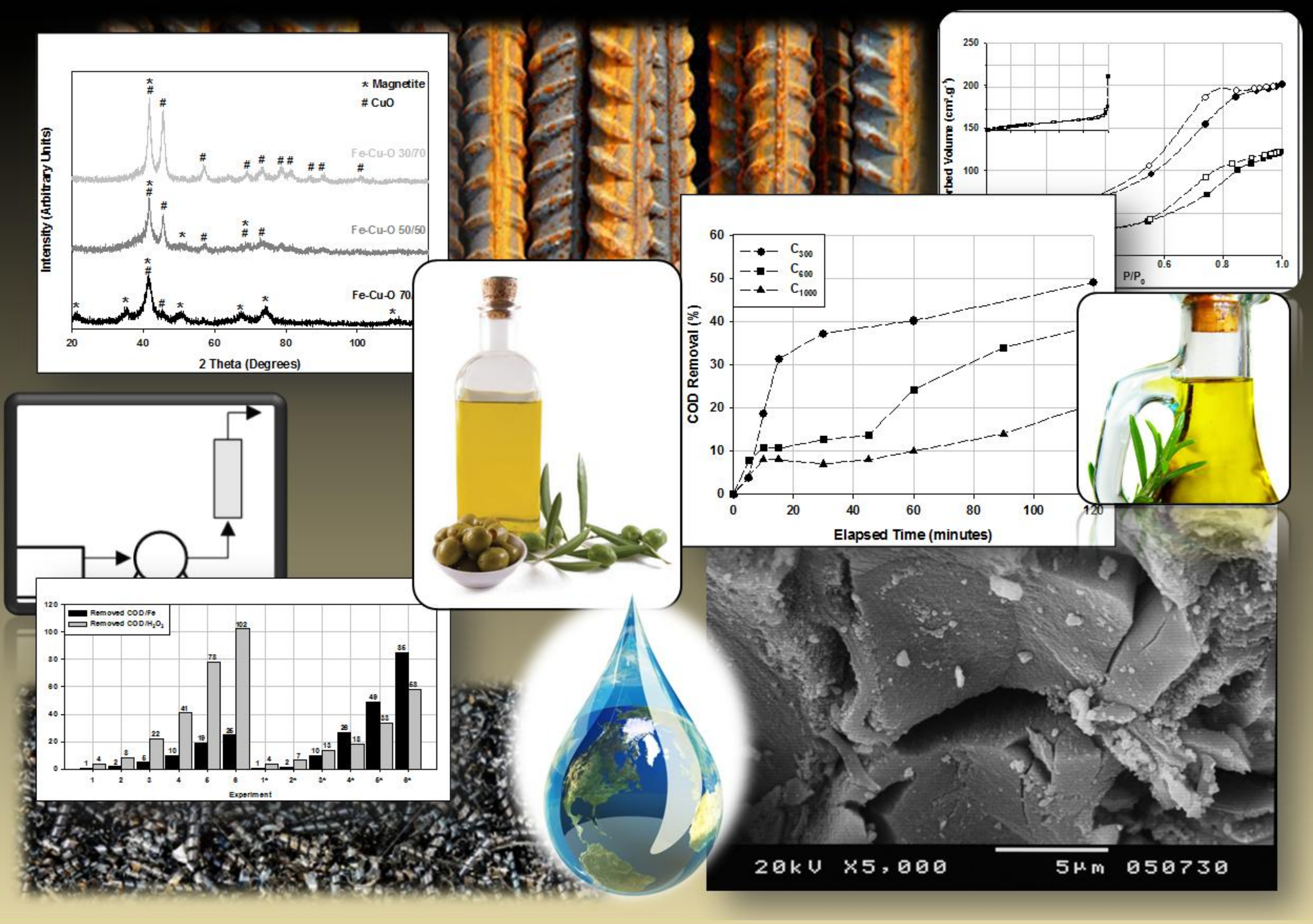

André Fernandes Rossi

FENTON'S PROCESS APPLIED TO WASTEWATERS TREATMENT

HETEROGENEOUS AND HOMOGENEOUS CATALYTIC OPERATION MODES

Ph.D. Thesis in Chemical Engineering supervised by Prof. Rosa Maria Quinta-Ferreira and submitted
by the Chemical Engineering Department, Faculty of Sciences and Technology, University of Coimbra.

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UNIVERSIDADE DE COIMBRA

DEPARTMENT OF CHEMICAL ENGINEERING
FACULTY OF SCIENCES AND TECHNOLOGY
UNIVERSITY OF COIMBRA

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DEQ – FCTUC
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Dissertation by
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“So you run and you run to catch up with the sun but it's sinking,
Racing around to come up behind you again.
The sun is the same, in a relative way, but you're older,
Shorter of breath and one day closer to death.”

Stanza from the song “Time”, composed by Roger Waters, David Gilmour, Rick Wright and Nicholas Mason (Pink Floyd).

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Since Portuguese is my mother tongue, as well as of those to whom I would like to express appreciation, this section is going to be written in this language.

Agradeço pela perseverança e crença que minha orientadora, a **professora Rosa**, sempre teve em mim...

...pela constante disponibilidade do **Rui**, de valor inestimável.

A quem começou esse doutorado por mim, **meus pais**, **Léo** e **Rosane**, novamente agradeço pela educação que me deram.

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Finalmente, deixo explícita a minha admiração tanto pelo povo quanto pela cultura de **Portugal**. Meu muito obrigado pelos vinhos, comida, fados e exemplos de companheirismo que nesse país encontrei. Como brasileiro, já conhecia o significado da palavra saudade. No entanto, agora terei mais motivos pra senti-la; um tempo tão bom que vivi ao longo desses anos de estudo.

André Fernandes Rossi

ABSTRACT

Water resources are not infinite. If even nowadays some people do not have proper access to this vital supply, humanity must do much more effort aiming its preservation in consideration with the future of the generations to come. Avoiding all types of pollutants from contaminating water cycles is currently one of the current utmost matters to be faced by government policies. Research on wastewaters treatment have been dealing this regard over many years now, strongly contributing with solutions to the related problems.

The most frequent remediation techniques to several kinds of effluents are the biological treatments, where microorganisms consume the organic charge – thus requiring biomass adaptation when there are changes on substrates composition. Drawbacks emerge when non-biodegradable or toxic effluents must be dealt with. This, sometimes, makes it impossible to treat effluents by activated sludge, especially when the effluent is not available all over the year for bacteria to have time to get acclimated. Therefore, accordingly to the kind or content of the residues requiring remediation before discharge, different approaches may be considered instead.

Portugal alone produced 80 kilotons of olive oil in 2012. In the same year, the World's production exceeded 3.3 megatons, produced from fruits gathered from over 750 million trees spread all over the globe (most of it at the Mediterranean region). This elevated and concentrated production generates huge amounts of different effluents, summing up the so called olive mills wastewaters (OMW). These rejects simultaneously present the two imperative characteristics that renders biological option unsuccessful for environmental legislation achievement: toxicity to microorganisms (due to the presence of phenolic acids) and seasonality (since the crop of the fruits occur for approximately four months of the year). Consequently, it is necessary to find alternative treatments capable of abating these wastewaters' organic charge at any period for as long as it is necessary.

Solution circumventing the mentioned inconveniences are chemical treatment technologies, where the advanced oxidation technologies (AOPs) are included. These last are based on an oxidative reagent able to degrade the aimed compounds, either by complete elimination or by reducing their environmental harmfulness. Parameters such as chemical oxygen demands (COD), total organic carbon levels (TOC), total phenolic content (TPh), biochemical oxygen demand (BOD), eco-toxicity (EC_{20} and EC_{50}), amongst others, supply key information for these processes' efficiency assessment, that may be presented as remediation alternatives after proper judgment of experimental results.

Hydrogen peroxide (H_2O_2) is a common reactant when it comes to wastewater oxidative treatments. Although it is a highly oxidative species, further activation by cleavage into hydroxyl radicals (•OH) can be achieved by the presence of ozone, UV-light or transition metals. In particular, when this excitation is caused by iron ions (usually Fe^{2+}), it is called Fenton's process, which is used as industrial wastewaters treatment with great economic advantages, especially for occurring under normal conditions of pressure and temperature. Besides, the non-selectivity of the Fenton's radicals assures that several kinds of effluents can be oxidized by these systems.

The Fenton's oxidation of a synthetic solution comprised by a few phenolic acids commonly found in OMW was studied. New results were introduced to the scientific community, obtained by the use of ceramic solids and low cost materials tested as heterogeneous catalysts. The classical process, in homogeneous phase, was also appraised and compared with a different approach of it, achieving interesting results regarding the reduction of sludge formation and reactants yields. Continuous operation modes were also performed in a tubular reactor, reaching good organic charge removals. The operating conditions were planned in a way to allow comparisons amongst several experiments.

In this thesis, the calcination temperature of ceramic catalysts is the first subject to be evaluated. Its study shows that the temperature of 300 °C produced the most active solids. An iron-cerium solid at the molar proportion of 70/30 can be highlighted amongst the other ceramic solids by its superior oxidative promotion (which might be related to its higher surface area, 188 $m^2.g^{-1}$): complete phenolic destruction, 49 % COD removal and 45 % TOC abatement. Moreover, the effluent's biodegradability was greatly enhanced and had its toxicity removed. Other researches using the same methodology of catalyst preparation comprised iron-copper and iron cobalt solids used at the same operation conditions, but without such success.

Low cost materials recycling is another theme presented in this document. The attempt of using Fenton's sludge as catalyst (directly, after calcination and as iron precursor), although resulting in active solids, did not succeed on the biodegradability enhancement, being discarded. On the other hand, zero valent iron (ZVI) gathered from two sources presented outstanding catalytic performances in batch (from 10 minutes to 2 hours) and continuous reactions (stable organic charge removals up to 158 hours of operation).

Finally, the homogeneous Fenton's reaction is appraised in order to generate results linking it to the heterogeneous process. In the same chapter, a different approach for the classical Fenton's oxidation is performed, showing a great enhancement of the overall efficiency considering the sludge formation reduction and reactants yields augment.

RESUMO

Os recursos d'água não são infinitos. Se até hoje em dia algumas populações não têm acesso decente a este recurso vital, a humanidade precisa se esforçar mais com o objetivo de preservá-lo em consideração às gerações vindouras. Evitar a contaminação dos ciclos aquáticos por qualquer tipo de poluente é uma das grandes preocupações atuais. Pesquisas sobre tratamento de águas residuais têm lidado com esse assunto ao longo dos últimos anos, contribuindo fortemente com soluções para os problemas relacionados.

As técnicas de remediação mais frequentemente utilizadas na remediação de diversos efluentes são as depurações biológicas, nas quais microrganismos consomem a matéria orgânica – requerendo, assim, adaptação da biomassa quando existem variações na composição do substrato. As desvantagens destes processos surgem quando águas residuais não biodegradáveis ou tóxicas precisam ser tratadas. Isto, algumas vezes, torna impossível a utilização dos sistemas de depuração por lamas ativadas (especialmente quando o efluente não está disponível durante todo o ano para que as bactérias tenham tempo de se aclimatarem a ele). Portanto, de acordo com o tipo e conteúdo dos resíduos que exigem remediação antes de serem descarregados, abordagens diferentes precisam ser consideradas.

Portugal sozinho produziu 80 mil toneladas de azeite em 2012. No mesmo ano, a produção mundial excedeu 3 milhões de toneladas, produzidas com frutas colhidas de mais de 750 milhões de oliveiras espalhadas por todo o mundo (a sua maioria na região do Mediterrâneo). Esta produção elevada e concentrada conduz a quantidades enormes de diferentes efluentes que, juntos, geram os efluentes de lagares de azeite. Estes rejeitos apresentam, simultaneamente, duas características que tornam inviáveis as opções biológicas na obtenção de parâmetros legislativos relativos ao meio ambiente: toxicidade a microrganismos (pela presença de ácidos fenólicos) e sazonalidade (uma vez que a colheita das azeitonas ocorre por, aproximadamente, quatro meses ao ano). Consequentemente, é necessário encontrar tratamentos alternativos que sejam capazes de reduzir a carga orgânica destes efluentes em todos os momentos que forem necessários.

Soluções que contornam as inconveniências referidas são as tecnologias de tratamentos químicos, nas quais estão incluídos os processos avançados de oxidação. Estes últimos são baseados em um reagente oxidante capaz de degradar os compostos alvo, tanto pela sua completa eliminação como pela redução da sua periculosidade ambiental. Parâmetros como a demanda química de oxigênio, carbono orgânico total, conteúdo fenólico total, demanda bioquímica de oxigênio, eco toxicidade, entre outros, fornecem informações chave para medir a eficiência destes processos, que podem ser apresentados como alternativas de remediação após uma análise adequada dos resultados experimentais.

O peróxido de hidrogênio é um reagente frequentemente utilizado quando se trata de processos oxidativos de águas residuais. Embora ele já possua uma capacidade reativa elevada, o seu potencial oxidativo pode ser aumentado ainda mais pela sua quebra em radicais hidroxila – o que pode ser alcançado na presença de ozônio, luz ultravioleta ou

metais de transição. Em particular, quando esta excitação é causada por íons de ferro (geralmente Fe^{2+}), dá-se o nome de processo de Fenton. Tal operação tem diversas aplicações industriais envolvendo o tratamento efluentes com vantagens econômicas, especialmente por ocorrer sob condições normais de temperatura e pressão. Além disso, a não-seletividade do reagente de Fenton assegura que contaminantes bastante distintos sejam igualmente oxidados.

No presente trabalho, foi estudada a oxidação de Fenton aplicada a uma solução sintética composta por alguns ácidos fenólicos comumente encontrados em efluentes de lagares de azeite, trazendo novos resultados à comunidade científica, fazendo recurso a sólidos cerâmicos e materiais de baixo custo testados como catalisadores heterogêneos. O processo, na sua forma clássica (fase homogênea), também foi avaliado e comparado usando-se uma abordagem diferente que permitiu alcançar resultados interessantes no que diz respeito à redução da formação de lamas e rendimento dos reagentes. O modo de operação em contínuo foi testado com o uso de um reator tubular, mostrando boas remoções de carga orgânica. As condições de operação foram planejadas de forma a permitir comparações entre as diversas experiências.

Nesta tese, a temperatura de calcinação aplicada na produção de catalisadores cerâmicos é o primeiro assunto a ser avaliado. O seu estudo mostrou que a temperatura de 300 °C é a mais propícia para gerar sólidos mais ativos. Um catalisador composto por ferro e cério na proporção molar de 70/30 pode ser realçado entre os demais sólidos cerâmicos pela sua promoção de graus de oxidação superiores (que pode ser associada à sua maior área de superfície: 188 $m^2.g^{-1}$): destruição completa dos ácidos fenólicos, 49 % de redução de demanda química de oxigênio e 45 % de remoção de carbono orgânico total. Para além disso, a biodegradabilidade do efluente foi grandemente aumentada, verificando-se a eliminação da sua toxicidade. Outras pesquisas foram realizadas usando a mesma metodologia de preparação de catalisadores compostos por ferro/cobre e ferro/cobalto sob as mesmas condições operacionais, mas sem o mesmo sucesso.

A reciclagem de materiais de baixo custo é outro tema apresentado neste documento. A tentativa de se utilizar lamas de Fenton como catalisadores (diretamente, depois de serem calcinadas e como precursoras de ferro), mostrou que, apesar de estas tratarem-se de sólidos cataliticamente ativos, a sua interferência na biodegradabilidade compromete a sua utilização, sendo, por isso, descartadas. Por outro lado, ferro zero-valente obtido de diferentes procedências teve excelentes performances catalíticas em regimes descontínuo (com tempos de reação de 10 a 120 minutos) e contínuo (apresentando remoções de carga orgânica estáveis até 158 horas de operação).

Finalmente, a reação de Fenton em fase homogênea foi estudada com o intuito de gerar resultados relacionáveis ao processo heterogêneo. Neste mesmo capítulo, é abordada uma metodologia diferente da oxidação clássica de Fenton, demonstrando uma melhora expressiva na eficiência geral do processo (considerando a redução da formação de lamas e aumento do rendimento dos reagentes).

RESUMEN

Los recursos de agua disponible son limitados. Si hasta los días de hoy algunos no tienen acceso a este recurso vital, la humanidad hay que pelear más para preservarlo en consideración a las generaciones del futuro. Evitar cualquier tipo de contaminación de los ciclos acuáticos es una de las grandes preocupaciones actuales. Investigaciones sobre el tratamiento de aguas residuales tiene contribuido fuertemente con soluciones relacionadas a esta cuestión.

Las técnicas de remediación de diversos efluentes más frecuentemente utilizadas son los tratamientos biológicos, en los cuales microorganismos consumen la materia orgánica – necesitando, así, adaptación de la biomasa cuando existen variaciones en la constitución del substrato. Desventajas surgen cuando aguas residuales que no son biodegradables o tóxicas necesitan tratamiento. Esto, algunas veces, torna imposible la utilización de sistemas de depuración por lamas activadas (especialmente cuando el efluente no está disponible por todo el año para que las bacterias tengan el tiempo necesario para aclimatarse a él). Luego, de acuerdo con el tipo e lo que está contenido en los residuos, diferentes soluciones han que ser consideradas.

Portugal solo produjo 80 mil toneladas de aceite de oliva en 2012. En el mismo año, la producción mundial excedió las 3300 toneladas, producidas con frutas cosechadas en más de 750 millones de oliveras (localizadas, en su grande mayoría, en la región Mediterránea). Esta grandiosa y concentrada fabricación genera enormes cuantidades de diferentes efluentes que presentan, simultáneamente, dos características que inhiben la utilización de tratamientos biológicos para obtener parámetros legislativos considerando el ambiente: toxicidad para los microorganismos (garantida por los ácidos fenólicos) y estacionalidad (una vez que las aceitunas son cogidas por cuatro meses al año). Como consecuencia, es preciso encontrar tratamientos alternativos capaces de reducir la carga orgánica de estos efluentes a cualquier momento y por tanto tiempo cuanto necesario.

Soluciones que contornan las inconveniencias mencionadas son las tecnologías de tratamientos químicos, en las cuales están incluidos los procesos avanzados de oxidación. Estos se basan en un reactivo oxidativo que degrada los componentes deseados, o por su completa eliminación como por la reducción de su peligrosidad ambiental. Parámetros como la demanda química de oxígeno, carbono orgánico total, contenido fenólico total, demanda bioquímica de oxígeno, eco toxicidad y otros, proveen informaciones para medir la eficiencia de estos procesos.

El peróxido de hidrógeno es un reactivo muy utilizado por los procesos oxidativos de aguas residuales. Su potencial de oxidación puede ser aumentado con su transformación en radicales hidroxilo – lo que puede ocurrir en la presencia de ozono, luz ultravioleta o metales de transición. Cuando esta reacción es causada por iones de hierro (usualmente Fe^{2+}), es llamada de proceso de Fenton. Esta operación tiene muchas aplicaciones industriales ligadas al tratamiento de efluentes con ventajas económicas, especialmente por no necesitar aumentos de temperatura y presión. Además, la non-selectividad del reactivo de Fenton hace con que los contaminantes muy distintos sean igualmente destruidos.

La oxidación de Fenton aplicada a una solución sintética composta por algunos ácidos fenólicos que pueden ser encontrados en efluentes de la producción de aceite fue estudiada. Nuevos resultados son presentados a la comunidad científica, obtenidos por el uso de sólidos cerámicos y materiales de bajo precio testados como catalizadores heterogéneos. El proceso en forma clásica, en fase homogénea, también fue investigado y comparado con un nuevo enfoque diferente del propio, alcanzando resultados interesantes con respecto a la reducción de formación de lamas y rendimiento de reactivos. La manera de operación en continuo fue testada en un reactor tubular, mostrando buenas remociones de carga orgánica. Las condiciones de operación fueron planeadas de forma a permitir comparaciones entre los diversos experimentos.

En esta tesis, la temperatura de calcinación utilizada en la producción de catalizadores cerámicos es el primer asunto a ser considerado. Su estudio muestra que la temperatura de 300 °C es la más propicia a generar sólidos más activos. Un catalizador compuesto por hierro y cerio en la proporción molar de 70/30 puede ser apuntado entre los demás sólidos cerámicos por la superior promoción de oxidación (que puede ser ligada a su más grande área de superficie: 188 $m^2.g^{-1}$): completa destruición de los ácidos fenólicos, 49 % de reducción de la demanda química de oxígeno y 45 % de remoción del carbono orgánico total. Además, la biodegradabilidad del efluente fue aumentada y su toxicidad fue eliminada. Otras pesquisas utilizando la misma metodología de preparación de catalizadores compuestos por hierro/cobre y hierro/cobalto y las mismas condiciones operacionales, pero sin el mismo suceso.

La reciclaje de materiales de bajo precio es otro tema presentado en este documento. La tentativa de utilizar lamas de Fenton como catalizadores (directamente, después de calcinadas y como precursoras de hierro), mostró que la actividad catalítica no compensa su interferencia en la biodegradabilidad. Por otro lado, hierro cero-valiente obtenido de diferentes maneras presentó excelentes performances catalíticas en régimen discontinuo (con tiempos de reacción entre 10 y 120 minutos) y continuo (presentando remociones de carga orgánica estables hasta 158 horas de operación).

Finalmente, la reacción homogénea de Fenton fue estudiada con el intuito de generar resultados que la relacionasen al proceso heterogéneo. En este mismo capítulo, una metodología diferente de la oxidación clásica de Fenton es aplicada, mostrando una expresiva mejora en la eficiencia global del proceso (considerando la reducción de la formación de lamas y aumento del rendimiento de los reactivos).

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NOMENCLATURE

AOP – Advanced oxidation process

BOD_5 – Biochemical oxygen demand (in five days), mg $O_2.L^{-1}$

COD – Chemical oxygen demand, mg $O_2.L^{-1}$

CSTR – Continuous stirred tank reactor

DOE – Design of experiments

FBR – Fixed bed reactor

HPLC – High pressure liquid chromatography

OMW – Olive mill wastewater

OUR – Oxygen uptake rate

ORP – Oxidation-reduction potential

S_{BET} – BET surface area, $m^2.g^{-1}$

SEM – Scanning electron microscopy

TOC – Total organic carbon, $mg.L^{-1}$

TPh – Total phenolic content, $mg_{gallic\ acid}.L^{-1}$

XRD – X-ray diffraction

UV – Ultraviolet

ZVI – Zero valent iron

Greek symbols

θ – Diffraction angle (º)

λ – Wavelength (nm or Å)

Part A. **Thesis Scope and Outline**

The manuscript of the present work begins describing our planet's situation regarding our water supplies. In order to guarantee the renewing of this resource and respect its cycle without interfering by contaminating it, one problem is addressed: industrial wastewaters production. To be short, they are identified as one of the main water streams contamination causes. Therefore, treatment processes are presented, leading the reader to the advanced oxidation processes (AOP) as alternatives where biological methodologies can't be applied. Only then the focus of this document emerges: the Fenton's reaction. After the discussion about its advantages and drawbacks, a scheme of the chapters is revealed.

Since the present work is a continuation of many other investigations, including some of our research group, a literature review comes as the second chapter. Inside it, the reader will be led across results presented on recent and not-so-recent publications, being informed about technological progresses regarding the Fenton's reaction.

I. Introduction

Wastewaters remediation by the Fenton's process is the utmost subject of this document. The manuscript begins by stating some of the problems faced by society nowadays. Around the world, the water problem is one of mankind's greatest issues, along with manners to avoid the contamination of this vital resource's cycle. Through its wastes and effluents, the industry can be pointed out as one of the main sources of pollution. Yet, on the other hand, the operation of this sector is imperative for all human beings' known needs after centuries of technological development. Therefore, these unwanted rejects must not reach watercourses untreated and, to do so, satisfying legislation limits is mandatory.

Chemical processes arise as remediation systems for industries to fulfill their good conduct – sometimes optional, sometimes necessary. Advanced oxidation processes (AOPs), in which the Fenton's process is situated, are addressed as viable alternatives when the most common biological treatments are not able to achieve the necessary parameters.

The continuation of this chapter will further describe the referred questions and processes, culminating on the utility and advantages of the Fenton's reaction application to wastewaters treatment.

I.1. Water and environmental concerns

More than 70 % of our planet's surface is covered by water. Yet, when we look closely to the actual situation, less than 3 % of the total water volume is freshwater and most of it is frozen in ice caps and glaciers. Only 1 % of the total water resources on earth are available for human use.

It is not difficult to imagine, relating these data with the World's population growth, that, somewhere in the future, water will be a very scarce resource. Since there is so little to share with so many, water misuse can be pointed out as one of nowadays society major problems and the wasteful manners of human kind definitely do not help the situation. Saving water, this often underestimated treasure of our planet, and preventing its regenerating cycle from becoming polluted are matters of great concern – a preoccupation that only rises, especially when charts point the lack of this resource in a coming future. The burden is on men's shoulders and becomes heavier every day with the omission of information and, most importantly, awareness of all people.

The industries, in the rush for profitable periods, tend to spend the minimal amount of money necessary to get rid of their effluents. Legislation and supervision, therefore, have to make sure that wastewaters are being treated accordingly to avoid environmental problems. Cheap and efficient oxidation processes can be useful for both sides by reducing the costs of proper disposal of polluted streams and by reducing damages caused to the environment.

High amounts of effluents are produced daily by several types of industries. Every production line has its own wastewater – each with its own composition and, therefore, its own most indicated treatment. If those polluted streams are discharged untreated or with inefficient depuration in the natural resources, serious environmental issues may be caused. The application of successful processes capable of removing not only toxic compounds but every content that might cause environmental changes is of major importance to ensure safe disposal of wastewaters.

Biological treatments are the most used due to attractive costs and proper organic matter removal, but not all kinds of effluents can be remediated by them. The presence of toxic compounds or the seasonal character of some effluents may disable their application. This way, it is necessary to appeal to other degradation techniques, such as chemical treatments. In this matter, advanced oxidation processes (AOPs) have been widely used by the industry for several years. One of them is the Fenton's process, highlighted by the low costs associated and non-selectivity of the oxidative species generated along chain reactions.

A scientist called Henry John Horstman Fenton discovered this process in the end of the 19th century with the oxidation of tartaric acid into dihydroxymaleic acid by hydrogen peroxide in the presence of ferrous ions (Fenton, 1894). Mechanisms for this reaction were suggested more than thirty years later, in 1932, in two lines: formation of hydroxyl radicals (•OH) followed by autocatalysis (Equations I.1, I.2 and I.3) by Haber and Weiss (1932), while Bray and Gorin (1932) proposed the formation of the ferryl ion (FeO^{2+}) combined with additional equilibrium to explain the presence of Fe^{3+} (Equations I.4, I.5 and I.6). However, although these two mechanisms are presented in the literature, the one involving hydroxyl radicals is much more accepted and referred.

Haber and Weiss mechanism:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad \text{(Eq. I.1)}$$

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad \text{(Eq. I.2)}$$

$$HO_2\bullet + H_2O_2 \rightarrow O_2 + \bullet OH + H_2O \qquad \text{(Eq. I.3)}$$

Bray and Gorin mechanism:

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \qquad \text{(Eq. I.4)}$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 \qquad \text{(Eq. I.5)}$$

$$Fe^{2+} + FeO^{2+} + 2\,H^+ \rightarrow 2\,Fe^{3+} + H_2O \qquad \text{(Eq. I.6)}$$

The present work focuses on wastewaters treatment by the Fenton's process. This system will be addressed in further details on the next sections, presenting its characteristics, advantages and drawbacks. Following previous investigations of our research group, an olive mill simulated wastewater was used as a model solution. Its oxidation through hydroxyl radicals generated by several hydrogen peroxide concentrations, activated by different catalysts will be evaluated and discussed.

I.2. Motivation and scope

Solutions and new alternatives development aiming industrial wastewaters treatment, finding more sustainable pollutants depuration, costs reduction and related subjects are the main scopes of this document. Laboratorial experiments comprising the Fenton's oxidation of synthetic effluents were performed in order to provide a database about the optimization of the tested systems.

Although AOPs are able to treat several types of effluents, this work focuses on the remediation of olive mill wastewaters. The selection of these wastewaters was based on the elevated production in Mediterranean countries – such as Portugal. The referred region can be seen in Figure I.1. These countries (specially Spain, Italy and Greece) account for the vast majority of the world's olive oil production (FAOSTAT, 2014). Table I.1 displays a list of the five top producers plus Portugal (which is the 9th greatest producer in the world), with data between the years of 2008 and 2012, based on information acquired from the Statistics Division of the Food and Agriculture Organization of the United Nations. According to Lopez-Villalta (1998), there are approximately 750 million productive olive trees (Olea europea L.) around the world, mainly concentrated in the Mediterranean region.

Figure I.1. Map of the Mediterranean region.

Green olives are picked from the end of September until the middle of November, while blonde and black olives can be picked from this last date until early February. As soon as the fruits are harvested, the oil extraction is performed – which means that its production has the same period of the crop (from late September to early February, comprising about 4 months per year), as is the availability of this industry's wastewater.

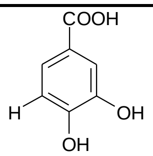
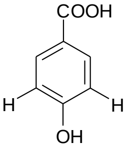
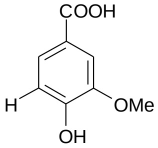
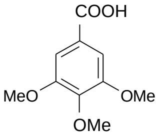
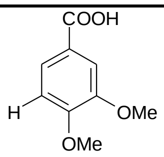
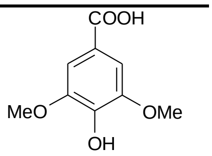
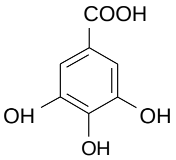
Table I.1. List of countries with the highest olive oil productions in the World, in thousands of tons (and their percentage of the total amount), for the years between 2008 and 2012.

Year	Spain	Italy	Greece	Syria	Tunisia	Portugal	World
2008	1,045 (39.5 %)	564 (21.3 %)	328 (12.4 %)	156 (5.9 %)	160 (6.1 %)	59 (2.2 %)	2,644
2009	1,247 (43.4 %)	517 (18.0 %)	305 (10.6 %)	168 (5.9 %)	150 (5.2 %)	68 (2.4 %)	2,872
2010	1,498 (45.6 %)	527 (16.0 %)	341 (10.4 %)	195 (5.9 %)	175 (5.3 %)	68 (2.1 %)	3,284
2011	1,585 (46.8 %)	543 (16.0 %)	331 (9.8 %)	208 (6.1 %)	112 (3.3 %)	83 (2.5 %)	3,388
2012	1,384 (41.7 %)	572 (17.2 %)	350 (10.5 %)	200 (6.0 %)	193 (5.8 %)	80 (2.4 %)	3,320
Total	6,760 (43.4 %)	2,723 (17.7 %)	1,656 (10.7 %)	928 (6.0 %)	790 (5.1 %)	358 (2.3 %)	15,508

Analyzing the data on the table above, we can see that Portugal alone produced 80,000 tons of olive oil in 2012. This number might give an idea of how much olive mill wastewater there is to treat in a short period. The preoccupation that rises from these numbers is the adverse effects on the environment associated with olive oil production. The olive tree culture and industry processing stages produce large amounts of by-products (Niaounakis and Halvadakis, 2004). These large amounts of seasonal bio-recalcitrant wastewaters (coming from the vegetation water and the soft tissues of olive fruits mixed with the water used in different oil production stages), plus the industry wash-waters, comprise the referred olive mill wastewaters (OMW). These effluents affect the environment due to their elevated organic charge (chemical oxygen demand values can go up to 170,000 mg O^{2}.L^{-1}) and polyphenolic content (up to 24,000 mg.L^{-1}). As results, high ecotoxicity and antibacterial effects are characteristics that, allied with seasonal production, constitute strong biological barriers for its remediation (Chatzisymeon et al., 2013).

A compilation of thirty identified phenolic compounds found on these effluents have been presented by Niaounakis and Halvadakis (2006), as well as the association between the phytotoxicity low biodegradability and its phenolic content. In this regard, our research group came up with an olive mill synthetic wastewater. Its composition comprises a mixture of some of these common phenolic acids, presented in Table I.2.

Table I.2. Phenolic acids used as model compounds to simulate olive mill wastewaters.

Name	Molecular formula	Structure
Protocatechuic acid	$C_7H_6O_4$	
4-hydroxybenzoic acid	$C_7H_6O_3$	
Vanillic acid	$C_8H_8O_4$	
3,4,5-trimethoxybenzoic acid	$C_{10}H_{12}O_5$	
Veratric acid	$C_9H_{10}O_4$	
Syringic acid	$C_9H_{10}O_5$	
Gallic acid	$C_7H_6O_5$	

Therefore, the main objectives of studying the Fenton's process applied to the remediation of the referred synthetic olive mill wastewater had the following objectives:

- Finding new alternatives to these effluents' treatment.
- Cost reduction of the overall process, drawing the industry attention.
- Safer disposal of unwanted rejects.
- Investigating sustainable and renewable technologies, with the possibility of integrating industry's leftovers with wastewater treatment.
- Early development of promising systems based on the oxidative power of the Fenton's reagent.

A few words must be said in what regards some fundamental options of this work. Firstly, the selection of the same polluted liquid that was constantly submitted to the Fenton's technology was performed, reaching a synthetic mixture of phenolic acids to mimic OMW. The basis of this decision was to highlight the principal goal of this thesis: look for alternatives capable of overcoming the main drawback of the conventional Fenton's reaction – its iron sludge production. This way, comparative studies addressing different operating batch/continuous modes and several heterogeneous/homogeneous conditions would mainly search for better catalysts and systematic parameters/methodologies. Otherwise (in the case of using real effluents), the compositional variations would interfere and probably deviate somehow the proposed ultimate target. Knowing that the wastewaters diversity require specific studies, future work will embrace real polluted streams.

Moreover, it should be pointed out that in some cases a thorough analysis comprised several chemical, biological and toxicological parameters. On the other hand, some situations' results showed that the experiment choices did not motivate subsequent application of the overall analytical tools. In other words, when the catalytic activity was found to be too low or when the biodegradability was being affected by the tested solid, the planning of further studies comprising the same materials/methods were dropped in order to give space to more promising alternatives – since there are many possibilities to be tested. Likewise, concerning solid catalysts behavior, morphological and textural properties were sometimes more extensively analyzed than in other circumstances.

I.3. Document's structure

The present work can be regarded under three main branches over the same basic principle: the search of environmentally sustainable systems allowing in-situ applications of this technology that would ease the industrial management by presenting low operation costs. In this context, alternatives to avoid or reduce the iron sludge generated on the classical methodology were the driving force for the studies that embraced the following general items:

- Heterogeneous operation based on iron ceramic catalysts.

- Integration of solid wastes and wastewaters remediation by using leftovers materials as sources of iron for the Fenton's oxidation.

- Trials that had close monitoring of the oxidant decomposition under the conventional and modified Fenton's processes, rendering careful control and H_2O_2 addition and achievement of conditions that require low iron concentrations.

This document is divided into five parts. A brief description of each one will be stated on the next sections, tackling a few of the subjects discussed into the comprised chapters.

I.3.1. Part A: Thesis scope and outline

The prelude of this work contains one introductory chapter, stating part of the pollution problem faced by today's society. Briefly approaching our vital water resources and the environmental concerns, the first chapter presents the industrial activity as a topic that needs close attention – giving major focus to olive oil production.

The rise of AOPs as proper wastewater remediation solutions when biological methodologies do not apply is mentioned and, in this regard, the Fenton's process is introduced in short words. Once the application of this system is not a cutting edge technology, previous accomplishments found on the literature are discussed on the next chapter, where the reader is informed about its technological progress.

I.3.2. Part B: Ceramic catalysts

To start the discussion about pioneer experimental results achieved, chapter III presents a ceramic catalyst comprised by iron and cerium oxides. The interference of its calcination temperature on the Fenton's process overall efficiency is appraised and thoroughly addressed.

Chapter IV mentions another ceramic catalyst composed by iron and copper oxides. Since the selection of the most indicated calcination temperature was already presented on the previous chapter, this part of the manuscript investigates Fe:Cu molar proportions in order to assess the generated solid's efficiency regarding organic charge removal. Moreover, this chapter encompasses a discussion about the synergistic effect of co-oxidation, studied through the comparison of the oxidation of two phenolic solutions with different phenolic contents.

The last chapter of Part B addresses an iron-cobalt ceramic solid, which presented poor activity as Fenton's catalyst but was able to increase the treated solution biodegradability.

I.3.3. Part C: Low cost materials

In this part of the thesis, environmental preoccupations were discussed. Chapter VI addresses the recycling of Fenton's sludge as Fenton's catalysts. Since this material is not a ceramic catalyst, the calcination temperature was studied once more in order to find out how to produce a more efficient solid. Although some of the studied solids presented high activity as oxidant-inducer, the biodegradability was affected and, since the Fenton's treatment is often used as a pre-treatment, the solids were discarded of further investigation.

Yet, the application of Fenton's sludge to wastewaters treatment was pondered for a second time with a different approach: its iron was extracted and utilized to produce a ceramic solid similar to the best catalyst already found: Fe-Ce-O. Even though the organic charge removal profiles for these two solids were alike, the biodegradability was again affected when the Fenton's sludge was the precursor.

This way, another low cost material is considered and analyzed: chapter VIII uses zero valent iron (ZVI), from construction site bars that were converted into shavings, as Fenton's catalysts. The good results presented by these cheap and effective catalysts motivated further investigation and they were tested in packed bed continuous reactors (chapter IX).

I.3.4. Part D: Homogeneous process and comparative studies

The continuation of this research encompasses a discussion amongst ceramic catalysts' results and low cost materials activities with the comparative link supplied by the classical Fenton's process. Firstly, many parameters are studied and evaluated for the homogeneous reaction. A different approach to the regular methodology is introduced and its advantages are highlighted in chapter X.

Chapter XI performs the link referred on the last paragraph, approaching previous subjects by different perspectives.

I.3.5. Part E: Conclusions and forthcoming work

The final movement of the document start with direct and prompt statements about the main findings previously displayed. Afterwards, pieces of possible work that might be performed in the future give the final dismiss in the end of chapter XII.

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II. Literature review

This chapter introduces and describes the classical Fenton's process and some evolutional steps taken by the scientific community. Therefore, both homogeneous and heterogeneous regimes are discussed. Here, the reaction optimization is addressed regarding parameters such as catalysts types and their ideal loads, oxidant agent concentration, pH and temperature of the reaction medium.

II.1. Classical Fenton's process

II.1.1. Reviews of the homogeneous Fenton's process

Based on the oxidant power of hydrogen peroxide (H_2O_2) catalyzed by iron ions to endorse the formation of hydroxyl radicals (•OH), the Fenton's process (Fenton, 1894) is a very promising Advanced Oxidation Process (AOP) due to the high mineralization promoted at mild conditions of both temperature and pressure. This treatment technique is, generally, very effective in the depuration of bio-refractory wastewaters (Bautista et al., 2008). The Fenton's process has been widely studied in the last years and its efficiency depends on several parameters, such as pH, concentrations and type of iron ions and hydrogen peroxide amounts (Neyens and Baeyens, 2003). This technology has been, above all, applied in the depuration of agro-industrial wastewaters, once these, due to its seasonality and high toxicity, cannot be properly treated by traditional biological processes. In this domain, Fenton's has been widely used in the treatment of winery effluents (Mosteo et al., 2006; Mosteo et al., 2007; Anastasiou et al., 2009, Lucas et al., 2009) and of those coming from the production of olive oil (Rivas et al., 2001; Ahmadi et al., 2005; Cañizares et al., 2007; Gomec et al., 2007; Kallel et al., 2009a; Kallel et al., 2009b).

Fenton's reagent was discovered about 115 years ago when a scientist called H. J. H. Fenton reported that ferrous ions strongly promoted the oxidation of tartaric acid by hydrogen peroxide (Fenton, 1894). Only several years later Haber and Weiss (1934) proposed that the hydroxyl radicals are the responsible moieties for the oxidant power of such a system. It is then suggested that the Fe^{2+}/Fe^{3+} catalysts are able to promote hydrogen peroxide decomposition leading to the formation of hydroxyl radicals, which are highly reactive with a wide range of organic pollutants.

One of the main advantages of the Fenton treatment is the fact that it does not request energy input as hydrogen peroxide is reactive at ambient conditions of pressure and temperature. Additionally, it requires short reaction times besides using easy-to-handle reagents. The main drawback is related with the fact that the homogeneous catalyst cannot be effortlessly retrieved from the effluent, demanding, thus, a separation step, leading to ferrous sludge – a waste entailing further management.

The high scientific and industrial interest upon this treatment process led to intense research in this field Table II.1 resumes the reviews published in the last years regarding the Fenton process.

Neyens and Baeyens (2003) reviewed the various reactions constituting the overall kinetic pathway of Fenton's with all possible side reactions. Moreover, the relation between the several operating parameters (pH, hydrogen peroxide and catalyst concentration) was summarized.

Table II.1. Fenton's process literature reviews.

Reference	Title	Main topics covered/comments
Neyens and Baeyens (2003)	A review of classic Fenton's peroxidation as an advanced oxidation technique.	This paper reviews the various Fenton reagent reactions constituting the overall kinetic scheme. It also summarizes previous publications on the relationship between the dominant operating parameters.
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, identity and characteristics of degradation by-products and intermediates, and possible degradation pathways are covered and discussed.
Bautista et al. (2008)	An overview of the application of Fenton oxidation to industrial wastewater treatment.	This review provides updated information on the application of the Fenton's process for the treatment of industrial wastewaters.
Hartmann et al. (2010)	Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials.	Iron-containing pillared clays as well as micro and mesoporous (alumino-) silicate catalysts prepared by ion-exchange, impregnation or direct synthesis for the degradation of organic compounds are the center of this discussion. Moreover, the treatment of more complex waste streams is reviewed. Catalyst stability and reaction conditions influences are also addressed.
Ramirez et al. (2010)	Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review.	In this paper, the use of pillared clays in heterogeneous photo-Fenton-like advanced oxidation for wastewater treatment is reviewed. Particular attention is given to the effect that the main operating conditions have on the process' performance. Emphasis is given to the type of catalyst used and its synthesis conditions.
Umar et al. (2010)	Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate.	The application of Fenton and Fenton related processes as landfill leachate treatments has received increased attention in the last decade. The Fenton's process is highly reliant on reaction conditions and leachate composition. Appropriate molar ratio of Fenton's reagents and initial pH are the two most important factors to achieve maximum COD removal performance.

Hydrogen peroxide-based advanced oxidation treatment processes for the abatement of aqueous pesticides are listed by Ikehata and El-Din (2006). Remarkable performances of various versions of photo-assisted Fenton and electrochemical Fenton processes have demonstrated the degradation of those compounds. Those studies have demonstrated that the acute toxicity can be diminished, in some cases, through treatment with various Fenton-type processes.

Since Fenton's peroxidation treatment plants design and construction are simple and the process does not imply significant operating problems, its application to real wastewaters becomes of industrial interest. Bautista et al. (2008) summarized the state of the art on the application of the Fenton technology to the treatment of industrial effluents. This process has demonstrated to be a feasible treatment for the abatement of a wide diversity of pollutants, representing an interesting solution whenever the traditional biological methodologies fail due to the presence of recalcitrant or toxic pollutants.

II.1.2. Previous studies of homogeneous Fenton's process

In the following of this section, an overview of the published literature regarding the application of Fenton's process for the depuration of liquid effluents is presented.

Classical Fenton's oxidation treatment is an interesting technology entailing simple plants that comprise, generally, a stirred batch tank where pH is controlled within the range 3.0 to 3.5 and operate at ambient conditions of pressure and temperature. $FeSO_4$ salt is usually applied as Fe(II) source. At the end of the reaction, the effluent is alkalinized and discharged to a tank where the $Fe(OH)_3$ solids, formed by the pH raise, are separated by settling (Bautista et al., 2008). The optimal operational conditions are very dependent upon the type of pollutants to be degraded; therefore, intensive research has been performed in this field (Table II.2).

Fenton reaction is now known to be very effective in the removal of many hazardous substances from water and wastewater using model compounds such as humic acid (Voelker and Sulzberger, 1996; Centi et al., 2000; Wu et al., 2010), phenolic compounds (Chamarro et al., 2001; Heredia et al., 2001; Peres et al., 2004; Kavitha and Palanivelu, 2005; Zazo et al., 2005), dyes (Szpyrkowicz et al., 2001; Prato-García and Buitrón, 2011; Doumic et al., 2013) and herbicides (Rivas et al., 2004; De Laat and Le, 2006; Benitez et al., 2007). Several works have been also published regarding the application of the homogeneous Fenton's process in the abatement of actual liquid effluents with interesting results for streams from detergent and cosmetic industry (Bautista et al., 2007; Wang et al., 2008; Perdigón-Melón et al., 2010), olive processing (Rivas et al., 2001; Kotsou et al., 2004; Ahmadi et al., 2005; Dogruel et al., 2009; Lucas and Peres, 2009; El-Gohary et al., 2009; Mert et al., 2010), pulp and paper (Eskelinen et al., 2010; Wang et al., 2011, Merayo et al., 2013;) and textile (Szpyrkowicz et al., 2001; Kim et al., 2004; Yu et al., 2010).

Fenton's reagent efficiency is dependent, amongst other factors, upon pH, hydrogen peroxide and catalyst concentrations. Indeed, pH is a crucial operating parameter. At pH values higher than 4.0, Fe starts to precipitate as iron hydroxide ($Fe(OH)_3$) and H_2O_2 decomposition into oxygen and water is preferred (Szpyrkowicz et al., 2001); moreover, the enhancement on the formation of Fe(II) complexes at high pH leads to a drop of Fe(II) concentration (Benítez et al., 2001). For more acidic conditions, Fe(II) regeneration by the reaction between Fe(III) with hydrogen peroxide is inhibited (Pignatello, 1992). It is, thus, generally accepted that pH 3.0 is the most suitable operating value for this treatment process (Neyens and Baeyens, 2003). The optimum hydrogen peroxide concentration depends upon the specific contaminants; nevertheless, it is generally higher than the stoichiometric quantity theoretically needed to completely remove the effluents initial COD since part of H_2O_2 decomposes into water and oxygen via non-radical pathways (Southworth and Voelker, 2003). Even so, the oxidant concentration has to be carefully selected due to its well-known radical scavenger effect (Walling, 1975). The increase of high ferrous ion concentrations improves the large formation of hydroxyl radicals within a short period of time; nevertheless, Fe(II) itself can be hydroxyl radical scavenger. Generally, Fenton's reaction follows two stages, a first step characterized by a quick degradation (Fe^{2+}/H_2O_2) followed by a slower one (Fe^{3+}/H_2O_2) (Ramirez et al., 2005).

Table II.2. Previous studies about the homogeneous Fenton's process (part 1/2).

Pollutant	Operational conditions	Reference
Chlorophenoxy herbicides	pH = 3.0 $[Fe^{2+}]$ or $[Fe^{3+}]$ = 0.2 – 20 mM $[H_2O_2]$ = 0 – 500 mM	Pignatello (1993)
Fulvic acid	pH = 3.0 $[Fe^{2+}]$ = 1 – 2 μM $[H_2O_2]$ = 1 μM	Voelker and Sulzberger (2003)
Surfactant wastewater	pH = 3.0 $[Fe^{2+}]$ = 30 – 180 mg.L^{-1} $[H_2O_2]$ = 20 – 80 mg.L^{-1}	Lin et al. (1999)
Chloroaliphatic compounds	pH = 3.0 $[Fe^{3+}]$ = 5 mM $[H_2O_2]$ = 0.6 M	Watts et al. (1999)
Carboxylic acids	pH = 4.0 Fe^{3+} = 0.106 mmol $[H_2O_2]$/substrate = 1.5	Centi et al. (2000)
Formic acid, phenol, 4-chlorophenol, 2,4 – dichlorophenol and nitrobenzene	Fe^{2+}/compound = 0.01 – 1 H_2O_2/compound= 0 – 50	Chamarro et al. (2001)
Phenolic compounds	$[Fe^{2+}]$ = 1.45 x 10^{-4} M $[H_2O_2]$ = 0.724 – 5.80 mM	Heredia et al. (2001)
Olive oil mill wastewater	pH = 2.5 – 3.0 $[Fe^{2+}]$ = 0.01 – 0.1 M $[H_2O_2]$ = 0.2 – 1.0 M	Rivas et al. (2001)
Disperse dyes	pH = 1.0 – 12.0 $[Fe^{2+}]$ = 250 – 550 mg.dm^{-3} $[H_2O_2]$ = 300 – 600 mg.dm^{-3}	Szpyrkowicz et al. (2001)
Cork cooking wastewater	pH = 3.2 $[Fe^{2+}]/[H_2O_2]$ (wt.) = 1.5 $[H_2O_2]$ = 10 mg.dm^{-3}	Guedes et al. (2003)
Direct dyes	pH = 3.0 $[Fe^{2+}]$ = 0.0179 – 0.1339 mM $[H_2O_2]$ = 0.29 – 5.88 mM	Malik and Saha (2003)
Fermentation brines	pH = 3.0 – 4.0 $[Fe^{2+}]$ or $[Fe^{3+}]$ = 0.01 – 0.05 mM $[H_2O_2]$ = 0.20 – 1.0 mM	Rivas et al. (2003)
Green table olive wastewater	pH = 3.0 $[Fe^{2+}]$ = 0.5 g.L^{-1} $[H_2O_2]$ = 2.0 – 8.0 g.L^{-1}	Kotsou et al. (2004)
Wine distillery wastewaters	pH = 4.0 $[H_2O_2]:[Fe^{2+}]$ = 5 – 100 mol.mol^{-1} $[H_2O_2]$ = 0.0033 – 1.65 M	Beltrán de Heredia et al. (2004)
Pigment wastewater	pH = 3.0 $[Fe^{2+}]:[H_2O_2]$ = 0.1 mol.mol^{-1} $[H_2O_2]$ = 1000 – 5500 mM	Kim et al. (2004)
p-Hydroxybenzoic acid	pH = 2.0 – 5.0 $[Fe^{2+}]$ = 0.072 – 0.723 mM $[H_2O_2]$ = 0.72 – 14.49 mM	Peres et al.(2004)
Simazine	pH = 2.0 – 6.0 $[Fe^{2+}]$ = 0.05 – 0.40 M $[H_2O_2]$ = 0.002 – 0.008 M	Rivas et al. (2004)
Orange II	pH = 3.0 $[Fe^{2+}]:[H_2O_2]$ (wt.) = 0.05 – 0.2 $[H_2O_2]$ = 3 – 15 mM	Ramirez et al. (2005)
Olive oil processing wastewater	pH = 3.0 – 5.0 $[H_2O_2]:[Fe^{2+}]$ (wt.) = 1.67 – 8.33	Ahmadi et al. (2005)
Nitrophenols	pH = 3.0 $[Fe^{2+}]$ = 900 mM $[H_2O_2]$ = 3.7 – 6.8 M	Kavitha and Palanivelu (2005)
Phenol	pH = 3.0 $[Fe^{2+}]$ = 1 – 100 mg.L^{-1} $[H_2O_2]$ = 500 – 5000 mg.L^{-1}	Zazo et al. (2005)
Detergent	pH = 3.0 $[Fe^{2+}]$ = 0 – 122 g $[H_2O_2]$ = 0 – 400 cm^3	Perkowski et al. (2006)

Table II.2. Previous studies about the homogeneous Fenton's process (part 2/2).

Pollutant	Operational conditions	Reference
Atrazine	pH = 3.0 $[Fe^{3+}]$ = 0.2 – 1.0 mM $[H_2O_2]$ = 9.4 – 49.9 mM	De Laat and Le (2006)
Chemical laboratory wastewaters	pH = 2.0 – 5.0 $[COD]:[Fe^{2+}]$ = 2:1 – 8:1 $[COD]:[H_2O_2]$ = 1:9 – 1:1.5	Benatti et al. (2006)
Paper and pulp wastewater	pH = 3.0 $[Fe^{3+}]$ = 100 – 1000 mg.L^{-1} $[H_2O_2]$ = 100 – 1000 mg.L^{-1}	Tambosi et al. (2006)
Cosmetic wastewaters	pH = 2.0 – 4.0 $[Fe^{2+}]$ = 40 – 1000 mg.L^{-1} $[H_2O_2]$ = 2545 – 12725 mg.L^{-1}	Bautista et al. (2007)
2-chlorophenol	pH = 2.5 $[Fe^{2+}]$ = 3 – 70 mg.L^{-1} $[H_2O_2]$ = 200 – 700 mg.L^{-1}	Moya et al.(2007)
Tanning materials	pH = 2.5 $[Fe^{2+}]$ = 300 – 750 mg.L^{-1} $[H_2O_2]$ = 150 – 600 mg.L^{-1}	Lofrano et al. (2007)
Phenylurea herbicides	pH = 2.0 – 4.0 $[Fe^{2+}]$ = 0.05 – 0.1 mM $[H_2O_2]$ = 0.1 – 1 mM	Benitez et al. (2007)
Amination water effluent	pH = 3.0 – 11.0 $[Fe^{6+}]$ = 2 – 10 g.L^{-1} $[H_2O_2]$ = 4 – 20 g.L^{-1}	Martins et al. (2007)
Acid and reactive dyes	pH = 3.0 $[Fe^{2+}]$ = 4 mM $[H_2O_2]$ = 20 mM	Arslan-Alaton et al. (2008)
Surfactant wastewater	pH = 3.0 – 5.0 $[Fe^{2+}]$ = 600 mg.L^{-1} $[H_2O_2]$ = 60 – 180 mg.L^{-1}	Wang et al. (2008)
Olive mill wastewaters	pH = 3.0 – 4.6 $[Fe^{2+}]$ = 5 – 50 mM $[H_2O_2]$ = 20 – 200 mM	Dogruel et al. (2009)
Olive mill wastewaters	pH = 2.0 – 9.0 $[H_2O_2]:[Fe^{2+}]$ (mol.mol^{-1}) = 7.5:1 – 30:1 $[H_2O_2]:[COD]$ (wt.) = 0.35 – 1.75	Lucas and Peres (2009)
Olive mill wastewaters	pH = 3.0 – 5.0 $[Fe^{2+}]:[H_2O_2]$ (wt.) = 1:10; 1:20; 1:50 $[COD]:[\ H_2O_2]$ (wt.) = 0.1:4.4 – 0.1:1.1	El-Gohary et al. (2009)
Citrate and hypophosphite	pH = 1.3 – 6.8 $[H_2O_2]$ = 30 mM $[Fe^{2+}]$ = 260 mM	Huang et al. (2009)
Methylene blue	pH = 3.0 $[Fe^{2+}]$ = 0.5 – 2.0 mM $[H_2O_2]$ = 8.0 mM	Melgoza et al. (2009)
Textile wastewater	pH = 3.0 $[H_2O_2]:[Fe^{2+}]$ (wt.) = 3.0 $[Fe^{2+}]$ = 4 – 135 mg.L^{-1}	Yu et al. (2010)
Cosmetic wastewater	pH = 3.0 – 10.0 $[Fe^{2+}]$ = 1 – 5.5 g.L^{-1} $[H_2O_2]$ = 0.80 – 0.99 g.L^{-1}	Perdigón-Melón et al. (2010)
Olive oil mill effluent	pH = 2.0 - 7.0 $[Fe^{2+}]$ = 3000 mg.L^{-1} or $[Fe^{3+}]$ = 2500 – 4000 mg.L^{-1} $[H_2O_2]$ = 3000 – 3500 mg.L^{-1}	Mert et al. (2010)
Hydroxy and hydroxynitro derivatives of benzoic acid	pH = 3.0 $[Fe^{3+}]$ = 0.1 – 2.6 mM $[H_2O_2]$ = 5.2 mM	Nichela et al. (2010)
Humic substances	pH = 1.0 – 8.0 $[Fe^{2+}]$ = 0 – 240 mM $[H_2O_2]$ = 0 – 320 mM	Wu et al. (2010)

II.1.3. Advantages and drawbacks

Homogeneous Fenton’s process has shown interesting results when applied before biological treatments contributing for the effluents toxicity reduction and biodegradability enhancement (El-Gohary et al., 2009; Mert et al., 2010; Perdigón-Melón et al., 2010). Also, the addition of this subsequent step of chemical oxidation can be useful to refine the stream obtained after bio-processing in order to fulfill the regulatory restrictions regarding disposal (Kotsou et al., 2004). Some of the most important Fenton’s characteristics are the low energy requirements (satisfactory results may occur at mild conditions) and the fact that hydroxyl radicals can attack and oxidize organic and inorganic species without specificity due to their very high oxidative power. These radicals are very strong oxidants, with an oxidation potential of 2.8 V – 55 % higher than H_2O_2, its precursor. As displayed on Table II.3, previously presented by Hunsberger (1977), the hydroxyl radicals are the second strongest oxidative species.

Table II.3. Oxidation potential of most commonly reagents used in wastewater treatment (Hunsberger, 1977).

Specimen	Oxidation Potential (V)
Fluorine	3.03
Hydroxyl radical	2.80
Oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Potassium permanganate	1.68
Chlorine dioxide	1.57
Iodide	0.54

The weightiest drawback of homogeneous Fenton's process is the quantity of iron required for the reaction, which is well above the legal amount allowed to effluent discharge. Thus, it becomes necessary to precipitate the iron at the end of the process, which produces a large sum of sludge – a serious environmental problem (Hsueh et al., 2005). In the sense of avoiding this disadvantage and allowing catalyst recovery, many attempts have been made to use solid catalysts in the Fenton's process. In order to quote a few works dealing with Fe^{2+} regeneration from Fenton’s sludge found in the literature, iron-impregnated catalysts have been developed. Qiang et al. (2003) proposed the electro-regeneration which required the solid dissolution by lowering pH to values lesser than 1.0 followed by Fe^{3+} reduction into Fe^{2+} by applying an electrical potential. Meanwhile, Li et al. (2007) pointed out serious drawbacks to this methodology since the repeated use of the regenerated iron led to effluents with enormously high conductivity due to the extremely low pH needed to re-dissolving the sludge. Besides, it was verified the accumulation of a significant quantity of organic material. To avoid this, Cao et al. (2009) proposed that the iron sludge was firstly dewatered and baked at 350 – 400 ºC. To overcome the homogeneous Fenton’s drawbacks and facilitate the catalyst recovery, some attempts have been made to develop solids to catalyze the reaction as discussed in section II.2.

Yet, when it comes to the addition of a solid phase, the Fenton-like processes start to be approached and some of their uses will be discussed on the next section.

II.2. Fenton-like alternatives

The heterogeneous Fenton's process requires a metal-impregnated solid and, in this regard, finding new catalysts and evaluate their efficiency have been the objectives of many studies. Hereby, the state of the art of this technique will present information about the evolution of the search for heterogeneous catalysts used in these specific systems.

The interest upon the development of heterogeneous catalysts for the application on Fenton-like treatment technologies led to some research and, recently, two reviews were published in this field. Hartmann et al. (2010) sum up the works dealing with the application of porous materials as catalysts in Fenton-type reactions confirming the potential of this technology for wastewater treatment. Several fundamental questions that were still not satisfactorily answered are raised: (i) is adsorption of the reactants on the porous support beneficial for the Fenton process? (ii) Are the large molecules adsorbed in the pores of the catalyst or is leaching of iron species into the solution required for their degradation in the liquid phase? (iii) Can the reaction be performed truly heterogeneously?

Ramírez et al. (2010) reviewed the use of pillared clays as heterogeneous catalysts in photo-Fenton's reactions. An exhaustive analysis of the effect of each operational condition on the process performance was carried out. The use of integrated processes that combine AOP with biological treatments of wastewaters containing refractory compounds is referred as effective to achieve complete degradation of pollutants and seems to be attractive from an economical point of view.

Umar et al. (2010) revealed that the Fenton process shows environmental and economic advantages for landfill leachate treatment. This technology has been used successfully to mineralize a wide range of organic compounds.

Although the studied catalysts are solids that can be seen dispersed by the liquid phase while the reaction occurs, the heterogeneity of the reaction must be confirmed and proven because some catalysts are not stable enough to hold on to their active chemical groups, which, thus, are loosen from the solid phase and react homogeneously. Facing this event, the investigator is inquired to create solids with enhanced stability by, for example, changing preparation parameters. Otherwise, the chances of using it as a heterogeneous catalyst must be discarded.

When solids are used to catalyze Fenton's process, they present the advantage of being easily recovered. While some of them keep their activity and can still be reused several times with the same efficiency, others face great activity decrease due to various phenomena, such as metal leaching or adsorption of pollutants. In other words, chemical and physical stability under reaction circumstances is a *conditio sine qua non* for practical utility (Arends and Sheldon, 2001).

The above mentioned aspects will be taken into account over the rest of this section. Moreover, the remediation of wastewaters will be considered due to their importance, because even if a solid that presents great efficiency removing TOC, COD and improving biodegradability, probably will not have industrial applicability if it does not allow separation and reuse since its economic balance will not be favorable. Table II.4 presents a recollection of previous studies regarding Fenton's heterogeneous catalysts, together with the studied pollutants and references.

Table II.4. Previous studies about the heterogeneous Fenton's process.

Pollutants	Catalysts	Reference
4-chlorophenol (4CP)	Iron powder, graphite and activated carbon	Lücking et al. (1998)
N. A. - The authors investigated the hydrogen peroxide decomposition to evaluate the catalysts efficiency and study this reaction's kinetics	Fe^{2+} and Fe^{3+} complexed within diethylenetriaminepentaacetic (DTPA), ethylenedinitrilotetraacetic (EDTA), ethylenebis(oxyethylenenitrilo)tetraacetic (EGTA) and nitrilotriacetic (NTA) acids	Tachiev et al. (2000)
Trichloroethylene (TCE)	Goethite	Teel et al. (2001)
Cinnamic acid derivates: 4-hydroxycinnamic (p-coumaric), 3,4-dihydroxycinnamic (caffeic) and 4-hydroxy-3-methoxycinnamic (ferulic) acids	CuO, Fe_2O_3, Cu_2O, FeO and CuO.ZnO supported on γ-Al_2O_3	Mantzavinos (2002)
Phenol	Al-Fe and Al-Cu modified clays	Carriazo et al. (2003)
Disodium salt of 3,3-dioxobi-indolin-2,2-ylidine-5,5-disulfonate (indigo carmine dye, IC)	[Cu(ammonia)4]$^{2+}$, [Co(ammonia)6]$^{2+}$, [Ni(ammonia)6]$^{2+}$, [Cu(ethylenediamine)2]$^{2+}$ and [Cu(methylamine)4]$^{2+}$ supported on silica , alumina, silica-alumina (25% Al_2O_3), and cation-exchange resins	Gemeay et al. (2003)
Phenol	Extrudates of Al-Fe pillared clay	Guo and Al-Dahhan (2003)
N. A. - The authors investigated the hydrogen peroxide decomposition to evaluate the catalysts efficiency and study this reaction's kinetics	Modified polyacrylonitrile (PAN) fiber by a mixture of hydrazine (HD) and hydroxylamine (HA) treatment in order to activate functional groups (metal cations, namely Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+})	Ishtchenko et al. (2003)
Phenol	Fe-Al-pillared clays (Fe-Al-PILCs)	Letaïef et al. (2003)
N. A. - The authors investigated the hydrogen peroxide decomposition to evaluate the catalysts efficiency and study this reaction's kinetics	Iron oxide nanoparticles immobilized in alumina coated mesoporous silica	Lim et al. (2005)
1,1-dimethylhydrazine (UDMH)	FeZSM-5 zeolite	Makhotkina et al. (2006)
Textile wastewater	Fe_2O_3/carbon	Dantas et al. (2006)
Pentachlorophenol (PCP)	Electric arc furnace (EAF) dust and hematite (for comparison only)	Mecozzi et al. (2006)
Cinnamic acid	Fe-pillared montmorillonite	Tabet et al. (2006)
Lignin	FeZSM-5 zeolite	Makhotkina et al. (2008)
N. A. - The authors investigated the hydrogen peroxide decomposition to evaluate the catalysts efficiency and study this reaction's kinetics	Manganese ferrite nanoparticles ($MnFe_2O_4$)	Valdés-Solis et al. (2007)
Methylene blue dye	Fe^0/Fe_3O_4	Costa et al. (2008)
Orange II dye	$FeVO_4$	Deng et al. (2008)
Reactive Black 5 dye (RB5)	Fly ash from coal power plant as Fe^{2+} support	Flores et al. (2008)
Quinoline	H_2-treated goethite (αFeOOH)	Guimarães et al. (2008)
Methylene blue dye	Nb_2O_5/iron oxides	Oliveira et al. (2008)
Reactive Black 5 (RB5) and Orange II (OII) dyes	Fe_3O_4-poly(3,4-ethylene-dioxythiophene) (PEDOT) core shell nanoparticles	Shin et al. (2008)
4-chlorophenol (4CP)	Zero valent iron (ZVI)	Zhou et al. (2008)
Phenol	Multi-walled carbon nanotube supported Fe_2O_3 catalysts	Liao et al. (2009)
Rhodamine-B (RhB)	Iron oxide nanoparticles from polymeric resins produced by Fe^{2+}-citrate and Fe^{3+}-citrate complexes polymerization with ethylene glycol	Giraldi et al. (2009)
Fermentation wastewater	Polyferric sulfate (PFS)	Xing et al. (2009)
Quinoline	Cu-doped goethite	Guimarães et al. (2009)
Reactive Blue 137 organic dye	FeZSM-5 zeolite	Aleksić et al. (2010)
Rhodamine 6G	CuFeZSM-5 zeolite	Dükkanci et al. (2010)
Acid Orange II dye	Vanadium-titanium magnetite	Liang et al. (2010)
Formic acid	Nanoparticulate zero valent iron (nZVI)	Mylon et al. (2010)
2-chlorophenol (2CP)	Goethite	Plata et al. (2010)
Phenolic wastewater	Ce based solid iron catalyst at the molar ratio Fe/Ce of 70/30 (Fe-Ce-O 70/30)	Martins et al. (2010)
Cr(VI)	Red mud waste (mainly composition: Fe_2O_3, Al_2O_3, CaO and TiO_2) obtained from aluminum production	Costa et al. (2010)
Potassium acid phthalate (KHP) solution	NaY zeolite-supported nanoscale zero-valent iron (NZVI/NaY)	Wang et al. (2010)

A heterogeneous catalyst prepared from bentonite was studied by Djamel et al. (2006) in the remediation of a cinnamic acid contaminated solution by the Fenton's process. The bentonite, composed essentially of montmorillonite, was purified and pillared with iron. Homogeneous Fenton oxidation of the cinnamic acid solution experiments were also carried out to compare the efficiency of this catalyst. The authors studied the influence of pH and the ratios of Fe and hydrogen peroxide to cinnamic acid on its removal rate.

Control experiments showed that H_2O_2 alone could not remediate the cinnamic acid solution and the same conclusion was taken about the catalyst from the adsorption studies, in which the catalyst alone was added to the solution and only 2 % removal occurred. This, allied with the leaching tests, which proved that the catalyst is stable and almost none iron leaching occurred, confirms that the oxidation happens through heterogeneous Fenton process.

The evaluated pH values were 2.9, 4.0 and 5.0, being at the lower one the best efficiency for the process (for both homogeneous and heterogeneous catalysts). The heterogeneous catalyst presented better cinnamic acid removal results than homogeneous catalyst and the authors explained this lower efficiency of the dissolved iron ions by its complexation with the organic intermediates of the degradation, such as carboxylic acids. The 2:1 Fe/cinnamic acid molar ratio was the most efficient and the H_2O_2/cinnamic acid best molar ratio was 83:1.

It is important to notice that these authors measured the cinnamic acid content by spectrophotometry at the acid's specific adsorption band ($\lambda = 304$ nm), so the results show the removals of this compound only – and not its intermediates. Other analysis like COD, HPLC or TOC would say much more about the real content of the remaining solution and should be made before taking any conclusions about the treatment of this acid into account.

Searching for novel compounds to act as heterogeneous Fenton catalysts, Mecozzi et al. (2006) studied the activity of electric arc furnace (EAF) dust in the decomposition of pentachlorophenol. EAF dusts are industrial by-products generated in the production of steel and are some of the concerns of the metallurgic industry because of the dumping costs (usually stabilization followed by land filling). Emphasize that the composition of these dusts may vary greatly according to the operational conditions for the production of the metal in question is also important. In this case, the used EAF dust was obtained at the production of carbon steel and pelletized.

As a heterogeneous Fenton catalyst, the efficiency of EAF dust was evaluated decomposing a toxic pollutant found in contaminated soils and sands: pentachlorophenol (PCP), a preservative agent for woods and leathers and a powerful pesticide. Chloride and total organic carbon removals were evaluated, yielding up to 60 % and 49 %, respectively, for optimized reaction conditions. As the authors say: “using as a catalyst what is commonly considered as a waste, would be of economic interest considering the high costs required for its disposal”. The catalyst activity of the EAF dust was compared with hematite.

The composition of both catalysts was determined by energy dispersive X-ray analysis (EDS), showing that EAF dust has Cl, Zn, Fe, K, Pb, Ca and Mn while hematite contains only Fe of the above metals. SEM micrographs showed that the size and shape of the catalysts are also different: while EAF dust is spherical with different sizes, hematite has platelet shape within 12 to 20 µm of thickness. Leaching tests were conducted in a centrifuge, showing only traces of Pb, Fe and Mn, discarding the chances of homogeneous reaction. As chlorine ions were leached to the bulk solution, EAF dust received four washes with bi-distilled water so these ions would not interfere in the Cl removal results.

Through pH monitoring experiments, the authors showed that the best pH for TOC and chlorine removals from the PCP initial solution is 4, but due to the fact that this pH is hard to maintain constant, the chosen pH value was 2. This lower value also has good remediation of the PCP solution allied to the easier control of the solution pH.

The TOC removal over time was evaluated and the results showed that the first 6 hours of reaction yields most of the removal, but the reaction goes on and TOC values keep falling until 24 hours of reaction - further time has almost zero reaction rates.

Changing the H_2O_2:PCP and Fe:H_2O_2 ratios and the catalyst (EAF dust or hematite), several experiments were carried out to compare the efficiency of the process regarding to TOC and chlorine removals. The H_2O_2 stabilization using KH_2PO_4, which lowers dissolved metal concentrations through their precipitation or complexation (a good method to avoid the scavenger effects when using high metal catalyst concentrations, specially the EAF dust because of its composition), was also an observed parameter.

The 10:1 H_2O_2:PCP molar ratio experiment presented the best removal efficiencies: (i) for the EAF dust, 49 % for TOC and 57 % for chlorine when Fe:H_2O_2 molar proportion was 1:5 and 48 % for TOC and 61 % for chlorine when Fe:H_2O_2 was 1:1 (although this high metal concentration requires KH_2PO_4 stabilized H_2O_2); and (ii) for the hematite, 45 % and 55 % when the Fe:H_2O_2 ratio was 1:2. These results show that EAF dust can be used as a heterogeneous Fenton catalyst.

Dantas et. al (2006) evaluated the treatment of textile wastewater by adsorption and simultaneous heterogeneous Fenton process using Fe_2O_3/carbon composites that, besides having their part as catalysts on the Fenton oxidation, work as adsorbents as well. The studied catalyst showed high stability by allowing negligible iron leaching and it was demonstrated that the adsorptive capacity of these solids is enhanced by the superficial iron oxide content increase and that this catalyst can be effectively used in the treatment of textile wastewaters. This adsorption mechanism is an economic advantage because reduces the amount of hydrogen peroxide required for the treatment.

Nevertheless, if adsorption can be an advantage, it also can be a drawback – depending on the point of view. It can reduce costs with hydrogen peroxide but, on the other hand, once the catalyst adsorbs the pollutants, these are just passed from the liquid phase to the solid phase (instead of being degraded by oxidation), and the catalyst will, at a certain point, become saturated with pollutants and the reactor will require a new charge of clean catalyst. On the other hand, the adsorption can aid the oxidative process by pulling the organic compounds closer to the site where hydroxyl radicals are/will be generated from the activation of hydrogen peroxide (especially considering the very short half-life of these oxidative species).

Yet on the trial of finding new efficient solid catalysts for the Fenton oxidation, Oliveira et. al (2008) investigated the use of niobia (Nb_2O_5)/iron oxides for the treatment of the methylene blue dye artificial wastewaters. The results of the characterization of the novel material (power X-ray diffraction, chemical analyses, scanning electron microscopy and ^{57}Fe

Mössbauer spectroscopy) showed that the main iron oxides formed in the preparation of the catalysts were goethite and maghemite with small particles sizes. To quantify the hydrolization/oxidation, the electrospray ionization mass spectrophotometry method was used.

The preparation of these catalysts involved the addition of the desired mass proportion between iron and niobia salts, thus, two different catalysts were prepared with different niobia:iron oxide molar proportions (1:1 and 1:5). Plus, for comparative studies, a pure niobia catalyst was also prepared.

Three reaction pathways were evaluated: (i) the decomposition of the hydrogen peroxide into oxygen and water, (ii) the decomposition of hydrogen peroxide in the presence of organic compounds and (iii) the oxidation of the methylene blue dye. Studies by ESI-MS allowed the identification of intermediate compounds of the organic dye decomposition. Also, by atomic absorption, the iron leaching was assessed.

Regarding to H_2O_2 decomposition in the presence of the catalyst, the niobia/iron oxide 1:1 was the only one that showed strong activity, while the other catalysts (niobia iron oxide 1:5, pure iron oxide and pure niobia) did not decompose H_2O_2 significantly. As referred to the H_2O_2 decomposition in the presence of organic compounds and the niobia:iron oxide 1:1 solid catalyst, the pollutants phenol and drimaren red textile dye have proven to be reaction inhibitors and this inhibition might be related to the adsorption of the organic compounds on the active sites of the composite and/or their reaction with intermediate species in the H_2O_2 decomposition – delaying the reaction rate by more than twenty times as compared to the absence of these organic compounds. Finally, the discoloration rate of the methylene blue was evaluated, confirming the expected catalyst to present better results: niobia:iron oxide 1:1 showed much better discoloration than the other catalysts (pure niobia, pure iron oxide and niobia:iron oxide 1:5). Adsorption tests revealed that 15 % of the discoloration is obtained by adsorption contribution in the worst of the cases (niobia:iron oxide 1:5). Through leaching tests, the iron content in solution was found to be always very low, indication that the reaction occurs via heterogeneous mechanism.

Although wastewater discoloration is an important parameter, there are more subjects to deal with before choosing the correct treatment, such as the mineralization of the compounds into carbonic gas and water, once one can obtain complete discoloration of the effluent without getting rid of the refractory and harmful compounds generated through the oxidation process. Therefore, it is natural that for industrial applications, the aim of the treatment is the complete mineralization of the effluents (and not just their discoloration) before its discharge into water courses. In order to evaluate the mineralization pathways, the authors recurred once again to ESI-MS spectra and presented a scheme for the oxidation of the methylene blue dye by this system. These ESI-MS spectra suggested that total mineralization of the methylene blue dye is obtainable.

The reduction of iron oxides like Fe_2O_3, FeOOH and Fe_3O_4 using H_2 was studied by Costa et al. (2008) to prepare highly active systems for the heterogeneous Fenton process, namely Fe^0/Fe_3O_4. The ratios between the metal and the oxide were determined by Mössbauer spectroscopy and powder X-ray diffraction. The compounds formed by this process can easily be oxidized by atmospheric oxygen. The composites showed high activity while oxidizing the methylene blue dye through Fenton's process. Good values of TOC removal were achieved by the catalyst containing 47 wt. % of Fe^0: 75% after two hours of reaction. Conversion electron Mössbauer spectroscopy (CEMS) evaluations indicated that the catalyst was oxidized during the reaction.

These Fe_3O_4-based catalysts have some important physical-chemical characteristics that deserve to be discussed due to their importance in the Fenton's process. First of all, they contain $Fe^{2+}_{magnetite}$, which can donate an electron to initiate the Fenton reaction according to the Haber-Weiss proposed mechanism. Also, the structure of the magnetite has an octahedral site that can hold both Fe^{2+} and Fe^{3+} (this way, the iron can be oxidized and reduced back being in the same site). Finally, different metals can substitute the iron in the same structure in order to adapt the catalyst properties to various different active systems, according to the substitute metal and its content proportion.

In this case, the substitute metal analyzed was Fe^0 due to the low cost and the fact of being already used for several remediation processes (permeable reactive barriers, reduction of organochloro, dyes, pesticides, Cr(VI) and As). Also, the Fe^0 was studied as a replacement of Fe^{2+} because it has three electrons to participate in the reaction. However, this possibility was discarded because the reaction rate is very slow to transfer electrons from Fe^0 to H_2O_2 in a near neutral pH.

The same group of investigation has been focusing its attention on the magnetite-based catalysts, having already found out that the simple grind of Fe^0 and Fe_3O_4 powders raises significantly the activity of this catalyst and this increase is discussed as being in terms of thermodynamics: the electron transfer from Fe^0 to $Fe^{3+}_{magnetite}$, which regenerates $Fe^{2+}_{magnetite}$ (enhancing the Fenton reaction), is energetically favored. However, for further studies, the preparation of the catalyst involved more complex steps: the Fe^0/Fe_3O_4 was obtained by the controlled reduction of Fe_3O_4 with H_2. Afterwards, to identify and quantify the iron phases in the samples, Mössbauer spectroscopy was used. To assess the activity of the prepared catalysts, the authors compared their influence in the decomposition of H_2O_2 and, through the data obtained, one can observe that the most active composite was the one prepared involving the reduction with H_2 at 400 °C for two hours. By comparing CEMS analysis results, it can be seen that both Fe^0 and Fe_3O_4 are responsible for the decomposition of the H_2O_2 and it is worthy to take into account that the content of Fe^0 decreases from 56% to 48% while the Fe^{3+} content increases at the same proportion, meaning that the Fe^0 was oxidized to Fe^{3+} during the reaction.

The decomposition of methylene blue was then carried out, assessed by discoloration, to evaluate the production of non-colored intermediates in the oxidation, and total organic carbon, a measurement that shows how much of the organic compounds were completely oxidized (mineralized). Again, for both evaluation tests, the catalyst prepared with the H_2 reduction step at 400 °C for two hours showed the best results. Atomic absorption analyses did not show any significant concentration of soluble iron, meaning that the catalyst is stable and that the heterogeneous reaction takes place. Plus, the discoloration and the H_2O_2 decomposition reactions were interrupted by the removal of the catalyst, what confirms the just told conclusions. Fe^0/Fe_3O_4 400 °C/H_2 had 75% TOC reduction and the adsorption tests (same reaction conditions but without the addition of H_2O_2) showed only 10% TOC reduction.

$FeVO_4$ was tested as a new heterogeneous Fenton catalyst in the treatment of Orange II simulated wastewater by Deng et al. (2008). Unlike most catalysts, this one presented fine degradation results (93% after 60 minutes) at a non-acidic pH value, 6.1. Its preparation requires a final drying stage (calcination) at a certain temperature and the compounds formed through lower calcination temperatures showed better activity – explained by the higher BET surface area and pore volume of these solids. The authors tested initial pH values from 3 to 8, paying attention and discussing iron and vanadium leaching characteristics, acquiring thus interesting data regarding to catalyst stability: through operational conditions ([orange II] = 100 mg.L^{-1}, [$FeVO_4$] = 0.5 g.L^{-1}, [H_2O_2] = 15 mM, pH = 6.1), the iron leaching for catalysts calcinated at several temperatures (50, 100, 200, 300, 400 and 500 °C) were around 0.5 mg.L^{-1} within acceptable EU discharge standards (2 ppm). On the other hand, the leaching of vanadium ions was undesirably above those limits: approximately 2.5 mg.L^{-1}. The leaching patterns according to the calcination temperature were quite different for iron and vanadium ions: while the iron leaching decreased for higher calcination temperatures, the opposite occurred to the vanadium – leading to the use of lower calcination temperatures to be preferred, once the iron leaching is always very low and does not decrease much with lesser calcination temperatures (yet sustained by the data obtained indicating that the efficiency is also better for lower calcination temperatures). The argumentation of the authors is that this leaching is probably led by the acidification of the bulk caused by the formation of organic and inorganic acids generated during the oxidation process (explaining the pH decrease along the reaction). Even though vanadium ions migrated from the solid to the liquid phase more than it was likeable, it is intended to take the study of this catalyst forward because it presented good degradation and stability when reuse tests were carried out (up to six repetitive runs without significant loss of reactivity).

Core-shell nanoparticles of a polymer (PEDOT), chemical formulae Fe_3O_4–poly (3,4-ethylene-dioxythiophene), were studied by Shin et al. (2008) as heterogeneous catalysts for the Fenton reaction. That compound, compared with pristine Fe_3O_4 nanoparticles and commercialized iron oxide nanopowder, showed high efficiency in the degradation of Reactive Black 5 (RB5) and Orange II dyes. Other advantage of this polymer is that the iron leaching can be suppressed by its molecular coordination and it can be easily removed by a magnetic field.

The study of the pH effect on the oxidation revealed that the core-shell nanoparticles are able to enhance the catalytic efficiency, allowing the reaction to still occur at a wider pH range. Also, the calculated RB5 oxidation rate constant for the first ten minutes was much higher for the Fe_3O_4-PEDOT core-shell nanoparticles than for Fe_3O_4 nanoparticles and iron oxide nanopowder. The same order of efficiency was observed in the oxidation of the Orange II dye over the same reaction conditions. Comparing the catalytic degradation rate of the Fe_3O_4-PEDOT core-shell nanoparticles catalyst with the other previously studied, such as hydroxyl-Fe-pillared bentonite and Nafion/Fe–ion/carbon fabric composite, it shows better efficiency under the same conditions.

The iron leaching from the catalyst was calculated by measuring the concentration of residual iron ions after the Fenton reaction and it was found to be 0.6 ppm for both dyes, a small amount. When this same quantity of iron was used as homogeneous catalyst for the Fenton reaction under the same conditions, the oxidation was nearly zero within ten minutes, indicating that the discoloration of the azo dyes was mainly due to the heterogeneous reaction catalyst over the Fe_3O_4-PEDOT core-shell nanoparticles and that the homogeneous contribution in the discoloration was negligible.

The authors tested the same catalyst and hydrogen peroxide amounts for different dye (both RB5 and Orange II) concentrations and results showed a gradual decrease in discoloration efficiency with increasing dye concentration. As conclusion, the optimal dosage of core-shell nanoparticles for complete discoloration and mineralization in 10 minutes is 100 ppm per 0.1 mM dye concentration.

Fly ashes collected from a bituminous coal thermal power plant were impregnated with iron to be used as heterogeneous Fenton catalyst, due to its economic source (another waste that can be transformed in something useful) and high specific area (Flores et al., 2008). From the ashes and ferrous nitrate, five different catalysts were prepared (C1 by impregnation and C2 to C5 by ion exchange).

Sequential leaching tests showed that a small part of the iron content is lost; nevertheless the catalyst is quite stable under the studied conditions and one can say that the abatements observed in the experiments are due to heterogeneous Fenton reaction, once the adsorption studies also revealed that this phenomenon is negligible regarding to color and COD removals.

The authors calculated the stoichiometric amount of H_2O_2 required to completely oxidize the RB5 dye compound and used this amount, 10 % and 20 % H_2O_2 excess to verify which one is the best alternative to the process, concluding that the higher hydrogen peroxide concentration increased the RB5 degradation.

Catalyst load is another important parameter. Original fly ashes efficiency was compared with the one of prepared catalysts. It was proven that although fly ashes have iron content, it is too small to start a Fenton process. The catalysts could reduce COD in approximately 80 % and the color of the RB5 solution (except for one of them, prepared in alkaline media and mixture by ultrasonic energy).

Although this catalyst presented good results in the remediation of the RB5 dye, this study did not evaluate the toxic compounds that may be present in fly ashes, like furans and dioxins. This evaluation would only become important if the catalysts were prepared without the 500 °C calcination step because the mentioned toxic compounds are desorbed from different solids at 300 - 400 °C.

The degradation of 4-chlorophenol (4CP), a toxic pollutant, by heterogeneous Fenton reaction using zero valent iron (ZVI) as catalyst was studied by Zhou et al. (2008). This pollutant has antimicrobial properties and it is used as a preservative for woods, paints, vegetable fibers and leathers, as well as a disinfectant and raw material in the industrial synthesis of pesticides, fungicides, herbicides, insecticides, pharmaceuticals and dyes. Waste incineration, bleaching of pulp with chlorine and disinfection of drinking water can also generate 4CP. Due to its toxicity, this compound cannot be biodegraded becoming hard to remove it from the environment.

It is known that heterogeneous Fenton's process using iron supported catalysts have good efficiency in the remediation of CPs. In this study, the focus of the authors is the further investigation of the degradation kinetics and pathways of 4CP in a ZVI/H_2O_2 system, finding out the reaction intermediates and products.

Control experiments were carried out using only H_2O_2 or ZVI with the 4CP, as well as 4CP alone to check the decomposition of 4CP itself or by adsorption in ZVI or by decomposition from H_2O_2. These experiments revealed that there is almost no degradation by these means, proving that Fenton's high rate degradation is due to Fenton's mechanisms only and not by adsorption or H_2O_2 degradation.

To proceed with the experiments, the effect of the pH on the degradation of 4CP in ZVI/H_2O_2 system was evaluated. The experiments were conducted in the same conditions: 100 mg.L^{-1} of 4CP, 1 mM of H_2O_2 and 1 g.L^{-1} of ZVI, varying the pH to 3.0, 4.0, 5.0 and 6.5 (the actual pH of the solution without any adjustment). The two lowest pH values showed high efficiency and fast degradation of that compound. With pH 3.0, the full degradation occurred in just 8 minutes, while with pH 4.0 it took 22 more minutes. The two highest pH values were not able to fully degrade the 4CP solution. The experiment carried out with pH 5 presented only 6 % removal at 45 minutes and at pH 6.0, 4 % removal in 6 hours. The authors noticed some color changes during the reaction and commented that it may be due to the iron dissolution (which becomes lesser and lesser as the pH increases): while the pH 5 experiment turned from colorless to green and brown, the pH 6 reaction did not obtain any colors, being colorless during all the experiment. This hypothesis is confirmed by the H_2O_2 decomposition, which falls from 70 % in 45 minutes of reaction to only 12 % in 6 hours for the pH values of 5.0 and 6.5, respectively.

Another attempt to discover an efficient catalyst was made by Guimarães et al. (2009). The work evaluated the catalytic activity of goethites impregnated by Cu^{2+}. The incorporation of these cations on the solid structure (showed by Mössbauer spectroscopy data) improved the oxidation of quinoline by heterogeneous Fenton-like process using H_2O_2.

Three different goethite-based catalysts were prepared. One containing pure goethite, a second one consisting on goethite Cu substituted (GtCu) and a third one prepared with an extra step after the drying stage: heating at 350 °C for two hours with H_2 flow (reduced GtCu). These three catalysts were characterized by XRD, Mössbauer spectrophotometry, TPR and BET surface area measurements and then their efficiencies were evaluated in the decomposition of H_2O_2 into H_2O and O_2 and in the oxidation of a prepared quinoline aqueous solution through heterogeneous Fenton process – in which the GtCu and the reduced GtCu catalysts showed higher activities. Even though the mentioned catalysts have good activity, again it was noticed that the presence of organic compounds (in this case, ascorbic acid and phenol, used separately) strongly inhibits the decomposition of H_2O_2, explained by the competition of competitive process involving the adsorption of the organic compounds on the active sites of the composites and the reaction of the decomposition intermediates of the organic compounds with the intermediate species of the H_2O_2 decomposition – both of them reducing the formation of O_2.

Atomic absorption tests were performed to evaluate the leaching of Fe and Cu from the catalysts in order to assess the possibility of homogeneous reactions and the both metal concentrations were under the equipment sensibility limit – excluding the odds of homogeneous reaction occurrence and pointing the solid as stable.

The most active of the catalysts, reduced GtCu, also showed good results in the decomposition of quinoline through H_2O_2 oxidation. ESI-MS data reveals that the quinoline molecules are fragmentized along the reaction by successive hydroxylations. Also, the complete mineralization of quinoline was observed by the measurement of the total organic carbon in solution, reaching approximately 57 % TOC removal for the reduced GtCu catalyst in front of only half of this removal for the non-reduced GtCu catalyst, showing that the H_2 reducing step in the preparation of the catalyst enhances its activity. This enhancement might be due to the reduction of the Fe^{3+} as well as the Cu^{2+} to Fe^{2+} and Cu^{+} respectively, that are more active to form hydroxyl radicals (the compound responsible for the Fenton oxidation) through equations II.1 and II.2:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad \text{(Eq. II.1)}$$

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + \bullet OH + OH^- \qquad \text{(Eq. II.2)}$$

The controlled reduction of red mud with hydrogen (H_2) producing active compounds to be used in two different environmental applications – heterogeneous Fenton's reaction and reduction of chromium, Cr(VI), was investigated by Costa et al. (2010). Different compounds, principally Fe_3O_4, Fe^0/Fe_3O_4 and Fe^0, are formed depending on the temperature of reduction, i.e. 300, 400, 500 and 600 °C. The formed Al-, Si- and Ti-dispersed iron oxides showed high reactivity, so the temperature of reduction was investigated, regarding to this reactivity. As catalyst of heterogeneous Fenton reaction, the compounds formed by the H_2 reduction of red mud that had better efficiency in oxidation of the model dye methylene blue with hydrogen peroxide at neutral pH were the ones formed at 400 °C, due to the presence of the composite Fe^0/Fe_3O_4. An important aspect of this composite commented in the same paper is that it can be completely regenerated by simple H_2 treatment after becoming deactivated due to extensive use.

Another attempt to find a new and efficient solid catalyst for the heterogeneous Fenton process was made by Wang et al. (2010), having their focus on the NaY zeolite-supported nanoscale zero-valent iron (NZVI/NaY). The chemical oxygen demand removal ratio of a potassium acid phthalate (KHP) solution (425 ppm) at pH 3.5 achieved 79 %. The activity of this catalyst is close to the homogeneous one and presents less than 50 % iron leaching. Besides, the catalyst had good performances at wider pH ranges (1.7 to 5), what led the authors to conclude that the reaction is given mainly at the nanoparticles surface and not in the bulk, so its pH is not an important parameter as to the other catalysts.

The use of active nano-^{0}Fe, can be an enhancement factor for the Fenton's process, because it can generate Fe^{2+}. Its performance was compared with those of unsupported NZVI and $FeSO_4$ (classic homogeneous Fenton reaction) and the COD removal was very close for the three catalysts. After analyzing the leaching tests, the authors found out that, for the unsupported heterogeneous catalyst, the activity was almost totally due to the leached iron ions (homogeneous reaction, in this case). The supported catalyst showed much less iron leaching but the content of Fe^{2+} in the liquid phase increased due to the catalyst capacity of reducing Fe^{3+}. Even though the iron leaching is not negligible, the supported catalyst, when filtrated and washed after two batches of 120 minutes reactions, kept most of its activity, showing good stability that could reduce operational cost in practical applications significantly with its reusability.

Previous work from our research group pointed out the Fe-Ce-O as a promising heterogeneous Fenton catalyst (Martins et al., 2010). These studies were made upon an olive mill simulated wastewater comprising six of the most common phenolic acids usually present in this type of effluent and eight different catalysts were tested: Fe-Ce-O (laboratorial catalyst prepared by precipitation of the precursors salts of the metals at the molar proportion 80/20, 70/30, 50/50 and 30/70), Fe-Mn-O (commercial catalyst N-150 and laboratorial catalyst at the molar proportion 70/30), Fe-O and Ce-O. The reaction parameters, such as pH, hydrogen peroxide and catalyst loads were evaluated in order to optimize the process. Also, the molar proportions between the two metals of the catalysts, which can be changed during its preparation, were explored to find out the most active system. To assess the efficiency of the Fenton treatment, total phenolic content (TPh) and total organic carbon (TOC) removals after two hours of reaction were measured. Biodegradability enhancement and toxicity reduction were also aiming achievements so the Fenton's process could be a pre-treatment for the effluent before a biological final step. The adsorption of organic matter by the catalyst, the iron leaching from the solid to the liquid phase and, consequently, its stability during several reuses were analyzed in order to discover if the catalyst in question is, in fact, able to be used in this kind of application, since industry requires stable, recyclable catalysts.

As a result of all experiments, Fe-Ce-O 70/30 presented itself as the best catalyst and the optimized process parameters were pH 3, hydrogen peroxide concentration of 244 mM and catalyst load of 1 g.L^{-1}. At these conditions, the TPh abatement was complete and the TOC removal was up to 57 % in 120 minutes of reaction.

During this study, it is important to call attention to the fact that the Ce content improved the activity of the catalyst: yet the Fe-O catalyst presented better results than the Ce-O, the Fe-Ce-O catalysts in all molar ratios had better TPh abatement and TOC removal than Fe-O – being the Fe-Ce-O 70/30 the most active. This can be explained by the synergetic effect between these two metals related with the more efficient electron transfer due to the presence of the Ce (Chen et al., 2001; Rocchini et al., 2002).

Although even the most active catalyst (Fe-Ce-O 70/30) did not remove enough organic matter for the effluent to be disposed directly in the water courses, this pre-treated wastewater can be biologically processed in order to obtain higher TOC removal with the integrated treatments. This possibility was assured by the biological oxygen demand and respirometric tests, which showed that the pre-treated effluent is biologically consumable (BOD_5/COD ratio of 0.95) as compared to the initial effluent (BOD_5/COD ratio of 0.35), meaning that the toxic compounds for the biological treatments are transformed into innocuous molecules by the Fenton's process. To ensure that, toxicity of the initial and treated effluents were evaluated through luminescence techniques using the marine bacteria *Vibrio fisheri* and these tests showed that the Fenton's process is also successful in reducing the toxic compounds present in the wastewater.

The metal leaching from the catalyst to the liquid phase, an important issue, was evaluated through atomic absorption of Fe, since cerium oxide is reported to be insoluble in water. The evolution of iron leaching along the reaction for pH values of 2.0, 3.0 and 4.0 shows that the pH has great influence in this regard: at pH 2.0, the leaching reaches values up to 27 % of the Fe initially present in the catalyst, while at pH 3.0 and 4.0, this value decreases to 7 and 2 %, respectively.

As the iron leaching was not null, the heterogeneity of the Fenton's reaction becomes another question because the reaction may be occurring homogeneously due to the leached metals and not in the solid phase. To answer this doubt, the same amount of leached iron during the heterogeneous reaction was added as iron sulfate to react solved in the liquid as homogeneous catalyst. At this strictly homogeneous reaction, TOC removals were 89 %, 11 % and 19 % of the total mineralization obtained in the heterogeneous experiments at pH 2.0, 3.0 and 4.0, respectively. Even though at the most acidic condition the homogeneous TOC removal is very high, for higher pH values the heterogeneous contribution becomes stronger. Also, reinforcing the heterogeneous role in the reaction, the homogeneous tests were carried out using the maximum leached iron values; in other words, the concentration of iron due to the leaching at the heterogeneous process was always lower than that, meaning that the homogeneous contribution would not be as high as the percentages just mentioned.

Another question to solve is the adsorption of organic matter in the catalyst. This obstructs its active sites and only keeps in a different phase the compounds that should be oxidized. However, by elemental analysis this catalyst showed very low adsorption (only 1 % of the initial TOC present in the simulated wastewater), what indicates that the reduction of organic content was effectively obtained by its oxidation and not by adsorption.

In order to evaluate if the catalyst in study is able to be reused keeping its activity, four sequential batch runs were carried out with catalyst reuse. TOC and TPh analysis showed that the activity of the catalyst was not decreased and even a slight enhancement on the effluent depuration seemed to appear in the third reuse. This way, Fe-Ce-O 70/30 becomes an interesting solid to be adapted for industrial use as Fenton's catalyst for wastewater treatment, fully justifying the targets of the present project involving the investigation of adequate reaction systems to be implemented in real treatment plants for continuous heterogeneous operation.

II.3. Fenton-like processes in continuous operation

Literature concerning the continuous and semicontinuous operation of the Fenton-like process is not as vast as there are investigations about the batch mode. Therefore, the degradation of some specific pollutants cannot be found for research purposes. On the other hand, the remediation of other compounds have already been studied many years ago, as is the case of chlorophenols. Commonly used as pesticide, herbicide or disinfectant, this compound is a common priority organic pollutant in water. It is discharged by several industries and has particularities that encouraged its treatment to be broadly studied, such as toxicity (even at low concentrations), formation of substituted compounds during disinfection and oxidation processes (AOPs), phytotoxicity and ability to bioaccumulate in organisms. Advanced oxidation processes have proved their efficiency on the remediation of this pollutant, specially systems relying on the Fenton and photo-Fenton oxidative powers (Pera-Titus et al., 2004).

Although Lücking et al (1998) presented the degradation of chlorophenols through AOP in continuous mode, the Fenton's reaction was only tested batch-wise using iron powder as iron ions precursor (homogeneous catalyst). Nevertheless, graphite and activated carbons were shown to act as heterogeneous catalysts for the activation of H_2O_2. Since all tested activated carbons were also constituted by metals (iron, predominantly), they were materials able to start the oxidative reactions in the same way of other Fenton-like solids. The four activated carbons tested (and their iron content) were: RFZ (90.2 $mg.g^{-1}$), F-300 (4.91 $mg.g^{-1}$), ROW (4.51 $mg.g^{-1}$) and GCW (0.6 $mg.g^{-1}$). After being experimented, the organic charge removal presented by them can be closely related to their iron content, which orders as: RFZ (up to more than 40 % COD removal) >> F-300 (close to 25 %) ≈ ROW (close to 25 %) >> GCW (close to 10 %). Being so, it might be said that the search of new materials able to be used in continuous reactors as Fenton's catalysts could bring interesting new alternatives to the industry, which can also mean important achievements to the environment.

The same pollutant type, pentachlorophenol (PCP), had its remediation studied by Zimbron et al. (2011) in a combined reactor system in continuous operation. In their work, two stirred tank reactors (STR) were set up in sequence. The first reactor was used as a pre-treatment, where the Fenton's oxidation was carried out (residence time of 1.5 h with pH monitoring and control to 3.5, iron concentration of 200 µM and H_2O_2 at 220 to 370 µM). The outlet of the first reactor preceded a second one, a bioreactor with residence time of 5.5 or 10.0 h. To fulfill bacteria needs in order that biological depuration could occur, pH was raised to 7.0 and supplementary nutrient solution was added. At the tested conditions, all PCP degradation occurred on the chemical reactor (Fenton's oxidation), while all TOC consumption occurred on the bioreactor. Recycling tests also rendered interesting results, promoting further TOC abatement. Moreover, strong dependence of the Fenton's process on H_2O_2 concentration was observed, being highlighted the sensitivity of PCP degradation to the oxidant agent dose.

Another great concern of the wastewaters management area is related with the pharmaceutical compounds. Due to their huge variety, the task of finding a common remediation methodology is quite challenging. Therefore, chemical processes were never left out of the depuration systems, either as treatments or as pre-treatments that ensure safety and efficiency of biological plants as final treatment steps. Again, the AOP rise due to their high oxidative power and the Fenton's process is highlighted as an interesting alternative (Silva et al., 2004; Schrank et al., 2005; Klavarioti et al., 2009). Melero et al. (2009) presented a study of heterogeneous catalytic systems for the treatment of pharmaceutical wastewater using a Fenton-like nanocomposite catalyst: Fe_2O_3/SBA-15. Based on preliminary trials in batch stirred tank reactors (STR), reaction parameters (such as temperature, hydrogen peroxide and pH) were optimized in order to start continuous mode operation studies in a fixed bed reactor. To do so, the catalyst (initially in powder form) was extruded with sodium bentonite (an absorbent clay) to prepare pellets ranging from 1.0 to 1.6 mm. A stream containing 10.8 $g.L^{-1}$ of H_2O_2 (which is equivalent to twice the stoichiometric amount to fully oxidize the pollutant) at pH 3.0 and a feed flow of 0.5 $mL.min^{-1}$ was able to promote 50 to 60% TOC removal during 55 hours of reaction. Moreover, the biodegradability was enhanced by BOD_5/COD and average oxidation state (AOS) increase – preparing the outlet effluent ready for conventional biological treatment coupling.

The cloth industry corresponds to one of the major contributors to watercourses pollution (Kunz and Peralta-Zamora, 2002). Part of this sector's residues includes dyes, richly present on textile effluents. The previous sections (homogeneous and heterogeneous Fenton's processes) already pointed out many works relating the capability of applying the Fenton's oxidation on the remediation of several types of dyes. Mesquita et al. (2012) studied the degradation of the Chicago Sky Blue (CSB) dye in a packed bed reactor by a Fenton-like process. The impregnation of an activated carbon (Norit RX 3 Extra) with ferrous sulfate was used to produce the catalyst, which showed good performance both in catalytic activity (88 % dye conversion and 47 % TOC removal) and stability (less than 0.4 ppm of iron leaching) at 50 °C. The optimum H_2O_2 concentration was found to be 2.25 mM, which corresponds to twice the stoichiometric amount. The studied temperatures were 10, 30, 50 and 70 °C and, although the highest temperature presented higher dye conversion, 50 °C was the chosen one because no further TOC removal was observed after this temperature. The steady state was reached after 40-50 minutes and the same performance was attained in three consecutive cycles of 5 hours each on the treatment of a 0.012 mM CSB solution.

A solution of the model compound Alcian Blue-tetrakis (methylpyrinidium) was used to simulate another textile effluent and its remediation was studied by Duarte et al. (2013). In this work, the same technique mentioned on the paragraph above was used to produce a catalyst, used on a fixed bed reactor. To treat a synthetic mixture of dye at 0.01 mM, the best conditions were found to be: H_2O_2 concentration of 30 mM, pH of 2.5 and temperature of 50 °C. This way, more than 93 % of dye conversion and 54 % TOC removal could be attained at steady-state. Afterwards, the same conditions were applied on the treatment of a real wastewater and even better results were obtained: 97 % discoloration and removals of 74, 66 and 72 % for TOC, COD and BOD_5, respectively. Another remarkable result was the iron leaching, found to be less than 1.25 % of the total iron present in the catalyst after 60 h of operation.

The Fenton's reagent has also been used to treat a substance commonly found in the pharmaceutical, petrochemical and chemical industry, the phenol. Phenol and phenol-like compounds are highly toxic to microorganisms, present high COD and low biodegradability (Katzer, 1976). Therefore, chemical treatments are required, at least as pre-treatments before further biological depuration can be applied. In this regard, Martínez et al. (2007) evaluated the catalytic wet hydrogen peroxide oxidation of a phenolic effluent in a fixed bed reactor using an iron oxide supported over mesostructured silica (Fe_2O_3/SBA-15) as catalyst. Under optimal conditions, complete phenol abatement and 66 % TOC removal could be attained (residence time of 3.8 min, temperature of 80 °C, feed flow rate of 1 $mL.min^{-1}$, pH of 2.7 and initial concentrations of 1.0 $g.L^{-1}$ (phenol) and 5.1 $g.L^{-1}$ (H_2O_2, stoichiometric amount of H_2O_2 to achieve full phenol mineralization).

Botas et al. (2010) published a study of continuous Fenton-like for phenol depuration in a fixed bed reactor. The tested catalysts consisted on iron oxides (mainly hematite, Fe_2O_3) over different silica supports (mesostructured SBA-15 silica and non-ordered mesoporous silica). Direct incorporation of the metals during the synthesis or post-synthesis impregnation methods were used to immobilize the iron species. With different silica supports and immobilization techniques, 6 solids were used and their efficiency was compared according to their catalytic activity in terms of phenol and TOC abatements as well as stability over time. This work's results show that the synthesis methodology has great importance on the stability and dispersion of the active species, where direct synthesis, either in presence or absence of a structure-directing agent was highlighted as best option. Mesostructured Fe_2O_3/SBA-15 (solid synthesized with a structure-directing agent) resulted as the most active solid, with 65 % TOC removal, and Fe_2O_3/SiO_2(DS) (absence of structure-directing agent). The stability of these solids is another interesting characteristic, since their iron leaching was found to be low when compared to those prepared by impregnation (below 15 ppm against 130 ppm, respectively). The study mentioned on the last paragraph (Martínez et al., 2007) gave basis to the reaction conditions used: residence time of 3.8 min, temperature of 80 °C, feed flow rate of 1 mL.min^{-1}, pH of 2.7 and initial concentrations of 1 g.L^{-1} (phenol) and 5.1 g.L^{-1} (H_2O_2).

Ferentz et al. (2014) tested the deposition of Au nanoparticles in structured TiO_2 nanocrystals (4.5 to 30 nm) and observed stable activity to be increased from 2.0 to 2.8 times, according to the Au particle size. It was also observed that the smaller Au nanocrystals (3 to 4 nm) would aggregate, leading to deactivation after 50 h, while larger Au nanocrystals (7 to 8 nm) would last much longer, 300 h, without deactivation. Inside pH ranges from 2 to 3, neither Ti or Au leached from the catalyst during the catalytic wet peroxide oxidation (CWPO). At proper conditions (initial phenol concentration of 200 ppm, temperature of 80 °C, pH of 2.5, residence time of ≈ 16 minutes), the system was able to achieve 95 % mineralization.

Our research group has already started to investigate the Fenton's process at continuous operation, using iron shavings, zero valent iron (ZVI), as catalysts in a packed bed reactor to treat a simulated olive mill wastewater (Martins et al., 2013). One of the advantages of using iron shavings is its low cost and high reactivity as Fenton's catalysts. Additionally, this system includes a solid waste valorization that is benign for environment protection. In the mentioned work, other solids were tested as well, such as sepiolite and red volcanic rock, but those resulted as much less promising catalysts. In batch mode, interesting ZVI results were found on the abatement of model compounds (phenolic acids) from a synthetic effluent using 40 g.L^{-1} of iron shavings, 35 mM of hydrogen peroxide and pH 3.0 at room temperature: 94, 60 and 54 % TPh, TOC and COD removals, respectively. Moreover, these results were confirmed when the same conditions were applied to a real wastewater. High removals were also achieved in continuous mode for 158 h, in which a column was filled with ZVI and, with a flow rate of 1 mL.min^{-1} (residence time of 11.5 minutes), pH 3.0 and 35 mM of hydrogen peroxide (same conditions previously optimized in batch mode): 73, 44 and 39 % TPh, TOC and COD removals. This study showed that ZVI can be applied for wastewater treatment both in batch and continuous modes with high catalytic activity.

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Part B. **Ceramic Catalysts**

As the reader reaches the second part of this work, being already alarmed about the importance of water saving through wastewaters treatment and already presented to the Fenton's process alternative, ceramic catalysts arise as the next topic.

Several metal combinations have been tested as Fenton's catalysts, such as cerium, copper and cobalt (always coupled with iron). They will all be discussed on this part of the document, along with other investigated subjects as calcination temperature of the solids (chapter III) and the co-oxidation phenomenon (chapter IV).

III. Heterogeneous Fenton using ceria based catalysts: effects of the calcination temperature in the process efficiency[1]

The need of more efficient solid catalysts for the heterogeneous slurry Fenton's process led many investigators to research new compounds' activities. Ceria based iron catalysts have proved their good performance enhancing the removal of organic compounds, reducing toxicity and improving biodegradability in the depuration of phenolic wastewaters. This work evaluates the calcination temperature during the preparation of the catalysts – co-precipitation of the precursors salts, while reaction conditions previously optimized in our research group were adopted (pH = 3.0, 1.0 g.L^{-1} of Fe-Ce-O 70/30 as the catalyst, [H_2O_2] = 244 mM and 120 minutes of room temperature reaction) to treat a simulated wastewater comprising 0.1 g.L^{-1} of each of six phenolic acids commonly found in Olive Mills wastewaters. The three obtained solids were characterized regarding superficial area, average pore diameter and XRD. Catalysts calcinated at 300 °C, 600 °C and 1000 °C presented superficial areas of 188, 86 and 2 m^2.g^{-1}, respectively, and their average pore diameter are 66, 87 and 151 Å, correspondingly. As showed in the XRD, the increase of the calcination temperature promotes the cristallinity of the obtained solid – higher amount of prominent peaks, meaning that the catalysts have different states of valence for iron (Fe^{2+} or Fe^{3+}) and Ceria (Ce^{2+} to Ce^{4+}), what would explain their singular behaviors during the reaction. As expected, the solids with higher superficial areas had better performances in every aspect: more COD, TOC and phenolic acids removal, pointing the lowest calcination temperature as leading to a more efficient solid to enhance hydrogen peroxidation, involving, however, more metal leaching. The higher the calcination temperature is, the more oxidized the solid will become because the calcination occurs without atmospheric control and so the oxygen contained in the air will interfere on the valence of iron ions at the solid's surface. This means that a solid calcinated at a higher temperature will have increased Fe^{3+} content and, as can be found in the literature, Fe^{2+} is faster than Fe^{3+} at hydrogen peroxidation, explaining the initial higher efficiency of the catalyst calcinated at the lowest temperature. Toxicological and biodegradability studies were still performed and showed enhancement in all cases.

III.1. Introduction

People's needs, which once were simple, have greatly increased through ages. The meaning of the word "evolution" sometimes only encompasses the fulfilling of those needs, without noticing that this thirst becomes, in a certain way, an enemy of life itself. New products are being elaborated every day and, as the number of different substances that happen to be often in our daily activities increases, another necessity – not rarely forgotten, raises: to treat these compounds before disposal. Wastewater treatment, sooner than having practical

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[1] This chapter is based upon the publication Rossi, A.F.; Amaral-Silva, N.; Martins, R.C.; Quinta-Ferreira, R.M. *Appl. Catal. B-Environ.* 111–112 **2012**

application, is a scientific study that needs plenty of effort concerning the environment's welfare – giving priority to remediate the streams of discharge that will reach water courses in order not to damage them.

Fenton's oxidative reaction was discovered in the early 1890's. Basic mechanisms for the reaction were proposed only almost forty years later (Haber and Weiss, 1932; Bray and Gorin, 1932). Even today there is still a polemic argumentation over which pathways Fenton's reagent may have to oxidize compounds. Although the mechanisms are not well enlightened, this reaction became a very powerful method of wastewater treatment as an advanced oxidation process that has the advantage of occurring at mild conditions. Before reaching industrial scale, procedure studying and efficiency evaluation are fundamental so the system can be optimized to economically fit the meanings to an end. Homogeneous Fenton's process was firstly investigated and literature can be found in the remediation of different kinds of effluents: olive mill wastewaters (Ahmadi et al., 2005; Cañizares et al., 2007;. Gomec et al., 2007; Kallel et al., 2009), winery (Mosteo et al., 2006; Mosteo et al., 2008), pesticides (Wang and Lemley, 2003). Besides specific studies, there are also reviews and overviews that can be consulted to obtain overall knowledge comprising several aspects of the reaction separately, such as the works of Neyens and Bayens (2003) and Bautista et al. (2008).

Although different conclusions are taken according to the effluent being handled and the objective of the work (that may focus economic viability, remediation of the wastewater, biodegradability enhancement, color removal, among others), one will find that the most crucial problem laying at the homogeneous Fenton's process is the formation of ferrous sludge – another waste that will require a separation step and further treatment. Avoiding this unwanted drawback, heterogeneous Fenton's process is raising as the natural development of the former procedure. Instead of adding iron ion (Fe^{2+} or Fe^{3+}) precursors, such as the commonly used $FeSO_4.7H_2O$, $FeCl_3$ or $Fe(NO_3)_3.9H_2O$, the heterogeneous method lays that the iron catalyst will be present but not dissolved, being, instead, impregnated at the surface of a solid. Activated carbon (Dantas et al., 2006), polymer encapsulation (Shin et al., 2008), silica (Gemeay et al., 2003), clays (Carriazo et al., 2003; Letaief et al., 2003), metallic oxides (Costa et al., 2008; Guimarães et al., 2009) have been part of the vast investigation regarding iron supports. Our investigation group has recently screened heterogeneous catalysts based on cerium, manganese and iron oxides, finding promising results with the former one. Different molar proportions of iron-to-cerium were then tested and had their efficiencies evaluated, being possible to observe that the most active cerium based iron oxide has the proportion Fe/Ce of 70/30 (Martins et al., 2010). Cerium has proved its good efficiency in different advanced oxidation processes such as catalytic wet oxidation (Silva et al., 2003; Lopes et al., 2007), and ozonation (Martins et al., 2009).

Still aiming the optimization of the process, the present work encompasses another parameter in the preparation of the catalyst above-mentioned (Fe-Ce-O 70/30) that was not yet studied for this solid: the calcination temperature. Experiments results allowed the catalyst's efficiency assessment while treating a simulated olive mill wastewater comprising six of the most common phenolic acids found in this effluent.

III.2. Experimental

III.2.1. Catalyst preparation and characterization

Among the catalysts previously studied by our research group, Fe-Ce-O was highlighted due to its higher efficiency (Martins et al., 2010). This work used three different Fe-Ce-O 70/30 catalysts prepared at the laboratory by co-precipitation of an aqueous solution of the former metallic salts: iron nitrate (Riedel-de-Haën) and cerium nitrate (Riedel-de-Haën) containing the desired molar proportion, 70/30 (other ratios were tested before but this specific one showed higher efficiency). Precipitation is stimulated by an increase on the pH by the addition of 200 mL of a 3 M solution of sodium hydroxide. The precipitate is filtrated, washed with 2.5 L of distilled water, dried at 105 °C for two hours, powdered by manual milling and then calcinated during three hours, as the procedure proposed by Imamura et al. (1985) and Silva et al. (2003). As the present study has the intention of determining the best calcination temperature of the prepared solid regarding removals of TOC, COD and TPh, as well as toxicity annulment and biodegradability enhancement, three temperatures were chosen: 300, 600 and 1000 °C – which will name the catalysts as C_{300}, C_{600} and C_{1000}, respectively, to facilitate comprehension and further discussion.

In order to characterize these catalysts, they were submitted to the following analysis: (i) Brunauer-Emmet-Teller surface area (S_{BET}) determined by an accelerated surface area and porosimetry analyzer ASAP 2000 (Micrometrics) with nitrogen at –196 °C, (ii) X-ray diffraction (XRD) through a conventional and low angle X-ray diffractometer Philips model X-Pert, (iii) mercury porosimetry for porosimetry and pore size distribution assessment at a Poresizer 9320 (Micrometrics), (iv) gas (helium) picnometry in an AccuPyc 1330 (Micrometrics), (v) laser dispersion to particle size assessment (Malvern Mastersizer 2000 – Malvern Instruments) and (vi) scanning electron microscopy (SEM) with a JEOL JSM-5310.

III.2.2. Synthetic effluent stock solution confection

The preparation of the phenolic solution consists in the addition of 0.1 g of six phenolic acids (3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid) to distilled water and further fulfilling to 1 L. To overcome the low solubility of these compounds in water and ensure their dissolution, the solution is submitted to ultrasounds (Crest ultrasounds equipment) during 15 minutes. Afterwards, the pH of the solution is adjusted to 3.0 – with H_2SO_4 or NaOH, in order to obey previously obtained conclusions that affirm that this pH value leads to the best efficiency (Martins et al., 2010). With this methodology, a solution with the characteristics mentioned in Table III.1 was subsequently used.

As showed in Table III.1, the simulated wastewater has high toxicity (this parameter is explained in the next section) and low biodegradability (proven by respirometric tests and LUMIStox analysis), being inappropriate for biological depuration (Lopes et al., 2007) – which emphasizes the necessity of chemical treatment.

Table III.1. Characteristics of the synthetic effluent comprising six phenolic acids at 0.1 g.L^{-1} each.

COD (mg O_2.L^{-1})	1000 ± 80
BOD_5 (mg O_2.L^{-1})	279 ± 56
BOD_5/COD	0.28
TOC (ppm)	418 ± 8
pH	3.3 ± 0.1

EC_{20} (%)	4.5 ± 2.0
EC_{50} (%)	32.2 ± 2.0
Toxicity (%)	67.0 ± 8.0
Biodegradability (%)	2.0 ± 8.0

III.2.3. The Fenton's process itself

Reactions were carried out in 500 mL capacity glass reactors magnetically stirred in which 300 mL of the synthetic effluent stock solution were poured just before the addition of the required amount of catalyst. Then pH monitoring is started with a Crison MicropH 2000 probe inserted inside the reactor and continuously adjusted to 3.0 – with H_2SO_4 or NaOH. The reaction only begins with the slow addition of the desired volume of H_2O_2. At certain time intervals, samples were withdrawn by direct pipetting from the reactor to a vacuum filtration unit (funnel, kitassato and air pump) using a 0.45 µm pore diameter quantitative filter paper to remove the solid catalyst from the liquid phase. Immediately after filtration, NaOH 3 M is added to the filtrated sample in order to raise the pH above 9.5, stopping, this way, the reaction by quenching the remaining H_2O_2, since it interferes with some of the analytical techniques. Samples were then named and stored in the refrigerator at approximately 4 °C until being forwarded to analysis.

III.2.4. Analytical techniques – synthetic effluent and treated samples

Total organic carbon (TOC) analyses were conducted in a Shimadzu 5000 Analyzer coupled with an auto-sampler ASI – 5000A. Total phenolic content (TPh) was assessed colorimetrically by the Folin-Ciocalteu procedure (Folin and Ciocalteu, 1927; Silva et al., 2007) with a T60 U PG Instruments spectrophotometer for absorbance measurement. Standard Method 5220D was utilized to determine the chemical oxygen demand (COD) (Greenberg et al., 1985), in which WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer were used. Biochemical oxygen demand in 5 days (BOD_5) was measured by the 5210B method proposed on the Standard Methods (Greenberg et al., 1985), being the inoculums obtained from garden soil (Martins et al., 2009b). Toxicity assessment was evaluated through the light inhibition of the marine bacteria Vibrio fischeri after 15 minutes of incubation on the presence of the samples – being this analysis essential to infer about the ecosystems harm that may occur by the discharge into natural water courses of the potentially toxic wastewaters. A commercial analyzer LUMIStox (Dr. Lange), which operates according to the standard DIN/EN/ISO 11348, was used to carry out this procedure – consisting in the determination of the wastewater effective concentration that causes the inhibition of 20 % (EC_{20}) and 50 % (EC_{50}) of the bacteria by measuring the intensity of its light glowing before and after 15 minutes of contact with the sample. Also, a liquid static-static (LSS) respirometer was used to evaluate biodegradability and toxicity through respirometric techniques. Biodegradability assessment was made upon the oxygen uptake rate (OUR) of activated sludge (obtained from a winery wastewater treatment plant with volatile suspended solids between 3000 and 4000 mg.L^{-1}) while consuming a completely biodegradable compound (OUR$_{\text{acetic acid I}}$) and compared with the OUR of the same bacteria population being fed by the analyzed sample (OUR$_{\text{sample}}$), according to Equation III.1. Still using the same parameter, toxicity was measured by comparing the OUR while consuming acetic acid (OUR$_{\text{acetic acid II}}$) of the bacteria after being exposed to the potentially toxic sample, as in Equation III.2.

$$Biodegradability_{\%} = \left(\frac{OUR_{sample}}{OUR_{acetic\ acid\ I}}\right) \times 100 \qquad \text{(Eq. III.1)}$$

$$Toxicity_{\%} = \left(\frac{OUR_{acetic\ acid\ I} - OUR_{acetic\ acid\ II}}{OUR_{acetic\ acid\ I}}\right) \times 100 \qquad \text{(Eq. III.2)}$$

Oxidation/reduction potential (ORP) and pH monitoring were carried out with a Crison micropH 2000. A spectrometer Perkin-Elmer 3300 was used to quantify the iron leaching to the liquid phase.

In order to assess sample’s hydrogen peroxide content, QUANTOFIX® Peroxide 25 test strips were employed. Once the concentration in the bulk is much higher than the measuring kit’s sensitiveness, samples are diluted to 1:1000, 1:2000, 1:5000 and 1:10000. To each diluted solution, a strip is used to measure peroxide content. The given value is then multiplied to the corresponding dilution factor – the highest and the lowest results are discarded while the others have its media calculated. The use of four dilutions has the intention of diminishing errors (found out to be close to 15 % through peroxide stock solution concentration determination by the strips) and improving accuracy, since the result is given though color comparison between the used strip and a pattern – a sensitive analysis that depends on the manipulator’s decision. This procedure requires to be made without any delay due to the fast and spontaneous hydrogen peroxide decomposition.

III.3. Results and Discussion

III.3.1. Fresh catalyst characterization

Even though the composition of the three catalysts is the same, the change of the calcination temperature imposes singular properties to the resulting solid and these can be seen in Table III.2.

Figure III.1.A illustrates fresh catalysts' gas adsorption isotherms. According to Figueiredo and Ribeiro (1989): (i) C_{300} and C_{600} isotherms are correspondent to standard isotherms type IV, characterized by the hysteresis phenomenon and the presence of an elbow; a solid that presents this kind of isotherm usually has mesopores. (ii) C_{1000} isotherm corresponds to a standard isotherm type II, meaning that this solid either has no pores or has macropores. Numerical values are presented in Table III.2.

Table III.2. Catalysts characterization.

Catalyst	C_{300}	C_{600}	C_{1000}
Calcination Temperature (°C)	300	600	1000
B.E.T. Surface Area ($m^2.g^{-1}$)	188	86	2
Average Pore Diameter (Å)	66	87	151
Single Point Total Pore Volume ($cm^3.g^{-1}$)	0.311	0.189	0.008
Average Density ($g.cm^{-3}$)	3.99	5.41	5.72

Figure III.1.B shows the relation between pore volume and diameter. The curves indicate that C_{300} and C_{600} have most of their pores within diameters smaller than 100 Å, while C_{1000} has much greater ones. These data interpretation is ensured by the single point total pore volume, which decreases with the raise of the calcination temperature, and the opposite happens regarding the average density. Through Table III.2, one can conclude that C_{300}'s pores have a smaller diameter and large volume. The same happens to C_{600}, but for C_{1000} the pore diameters are wide their total pore volume is very small. This also explains the great differences between the surface areas: small amount of great sized pores leads to lower superficial area (C_{1000}) while a higher number of deeper pores (despite of the reduced diameter) "enlarge" the available surface (C_{300} and C_{600}).

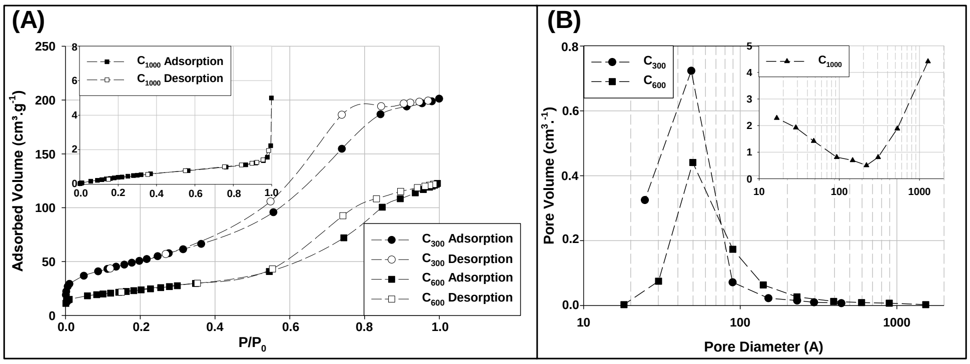

Figure III.1. Fresh solids characterization: **(A)** Gas adsorption isotherms (adsorbed volume versus relative pressure). Inlet: C_{1000} curves, which have a lower scale; **(B)** Pore size versus pore volume graphs. Inlet: curve for C_{1000}, which has a greater scale.

In order to evaluate another solid's aspect that might correlate its structure and catalytic behavior, X-Ray Diffraction characterization analysis was performed. While C_{300} shows a completely amorphous pattern without any cristallinity, C_{600} has an increase in both of these characteristics and C_{1000} is the opposite, exhibiting strong peaks, indicating that a higher calcination temperature leads to a more crystalline solid.

Cerium oxides present a quite important property during the calcination process. CeO_2 are capable of interacting with other metal oxides changing the metal valence state in the composite. The strong affinity and interaction between CeO_2 and Mn_2O_3 were discussed by Imamura et al. (1986). When these structures are in contact at temperatures over 150 °C, Mn^{2+} species begins to appear. We believe that the same process might occur when iron oxides are in contact with cerium oxide, explaining the reducing of Fe^{3+} (iron nitrate, the precursor) to Fe^{2+} (present in the catalyst). We also believe that this interaction might happen while the Fenton reaction occurs: as the iron begins to be oxidized, the cerium (which is in the same solid) might exchange electrons and enhance the catalyst overall activity.

III.3.2. Used catalyst characterization

After being used at Fenton's process, all catalysts were dried inside an oven at 105 °C and analyzed again to evaluate its properties and check for any changes. The results disposed in Table III.3 will be showed along this section and commented until the end of it.

Table III.3. Used catalysts characterization.

Catalyst	Used C_{300}	Used C_{600}	Used C_{1000}
Calcination Temperature (°C)	300	600	1000
B.E.T. Surface Area ($m^2.g^{-1}$)	175	128	5
Pore Diameter (Å)	69	71	91
Single Point Total Pore Volume ($cm^3.g^{-1}$)	0.299	0.227	0.011

Figure III.2.A illustrates used catalysts' gas adsorption isotherms. To the Used C_{300} and Used C_{600} isotherms are given the same classification (type IV: hysteresis and elbow, indications of mesopores). Only minor changes exist between used catalysts and the fresh ones. Yet former catalysts' isotherms remained almost unchanged, Used C_{1000} continues presenting a type II isotherm but with the hysteresis phenomenon type H3, classifying the solid as a non-rigid aggregate of particles in plate form, originating cleft-shaped pores.

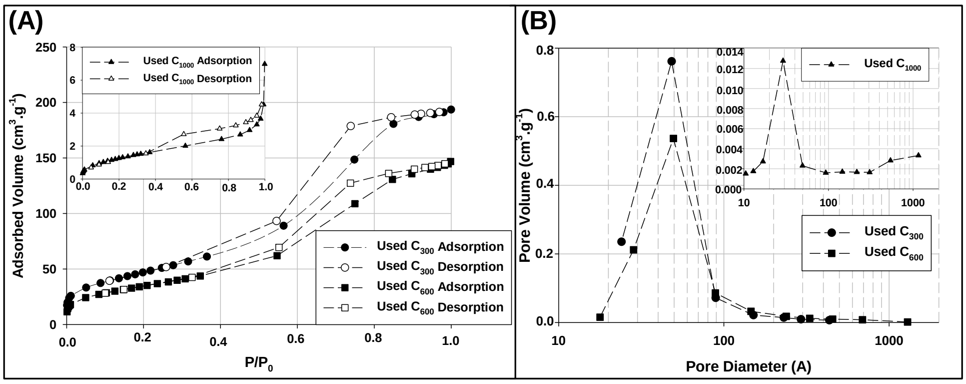

Figure III.2. Used solids characterization: **(A)** Gas adsorption isotherms (adsorbed volume versus relative pressure). Inlet: C_{1000} curves, which have a lower scale; **(B)** Pore size versus pore volume graphs. Inlet: curve for C_{1000}, which has a greater scale.

Comparing Used C_{300} and C_{300}, one may notice that pore diameter has slightly increased while single point total volume and B.E.T. area decreased – the opposite of what happened to the other solids after reaction. This fact can be explained by the change on the calcination temperature: higher values generate denser and more resistant solids, which will be confirmed by leaching tests, showed and commented in section III.3.4.3. Figure III.2.B shows the pore distribution for the used catalysts, where one can see that there are no significant changes.

All catalysts (fresh and used) have had their images at three different scales taken – namely, x350, x2000 and x5000 by SEM. The following sections (III.3.2.1, III.3.2.2 and III.3.2.3) will be used to show those images and include a brief discussion about them.

III.3.2.1. Fe-Ce-O 70/30 catalyst baked at 300 °C.

It is not hard to notice the “structure loss” over the reaction comparing pictures of fresh and used C_{300} – Figure III.3. On the fresh images (Figure III.3.A), the aggregates are bigger and have more “grainy attachments” while the used catalyst’s surface (Figure III.3.B) seems flat and with just a few small structures attached onto the aggregates.

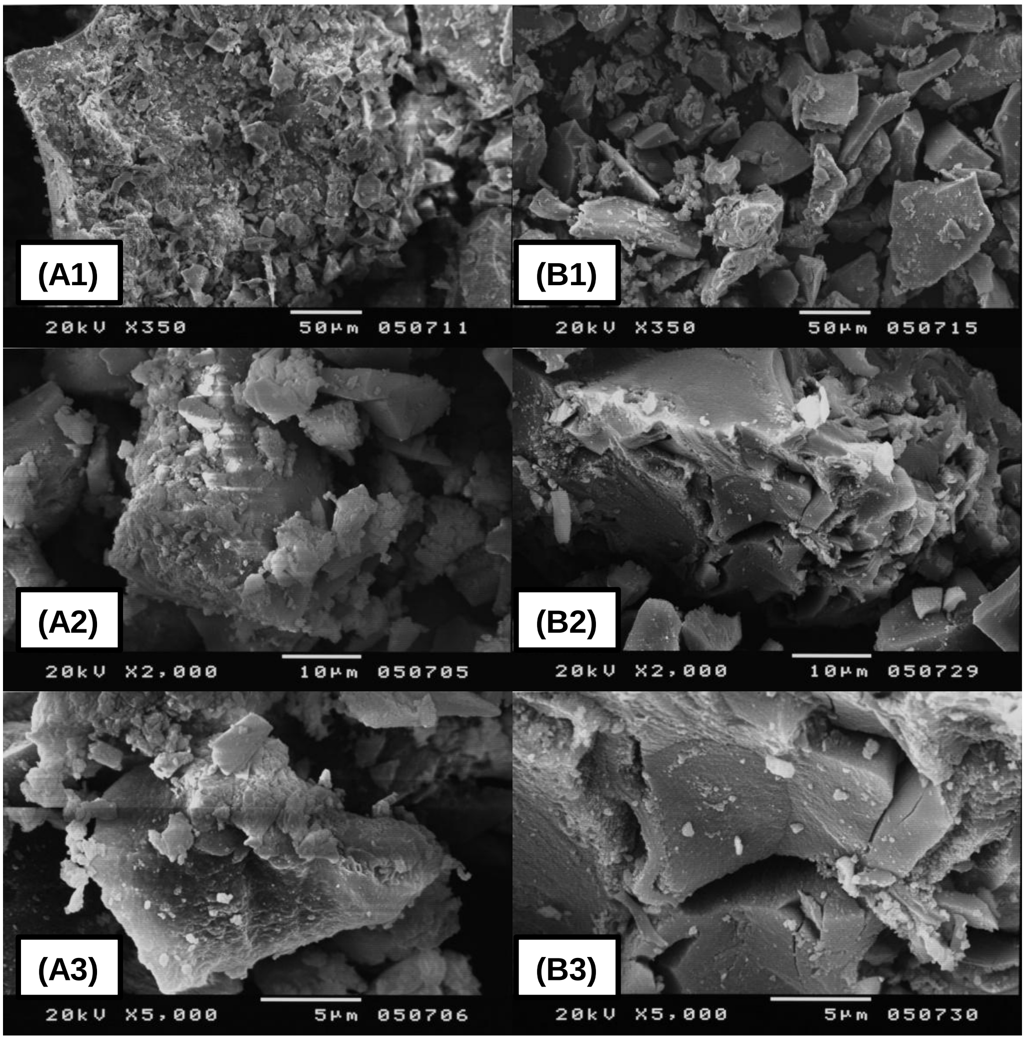

Figure III.3. SEM images showing several magnifications of fresh **(A)** and used **(B)** Fe-Ce-O calcinated at 300 °C.

III.3.2.2. Fe-Ce-O 70/30 catalyst baked at 600 °C.

On C_{600}'s images, one can see that the fresh catalyst (Figure III.4.A1) is not as homogeneous as the used (Figure III.4.B1). Although this indicates that the catalyst is broken into smaller pieces due to the reaction agitation, the higher magnitude pictures (Figure III.4.A2 against Figure III.4.B2 and Figure III.4.A3 against Figure III.4.B3) comparison shows that a considerable part of the grainy structures attached to the aggregates is still there.

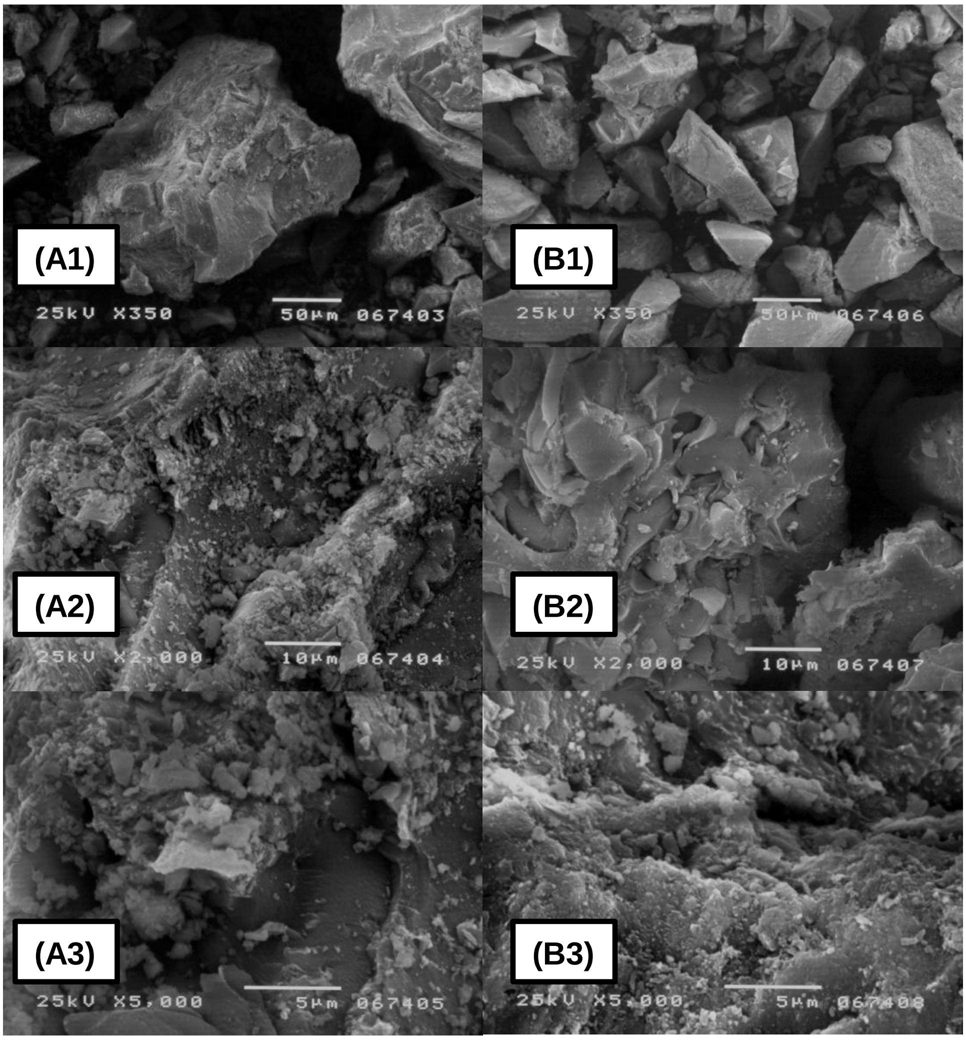

Figure III.4. SEM images showing several magnifications of fresh **(A)** and used **(B)** Fe-Ce-O calcinated at 600 °C.

III.3.2.3. Fe-Ce-O 70/30 catalyst baked at 1000 °C.

At last, C_{1000}'s illustrations (Figure III.5) reveal that the catalyst calcinated at the highest temperature is the one that remains with less significant structural changes. On a naked eye comparison, the aggregate's sizes for the fresh and used solids (Figure III.5.A and Figure III.5.B) seem closer and also the grainy surface aspect is kept.

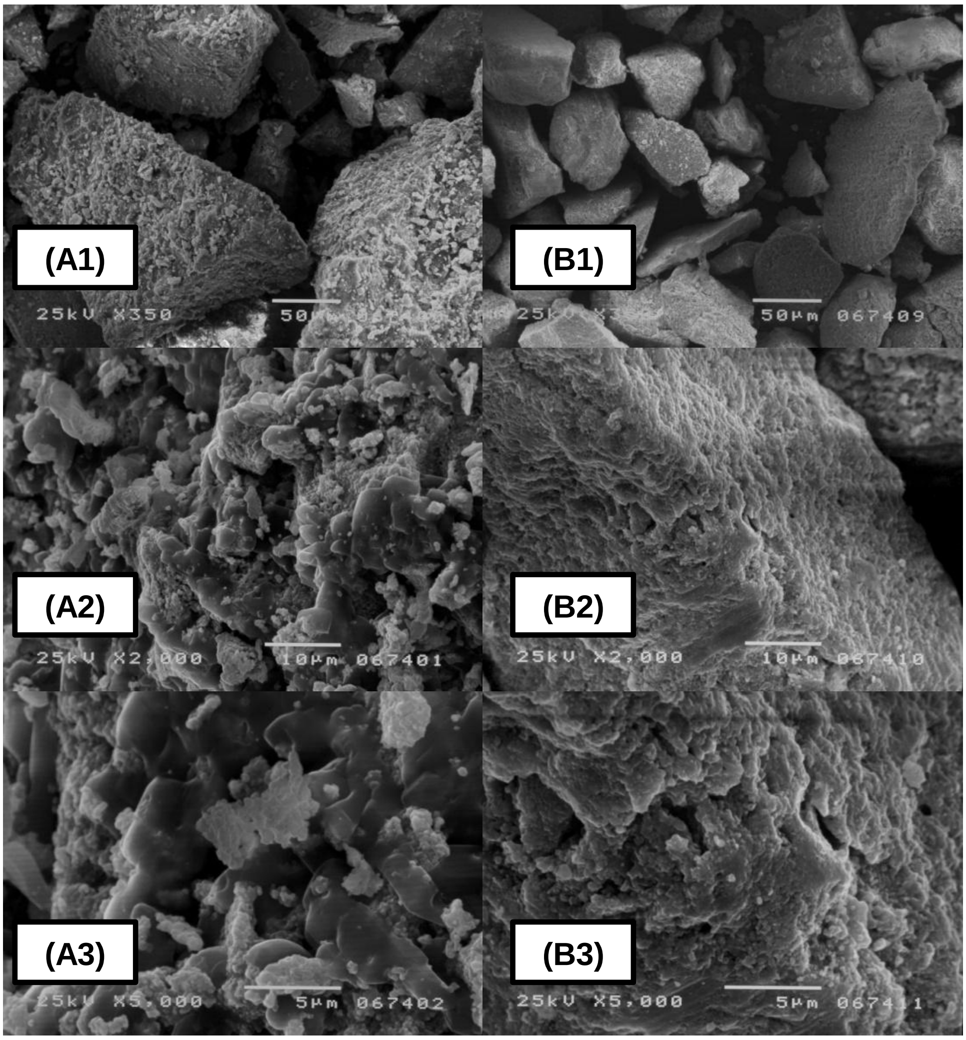

Figure III.5. SEM images showing several magnifications of fresh **(A)** and used **(B)** Fe-Ce-O calcinated at 1000 °C.

III.3.3. Preliminary Results

As our investigation group has worked with these kind of wastewater for a long time, plenty of experience has been acquired and optimal reaction parameters are already established, such as pH = 3.0, $[H_2O_2]$ = 244 mM and [Fe-Ce-O 70/30] = 1.0 $g.L^{-1}$. Other tests were useful to ensure that: (i) for the present catalysts at these conditions, the chemical regime is applied (negligible mass transfer resistances), (ii) hydrogen peroxide alone cannot significantly oxidize the compounds (without the addition of catalyst), (iii) the catalyst just by itself removed negligible organic matter by adsorption (without hydrogen peroxide addition) (Martins et al., 2010).

III.3.4. Influence of the calcination temperature

Next sections (III.3.4.1, III.3.4.2 and III.3.4.3) are reserved to discuss each catalyst's experiment, featuring Fenton's process efficiency assessment in every considered aspect.

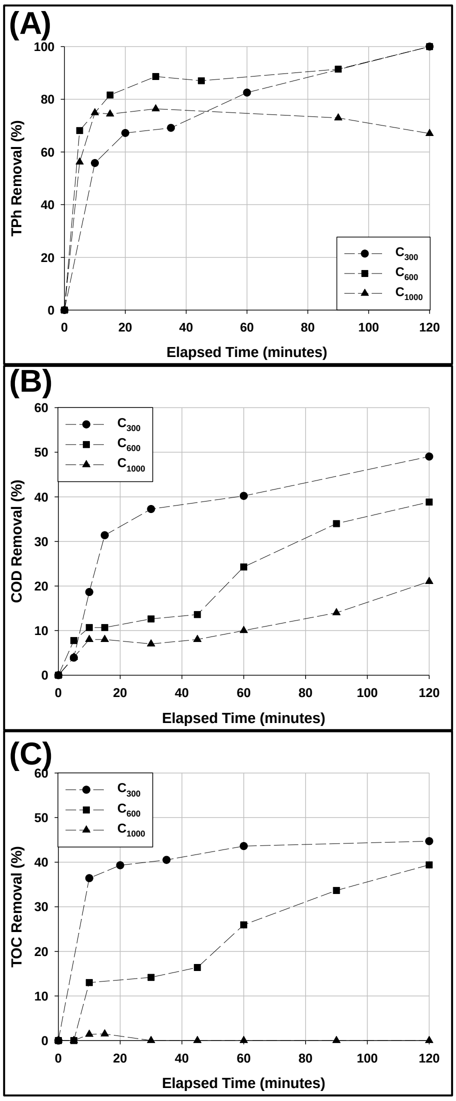

Figure III.6. Organic charge removal profiles along the experiments. **(A)** Total phenolic content; **(B)** Chemical oxygen demand; **(C)** Total organic carbon. Reaction conditions: [catalyst] = 1 g.L^{-1}, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C).

III.3.4.1. Organic charge depletion

As mentioned before, the synthetic effluent is composed by a mixture of six phenolic acids, with each one contributing for the increase on the TPh. It is already well known that Fenton's oxidation can easily break these aromatic bonds and this was once more observed in this work's results (Figure III.6.A), where C_{300} and C_{600} completely depleted these compounds. The reaction rate of phenolic destruction is high at the beginning of all experiments (over 70 % of the final removal is achieved in less than 20 minutes) and decays along the reaction probably due to the rapid concentration decrease and the formation of refractory phenolic by-products. As opposed to the other catalysts, C_{1000} was the only one that could not entirely remove the phenolic content (only approximately 70 % after two hours), pointing this solid's activity as the lowest. C_{1000}'s low activity was also observed regarding COD removal (Figure III.6.B). Its final depletion reached merely half of the one obtained by C_{600} (21 % and 39 %, respectively). The best result was attained by C_{300}, 49 %. Again, one can notice that the reaction rate decreases along time. This can be probably related to the intermediate compounds created during the experiment that become harder to oxidize as the reaction occurs, besides the fact of the arise of some refractory substances.

COD has a link with TOC and, therefore, their removals are meant to have some resemblances. Usually, TOC is removed after COD depletion, meaning that the effluent's organic substances are oxidized (COD removal), breaking molecules in smaller pieces until the limit, CO_2 and H_2O, when mineralization takes part (TOC removal). This can easily be noticed by analyzing Figure III.6.B and C. The first one shows the gradual reduction of COD, although in different levels, attained by the three catalysts. However, as shown in the second graph, when it comes to the C_{1000} related curve, negligible TOC reduction is observed – meaning that even though COD was reduced, no mineralization occurred, indicating that the reaction goes on toward oxidation but cannot get rid of small and more oxidized molecules to produce CO_2. Again, the best results for these removals were C_{300}'s, which are much higher than the others.

III.3.4.2. Biodegradability and toxicity assessment

As previous sections results showed, the organic load removal was not sufficient for the effluent to be directly disposed – therefore, further treatment is required. Being biological plants the most recommended, biodegradability enhancement and toxicity annulment gain great importance, since phenolic wastewaters are hardly consumable by microorganisms due to its high toxicity and low biodegradability.

Although all catalysts were able to completely (or almost completely) degrade the phenolic content, each of them presented different values of degradation by bacteria – biological oxygen demand in five days (BOD_5), meaning that not only the phenols are poisonous, but so the reaction intermediate compounds are.

As yet Fenton's reaction mechanisms are not fully traced, it is impossible to determine which molecules are harmful and which are not. Therefore, regarding final judgment, the most important sample in each experiment is its last point – at the end of the two hours reaction, because this treatment was optimized to this time. An important note is that one cannot ensure that from the beginning to the end of the reaction, the biodegradability or toxicity marches its way only increasing or decreasing. That depends on the compounds generated and eliminated by oxidation and yet is not possible to follow the bulk's (effluent) composition that closely.

BOD_5 is the primal and most reliable analysis, since toxicity through respirometry and LUMIStox sometimes creates confusion in the results discussion and affirmative conclusions are harder to be taken; besides, BOD_5 represents biodegradability examinations when the sample keeps in contact with a population of bacteria during five days – much longer than the 15 minutes of LUMIStox or the couple of hours that respirometry usually takes, analyzing, this way, not just the immediate impact but giving also time for the bacteria to recover from their exposition to a new media. This data set is presented in Table III.4 along with the respective COD values and the ratio BOD_5/COD, which represents the fraction of oxygen that can be oxidized biologically. The analysis of these data shows that the higher was the temperature that the catalysts had been exposed, the lesser was the toxicity removal after the experiments. C_{300} enhanced the BOD_5/COD ratio from 0.30 to 0.76. C_{600} was also able to elevate this value to 0.55 but, on the other hand, C_{1000} made the samples even harder to be oxidized by the microorganisms than the raw effluent, because toxic compounds may have been generated without being further degraded.

Table III.4. Biological oxygen demand after 5 days (BOD_5) compared with chemical oxygen demand (COD) along with the biological/chemical oxygen demand ratio. Left side: raw effluent. Right side: treated effluent (Experiment conditions: [catalyst] = 1.0 g.L^{-1}, [H_2O_2] = 244 mM, room temperature).

Raw Effluent			Treated Effluent			
BOD_5 (mg O_2.L^{-1})	279		Catalyst	BOD_5 (mg O_2.L^{-1})	COD (mg O_2.L^{-1})	BOD_5/COD
COD (mg O_2.L^{-1})	930		C_{300}	372	489	0.76
BOD_5/COD	0.30		C_{600}	349	630	0.55
			C_{1000}	0	790	0.00

LUMIStox values, in percentage, are displayed in Figure III.7.A (EC_{20}) and Figure III.7.B (EC_{50}). As discussed before, the raw effluent, by itself, presents a certain value of toxicity. A solution containing 4.5 % of it is able to inhibit 20 % of the bacteria Vibrio fischeri, while a concentration of 32.2 % is required to inhibit 50 % – that is the start line for all catalysts.

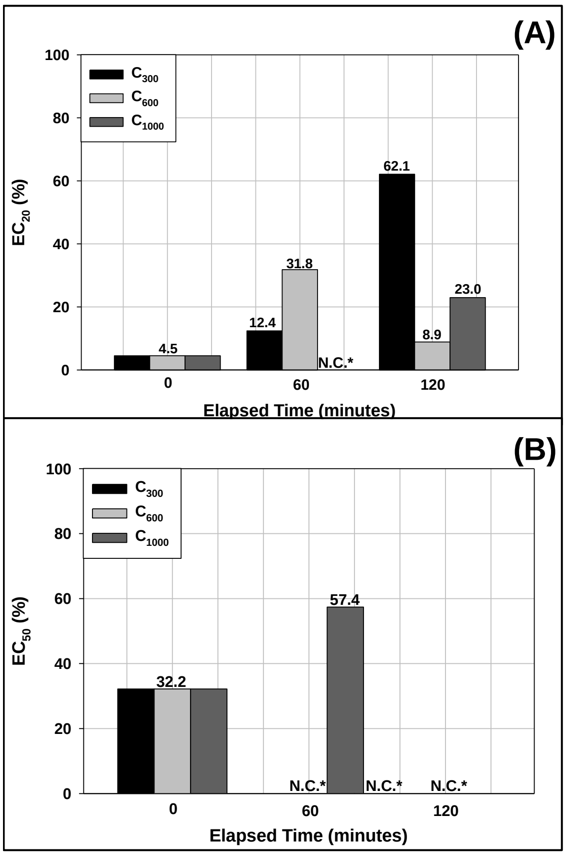

Figure III.7. Vertical bar plots along the experiments: **(A)** EC_{20} (%); **(B)** EC_{50} (%). *N.C.: non-calculated value.

Regarding C_{300}, one can see that the required amount of sample to restrain 20 % of the bacteria rises from 4.5 % to 12.4 % in one hour and to 62.1 % in two hours of reaction, meaning that the toxicity has been depleted during the experiment. Most likely, the concentration of the sample required to be in solution to inhibit 50 % of the bacteria is higher (as in this example). This way, because of the two non-calculated values (N.C.) of EC_{50} related to C_{300} (60 and 120 minutes), we can say that not even the pure sample would interfere sufficiently to inhibit 50 % of the bacteria – meaning that this catalyst was able to reduce the toxicity significantly.

At the first hour of reaction, C_{600} presented a good result, having elevated EC_{20} from 4.5 % to 31.8 % and a non-calculated value of EC_{50} that could be still explained as above. But, as the reaction continues for another hour, both values of EC_{20} and EC_{50} are non-calculated and, this time, there are two possible explanations to what could be happening: (i) either the sample is so toxic that even the slightest concentration would be able to inhibit 50 % of the bacteria, or (ii) the sample is not toxic at all and not even the pure sample would be able to inhibit 20 % of the bacteria.

C_{1000}'s results present a different perspective for the first hour of reaction: while EC_{50} rises from 32.2 % to 57.4 %, EC_{20} becomes non-calculated. This N.C. value might be justified by the fact that the sample is still sufficiently toxic to inhibit 20 % of the bacteria even at very low concentrations. This toxicity would be then reduced during the last hour of reaction, once EC_{20} reaches a value of 23 % and EC_{50} becomes non-calculated. Now, it can be compared to the C_{300}'s middle reaction time value. Thus, C_{300} seems to be the most effective catalyst facing eco-toxicity reduction. Once again, the peculiar Fenton's mechanisms for each catalyst do not allow behavior expectations for EC_{20} and EC_{50} patterns due to different intermediate compounds generation.

Respirometry analysis (data shown in Table III.5) confirms and concludes this work biological assessment: higher calcination temperatures generate less efficient solids to act as Fenton catalysts regarding further biological treatment. While C_{300} was able to completely deplete toxicity (from 67 % to zero) and greatly improve biodegradability (from 2 % to 70 %), other catalysts were not able to completely destroy toxic compounds (toxicity remains at 7 % for C_{600} and 10 % for C_{1000}) and their contribution to biodegradability enrichment is not as significant (18 % for C_{600} and only 4 % in the case of C_{1000}).

Table III.5. Toxicity and biodegradability values acquired through respirometry. Left side: raw effluent. Right side: treated effluent (Experiment conditions: [catalyst] = 1.0 $g.L^{-1}$, [H_2O_2] = 244 mM, room temperature).

Raw Effluent	
Toxicity	67 %
Biodegradability	2 %

Treated Effluent		
Catalyst	Toxicity	Biodegradability
C_{300}	0 %	70 %
C_{600}	7 %	18 %
C_{1000}	10 %	4 %

III.3.4.3. Catalyst stability and reaction heterogeneity

Biodegradability enhancement, toxicity annulment, COD, TOC and TPh removals are not the only factors that one may take into account while selecting a catalyst. A solid that has no resistance to maintain its active sites on their own spots is not proper for long-term industrial applications because it would have to be replaced over and over again, generating unnecessary waste of financial resources. Each catalyst of this work had its experiment's final sample analyzed to assess the amount of iron present in solution. This allows the evaluation of the iron leaching and the stability of the catalyst, presented in Figure III.8.A.

Reuse experiments of the same catalyst (Fe-Ce-O) were already carried out by our research group (Martins et al., 2010). This solid did not present significant activity changes even after several sequential feed-batch trials and, so that this matter will not be discussed in this paper.

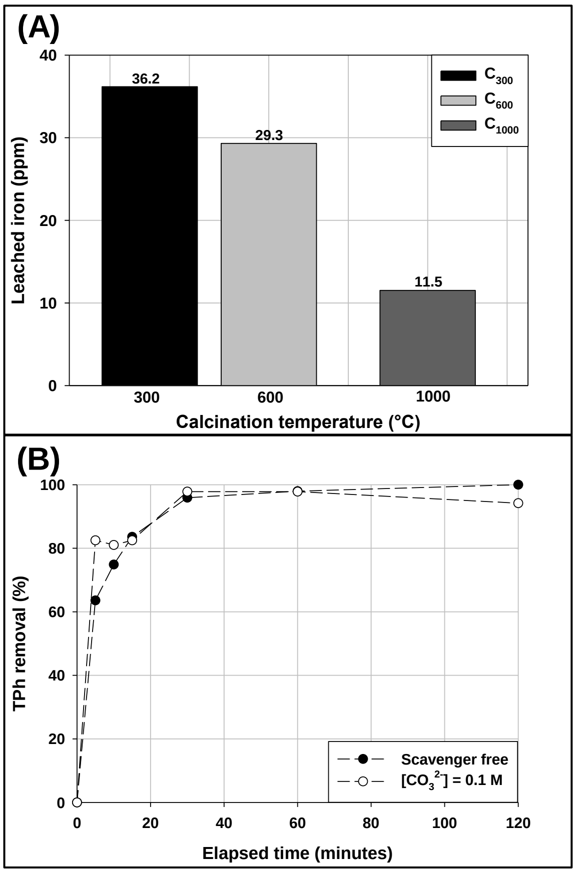

Figure III.8. Iron leaching bar plot for each calcination temperature **(A)** and total phenolic content removal profiles along the heterogeneity evaluation experiments **(B)**. Experimental conditions: [catalyst] = 1 $g.L^{-1}$, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C) and [CO_3^{2-}] = 0.1 M (when applicable).

To evaluate the role of the catalyst in the global reaction, new experiments with scavenger agents were performed, adding carbonates to the bulk, so that the reaction efficiency could be compared with the normal process – without any scavenger addition. No abatement on the process efficiency was observed with CO_3^{2-} addition, as shown for TPh removal in Figure III.8.B, pointing the reaction as mainly driven by surface oxidative reactions rather than by free-radical pathways.

C_{300} was the catalyst selected to be analyzed under scavenging effects for two reasons: (i) it was able to deplete more organic load, being, this way, easier to detect possible efficiency reduction; (ii) it presented the highest iron leaching, and, therefore, more homogeneous reactions were supposed to happen.

Oxidation/reduction potential (ORP) was also followed to evaluate the reaction's capability to oxidize organic matter. The three catalysts' experiments (Figure III.9.A) showed the same values of ORP (measured in the liquid phase), contrarily to the different catalyst behaviors towards COD, TPh and TOC removals, discussed above, revealing that degradation process is indeed mostly undertaken in the catalyst surface. This is strengthened when comparing the higher profiles of ORP of the homogeneous process that has its hydroxyl radicals on the bulk. Figure III.9.B shows the ORP difference between one experiment containing carbonates as scavenger and the normal reaction for the heterogeneous C_{300} catalyst. Through its analysis, one can say that there are indeed hydroxyl radicals on the bulk even for the heterogeneous process, although they have no significant contribution in the system efficiency.

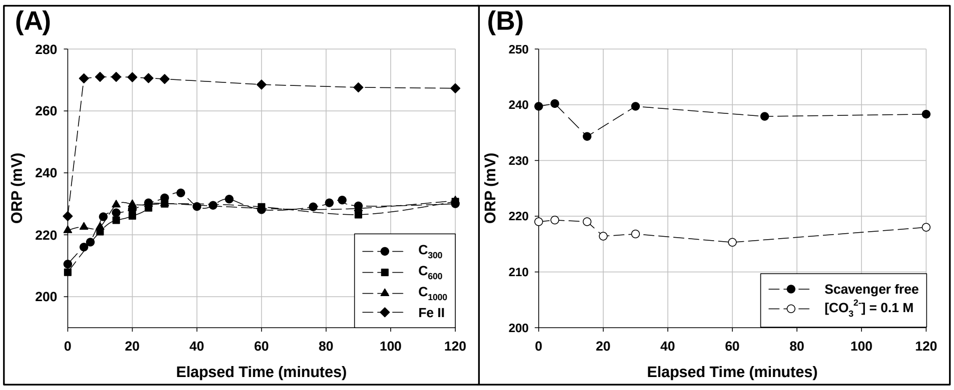

Figure III.9. Oxidation/Reduction Potential (mV) profiles along the experiments for all heterogeneous catalysts. Homogeneous process comparison **(A)** and scavenger experiment comparison **(B)**. Experimental conditions: [catalyst] = 1 g.L^{-1}, $[H_2O_2]$ = 244 mM, pH = 3.0, room temperature (~25 °C) and $[CO_3^{2-}]$ = 0.1 M (when applicable).

III.4. Conclusions

This work evaluates which is the best calcination temperature of a previously studied catalyst (Fe-Ce-O at the molar proportion of 70/30) facing a synthetic effluent treatment through heterogeneous Fenton's process. 300 °C, 600 °C or 1000 °C were the chosen temperature values. Regarding COD, TOC and TPh removals, C_{300} always presented the best results, followed by C_{600} and, at last, C_{1000} – which was the only catalyst incapable of promoting any TOC removal or to achieve complete phenolic content destruction. C_{1000}, besides providing lesser removals, also presented poor biodegradability enhancement and toxicity depletion. C_{600}, on the other hand, achieved a BOD_5/COD ratio of 0.55 at the end of the reaction, but even this value is not comparable to C_{300}'s: 0.76. C_{300} was then tested in carbonate containing bulk to check if the reaction pathways involved the exit of radicals from the solid's surface to the liquid phase and results indicate that the reaction is, indeed, heterogeneous, taking its place on the solid phase (hypothesis also pointed by ORP examination, which showed a lower potential on the bulk that did not contain carbonate). XRD analysis indicated that the higher the calcination temperature, the higher is the amount of Fe^{3+} on the resulting solid's surface, what might explain the better efficiency of C_{300} – the solid that contains more Fe^{2+}. Also concerning catalyst activity, ORP was followed, but this analysis did not showed significant values between the catalysts. Thus, this potential was not important before taking conclusions about the organic charge removal, reinforcing the fact of the reaction being taken on the solid's surface.

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IV. The composition effect of iron-copper composite catalysts in the Fenton's heterogeneous process efficiency and co-oxidation synergy assessment[2]

New iron-copper based solids prepared by co-precipitation had their efficiency in the heterogeneous Fenton's process investigated regarding organic charge removal and biodegradability enhancement. Different molar proportions between the two metals were used to assess the best one. Chemical oxygen demand (COD), total phenolic content (TPh), and biochemical oxygen demand in five days (BOD_5) were the parameters used for evaluation. Two solutions simulated olive mill wastewaters: one comprising six phenolic acids and another containing one extra acid. The efficiency of each catalyst was compared when facing both mixtures and the one containing more phenolic acids was further decomposed, maybe due to a co-oxidation synergistic effect related with the presence of more radicals. All solids proved to be fit for the reaction and the Fe-Cu-O 50/50 catalyst showed the best overall results regarding organic charge removals.

IV.1. Introduction

Fenton's process was discovered by H. J. H. Fenton in the end of the 19th century with the oxidation of tartaric acid into dihydroxymaleic acid by hydrogen peroxide in the presence of ferrous ions (Fenton, 1894). This reaction starts by the dissociation of the oxidant agent (H_2O_2) and the formation of highly reactive hydroxyl radicals (•OH). With elevated oxidation potential, 2.80 volts (Neyens and Baeyens, 2003), these radicals are able to attack compounds non-specifically, degrading them in a chain radical reaction – which makes the tracing of the full degradation pathway very hard to specify in a step by step form. Nevertheless, the basic start-up of the whole process was explained more than 80 years ago: production of hydroxyl radicals followed by autocatalysis (Haber and Weiss, 1932).

Nowadays, this reaction is an important process used for wastewater treatment, since it is able to oxidize both organic and inorganic compounds at mild conditions of temperature and pressure. The advantages of the Fenton process, besides the low energy requirement and cheap reactants, start with good organics abatement. Biodegradability enhancement is another benefit, since some wastewaters present toxic compounds and, therefore, are not able to be sent to biological treatment plants. This chemical reaction can degrade those substances, diminishing the effluent's toxicity. The same happens with seasonal wastes, which do not exist all over the year, discarding the chance of biological processes.

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[2] This chapter is based upon the accepted publication Rossi, A.F.; Martins, R.C.; Quinta-Ferreira, R.M. *Ind. Eng. Chem. Res.* **2014**.

The homogeneous Fenton peroxidation presents all these qualities, but also some negative points: high iron concentrations are required and this metal needs to be separated by precipitation, usually forced by pH elevation, which creates final sludge – another unwanted waste. Studies have been made to avoid those deficiencies, through the so called Fenton-like processes. These comprise the use of metals different from iron and the heterogeneous Fenton's process as well, in which the iron (or even other metal) is supported in a solid that will not dissolve into the bulk so it can be separated by simple filtration at the end of the reaction – not requiring pH increase and, thus, preventing the formation of sludge and reducing costs.

Previous studies from our investigation group analyzed the efficiency of several catalysts prepared by co-precipitation – as in Imamura et al. (1985). Interactions between cobalt, manganese and cerium with iron oxides were investigated and a catalyst composed by iron and cerium at the molar proportion of 70/30 (Fe-Ce-O 70/30) was highlighted (Martins et al., 2010). Further studies included determination of the most indicated calcination temperature for this solid, bringing out the catalyst baked at 300 °C for two hours (Rossi et al., 2012). The present work introduces a new catalyst also prepared by co-precipitation of iron and copper nitrates at five different iron/copper molar proportions: 0/100, 30/70, 50/50, 70/30 and 100/0. These solids were tested as catalysts for the Fenton-like process and their efficiency on the depuration of olive mill simulated wastewaters was compared – a very common effluent in Portugal.

All catalysts were evaluated on the oxidative reaction of two different simulated effluents. The first, containing 0.1 mg.L^{-1} of six phenolic acids and the other with one extra acid (gallic acid) at the same concentration. Since the Fenton's process is a radical reaction, the intention of this study is to compare if the presence of acids (and the products of their oxidation) would interfere in the oxidative power of the procedure. In a previous study, this comparison was made by Lopes et al. (2007), using the catalytic wet oxidation method. Altered oxidation behavior was observed when the pollutants were treated isolatedly from the others compared to mixed solutions. It was stated that the formation of free-radical intermediates might enhance the compounds degradation – the alleged co-oxidation process.

IV.2. Experimental

IV.2.1. Catalyst preparation and characterization

This work evaluated three different catalysts composed by different molar proportions between iron and copper (0/100, 30/70, 50/50, 70/30 and 100/0). Preparation procedure was obtained from Imamura et al. (1985). Firstly, 100 mL of a solution containing 15 g as the sum of both iron (Panreac 98 %) and copper nitrates (and Riedel-de-Haën 99 %) at the desired molar proportion was prepared. Co-precipitation was then induced by the addition of 200 mL of NaOH 3M – solution prepared using NaOH pellets (Panreac 98 %). The resulting mixture was washed several times with an ultrapure water system Milli-Q^{50} (Millipore), left to precipitate and its supernatant was filtered. When 2.5 L of washing water had been used, the final filtration was done to retain the metals at the paper-filter (Double Rings Qualitative filter papers - 102). The washing had the purpose to remove nitrates and the excess of NaOH.

The filter was left at an oven at 105 °C overnight and then the remaining solids were collected, smashed until the formation of a powder and calcinated at 300 °C for 2 hours. The temperature/time was chosen due to recent studies with a similar catalyst (Rossi et al., 2012). For discussion, the catalysts will be named Fe-O, Fe-Cu-O 70/30, Fe-Cu-O 50/50, Fe-Cu-O 30/70 and Cu-O.

Catalyst characterization included the following analysis: Brunauer-Emmet-Teller surface area (S_{BET}) determined by nitrogen adsorption at -196 °C in a Micrometrics ASAP 2000, X-ray diffraction (XRD) in an X-ray diffractometer Philips model X-Pert with Co Kα radiation under operation conditions of 40 kV and 35 mA. Data were collected from $2\theta = 20°–120°$ in 0.025° steps, mercury porosimetry and pore size distribution measurement at a Micrometrics Poresizer 9320 (penetrometer constant 10.683 $\mu L.pF^{-1}$, penetrometer weight 70.84 g, penetrometer volume 5.3905 mL, stem volume 0.392 mL, maximum head pressure 4.45 psia, room temperature) and gas picnometry at a Micrometrics AccuPyc 1330 (cell volume 12.2169 cm^3, equilibration rate: 0.0500 $psig.min^{-1}$, expansion volume 8.2518 cm^3, room temperature). The random errors associated with Micrometrics ASAP 2000 analysis (B.E.T. Surface Area, Average Pore Diameter and Single Point Total Pore Volume) are in the range of ± 0.1 %; for Micrometrics Poresizer (Porosity), ± 1.0 %, and, for Micrometrics AccuPyc 1330 (Average Density), ± 0.03 %.

IV.2.2. Synthetic effluent

One of our research group's major focuses are olive mill wastewaters (OMW). To simulate this kind of effluents, a solution containing 0.1 $g.L^{-1}$ of 6 phenolic acids commonly found in OMW was prepared. They are: protocatechuic acid (Acrós Organics, 97 %), 4-hydroxybenzoic acid (Sigma-Aldrich, 99 %), vanillic acid (Sigma-Aldrich, 97%), 3,4,5-trimethoxybenzoic acid (Sigma-Aldrich 99 %), veratric acid (Sigma-Aldrich, 99 %), syringic acid (Fluka, 97 %). Another intention of this work was to evaluate the synergy created by the addition of one extra acid to the synthetic solution, the gallic acid (Fluka, 98 %). This addition would increase the radicals present in the bulk after the beginning of the oxidation, since the Fenton process is based on a chain reaction. To ensure the dissolution of those compounds, the mixtures are submitted to ultrasounds (Crest ultrasounds equipment) during 15 minutes. Finally, the pH is adjusted to 3.0 since this is one of the well-known parameters required in order to optimize the procedure. Characteristics of these synthetic effluents are presented in Table IV.1, where the elevated organic charge and fairly low biodegradability for both solutions can be seen.

Table IV.1. Synthetic solutions characterization.

Solution	6 acids	7 acids
TPh ($mg_{phenolic\ acids}.L^{-1}$)	461 ± 9	610 ± 12
COD (mg $O_2.L^{-1}$)	1050 ± 21	1250 ± 25
BOD_5 (mg $O_2.L^{-1}$)	420 ± 42	544 ± 54
BOD_5/COD	0.40	0.43

IV.2.3. The Fenton's process

A 500 mL beaker was used to carry out the experiments containing 300 mL of the simulated olive mill wastewater. PH was checked with a Crison MicropH 2000 probe and corrected to 3.0 with NaOH or H_2SO_4 (Panreac, 96 %), if necessary. The catalyst was introduced at the concentration of 1.0 g.L^{-1} and magnetic stirring was started. One hour was given at these conditions without pH correction to evaluate the adsorption of the phenolic acids onto the catalyst. The pH increase due to the catalyst addition was measured and corrected only afterwards, once the reaction was about to start. A first sample was withdrawn in order to evaluate if the catalyst had adsorbed any organic charge. With the pH at 3.0, hydrogen peroxide (Panreac, 33 % - stabilized QP) was slowly poured at the concentration of 244 mM - these values were optimized in a previous work (Martins et al., 2010). At certain time intervals (15, 30, 60, 90 and 120 minutes), more samples were withdrawn by pipetting from the reactor to a filtration system (Buchner funnel, kitassato and air pump) using a 0.45 µm pore diameter quantitative filter paper to remove the solid catalyst from the liquid phase. PH was immediately raised to 10 to quench the remaining H_2O_2 and •OH, stopping the reaction. Reaction parameters were adopted in order to be able to compare these work's results with previous studies from our research group (pH, [H_2O_2] and [catalyst]). In those former tests, the chemical regime was verified (mass transfer resistances are not significant) and the oxidation of both phenolic solutions is not obtained with the absence of either the catalyst or the hydrogen peroxide.

Each catalyst was evaluated through total phenolic content and chemical oxygen demand removals from the phenolic synthetic solution (techniques described on the next section). To avoid experimental errors, each test was replicated and the mean values are presented on the figures, along with the corresponding error bars. The average error encountered for total phenolic removal was 1.1 % and for chemical oxygen demand removal this value was 0.7 %, representing very good agreement between experiments.

IV.2.4. Analytical techniques

A T60 U PG Instruments spectrophotometer was employed to detect the absorbance (wavelength = 765 nm) after applying the Folin-Ciocalteu method (Folin and Ciocalteu, 1927) to infer the total phenolic content (TPh), as described in the standard procedure 5500B (Greenberg et al., 1985). To connect the obtained values of absorbance and the phenolic content, a calibration curve have been prepared using several concentrations of the synthetic solution to acquire an expression that uses the given absorbance after the Folin-Ciocalteu procedure to infer the phenolic content in mg of phenolic acids per liter (mg$_{\text{phenolic acids}}$.L^{-1}). Since the variations of the absorption values is high, two ranges of concentrations were adjusted into two equations: the low range, calculated from solutions containing 12 to 300 mg$_{\text{phenolic acids}}$.L^{-1} (equation IV.1, with a correlation factor, R^2 of 0.9981) and the high range, from 300 to 1000 mg$_{\text{phenolic acids}}$.L^{-1} (equation IV., R^2 = 0.9997). Since the synthetic solution has a known concentration from approximately 450 mg$_{\text{phenolic acids}}$.L^{-1} for the case of six acids and 610 mg$_{\text{phenolic acids}}$.L^{-1} for the case of 7 acids, these ranges fit all needs of this work.

$$[TPh]\left(\frac{mg_{phenolic\ acids}}{L}\right)=\frac{(Absorbance-0.0049)}{0.0005} \quad \text{(Eq. IV.1)}$$

$$[TPh]\left(\frac{mg_{phenolic\ acids}}{L}\right)=\frac{(Absorbance-0.0591)}{0.0003} \quad \text{(Eq. IV.2)}$$

With the closed reflux standard method 5220D (Greenberg et al., 1985), the chemical oxygen demand (COD) was determined using a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer. Standard method 5210B (Greenberg et al., 1985) was used with inoculums obtained from garden soil to infer the biochemical oxygen demand in five days (BOD_5).

IV.3. Results and Discussion

IV.3.1. Catalyst characterization

XRD analysis shows that the catalysts are composed mainly by magnetite - Fe_3O_4 or $FeO.Fe_2O_3$, the most magnetic mineral found in nature (Harrison et al., 2002) and copper oxide, depending on the proportion of each sample – which can be seen in Figure IV.1.A. The most salient difference on the profiles regards the high peak presented at ~45 ° by the catalyst composed by higher copper proportion, Fe-Cu-O 30/70. This peak is related to copper oxide. It becomes smaller at the Fe-Cu-O 50/50 profile and almost absent in Fe-Cu-O 70/30. At ~42 °, there is a coincident peak for both magnetite and copper oxide and that is why the three catalysts present it in a quite similar level with small reductions when the iron proportion increases. Regarding the several other smaller peaks, we can see much more magnetite in the Fe-Cu-O 70/30 profile and copper oxides in Fe-Cu-O 30/70.

Figure IV.1.B shows the gas adsorption isotherms and, as we can see, the three analyzed solids present type IV isotherms – which, according to Figueiredo and Ribeiro (1989), are characterized by the hysteresis phenomenon and the presence of an elbow. Solids that present this type of isotherms usually have mesopores (pore size between 2 and 50 nm). When the composition of the solids and their pore diameters are compared (Figure IV.2), it seems that the augment on the copper content raises pore diameters: Fe-Cu-O 70/30 presents pores with an average diameter of 5.7 nm, while Fe-Cu-O 50/50 presents a value of 7.5 nm and, Fe-Cu-O 30/70, 15.7 nm.

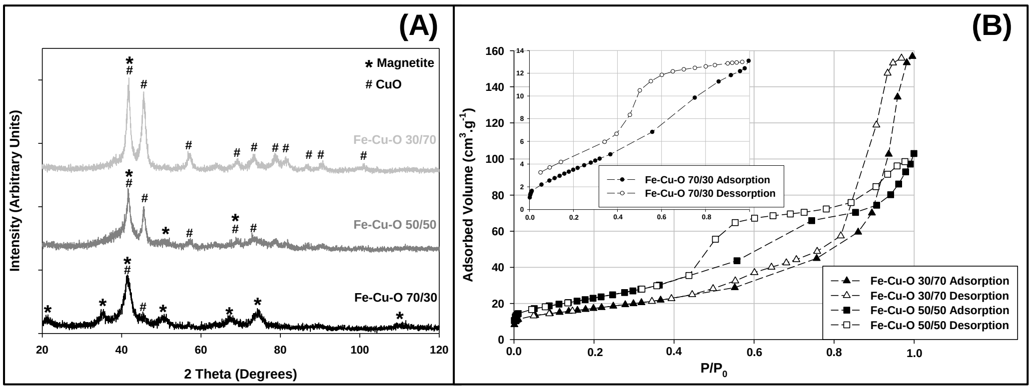

Figure IV.1. (A) X-ray diffraction profiles for catalysts Fe-Cu-O 70/30, Fe-Cu-O 50/50 and Fe-Cu-O 30/70. Magnetite and copper oxide coincident peaks have been marked, as indicated on the legend (***** for Magnetite and **#** for Cu-O peaks). **(B)** Gas adsorption isotherms (adsorbed volume versus relative pressure). Inlet: Fe-Cu-O 70/30 curves, which have a lower scale.

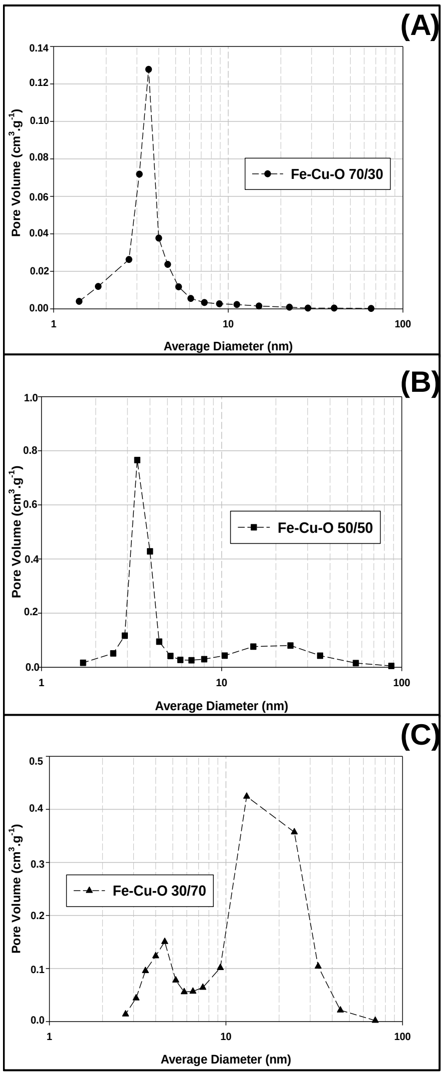

Figure IV.2. Pore size versus pore volume for the following catalysts: **(A)** Fe-Cu-O 70/30, **(B)** Fe-Cu-O 50/50 and **(C)** Fe-Cu-O 30/70.

Table IV.2 shows the data obtained from solids characterization. Both Fe-O and Cu-O were not analyzed since their results regarding organic charge removal as Fenton-like catalysts were poor.

Table IV.2. Catalysts characterization: solid's data.

Catalyst	Fe-Cu-O 70/30	Fe-Cu-O 50/50	Fe-Cu-O 30/70
B.E.T. Surface Area ($m^2.g^{-1}$)	14	85	62
Average Pore Diameter (nm)	5.7	7.5	15.7
Single Point Total Pore Volume ($cm^3.g^{-1}$)	0.0202	0.1594	0.2426
Average Density ($g.cm^{-3}$)	4.27	4.45	4.79
Porosity (%)	39	45	63

As Figure IV.2 shows, for both Fe-Cu-O 70/30 and Fe-Cu-O 50/50, higher pore volumes are found between pore with diameters of 3 and 4 nm. Fe-Cu-O 30/70, on the other hand, presents two pore volume peaks: one between 4 and 5 nm and another between 10 and 20 nm. Helium porosimetry indicates that for higher contents of copper the porosity is increased: Fe-Cu-O 70/30 has 39 % porosity, while Fe-Cu-O 50/50 has 45 % and, Fe-Cu-O 30/70, 63 %. Regarding BET surface areas, Fe-Cu-O 50/50 presents the larger value, 85 $m^2.g^{-1}$, while Fe-Cu-O 30/70 presents the intermediary value of 62 $m^2.g^{-1}$ and, Fe-Cu-O 70/30, only 14 $m^2.g^{-1}$.

IV.3.2. Organic charge depletion

By the adsorption tests, we detected that none or insignificant amounts of both TPh and COD were adsorbed by the catalysts in all cases. Figure IV.3.A and Figure IV.3.B displays the TPh removal profiles, where one can see that the oxidation curves for the simulated wastewater containing more initial compounds indicate a better process efficiency – enhanced results were found in all cases. Fe-Cu-O 50/50 is pointed out as the most active solid, removing 100 % of the phenolic content from solutions containing six and seven acids. This solid was followed by Fe-Cu-O 30/70, which could oxidize 85 % of the phenolic content from the solution containing seven acids solutions and 78 % from the solution containing six acids. Fe-O and Cu-O presented similar efficiencies in both cases: 68 and 66 % removals, respectively, from the seven acids solution, and 54 and 55 % phenolic content abatement from the solution containing six acids. The Fe-Cu-O 70/30 catalyst presented the most discrepant values when the TPh reductions from both solutions are compared: 95 % of the phenolic acids were removed from the solution containing seven phenolic acids when only 31 % were removed from the other solution – indicating a strong participation of the free radicals in solution, especially in this last case.

COD removal profiles are displayed in Figure IV.3.C and Figure IV.3.D. Regarding this parameter, catalysts efficiency order is the same for both COD and TPh abatements in the case of the seven acids solution. Being the most efficient, Fe-Cu-O 50/50 again topped this list, with 51 % COD removal. Regarding the six acids mixture, however, the best solid is the Fe-Cu-O 30/70 (42 % COD abatement). For the seven acids solution treatment, the remaining solids are as follows: Fe-Cu-O 70/30 (44 % COD depletion), Fe-Cu-O 30/70 (36 %), Fe-O (21 %) and Cu-O (9 %). Additionally, the order for the six acids solution oxidation, after the Fe-Cu-O 30/70 comes Fe-Cu-O 50/50 (36 %), Fe-Cu-O 70/30 (24 %), Fe-O (21 %) and Cu-O (15 %).

Being so, the optimal ratio between copper and iron to produce Fenton catalysts, regarding TPh and COD removals, is 50/50 – unless for COD reduction of the six acids mother solution, when the removal is 6% higher for the 30/70 ratio.

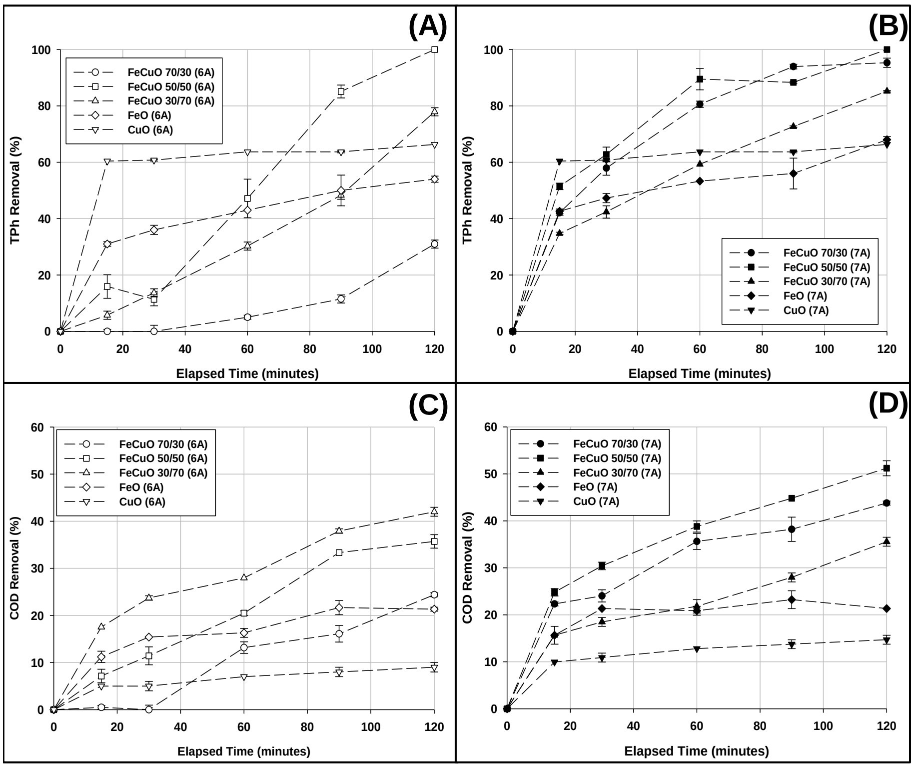

Figure IV.3. Organic charge removal profiles. **(A)** Total phenolic content removals for the six acids mother solution; **(B)** total phenolic content removals for the seven acids mother solution; **(C)** Chemical oxygen demand removals for the six acids mother solution and **(D)** Chemical oxygen demand removals for the seven acids mother solution. Experiments' conditions: [catalyst] = 1 $g.L^{-1}$, $[H_2O_2]$ = 244 mM, pH = 3.0, room temperature (~25 °C).

Through the analysis of all plots in Figure IV.3, it can be noticed that the percentage removals of COD and TPh are significantly higher when more acids comprise the mother solution. The treatment enhancement might occur because the radicals present in the reaction mixture can collaborate to the augment on the oxidizing potential in a synergistic manner.

As mentioned by Fukuchi et. al. (2014), the gallic acid can act as a reducing agent, which could reduce Fe(III) to Fe(II) and/or Cu(II) to Cu(I). Since this compound was only present on the seven acids mother solution, the metal's valence alteration could increase the Fenton's efficiency, since the reduced forms of the metals are able to generate hydroxyl radicals faster and, therefore, increase the oxidation of the other compounds in solution. Yet, it is mandatory to mention that although the concentrations of gallic acid by Zhu were much higher, it could only increase the efficiency of the used system in about 8 %. Besides, only the removal of a single compound was analyzed, not the full degradation of the broken molecules – such as in the present work. Therefore, this fact could only explain a small part of the system's oxidative power differences presented here – being, still, the co-oxidation responsible for the majority of the changes.

IV.3.3. Biodegradability assessment

Since the phenolic composition of olive mill wastewaters presents low biodegradability to bacteria, biological plants are not recommended to treat these effluents directly. As the mother solutions also has this characteristic, something desirable from the Fenton treatment is to enhance those parameters (BOD_5, COD and the BOD_5/COD ratio). Yet, although Fe-Cu-O catalysts reached good COD removals, the BOD_5/COD ratio was reduced from 0.45 to less than 0.25, indicating that the biodegradability was somehow affected (what can be seen in Table IV.3). The presence of leached copper cannot be pointed as the cause of this because the catalyst without this metal, Fe-O, also presented a similar BOD_5 result. Intermediate compounds might be refracting the biological consumption of the organic charge. Since the composition of all catalysts is qualitatively the same (copper and iron oxides), the oxidation pathways might have been similar and this would explain the biodegradability loss for all cases.

Table IV.3. BOD_5/COD results after each 2h experiment. Reaction conditions: [catalyst] = 1 g.L^{-1}, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C).

Catalyst	Fe-Cu-O 70/30	Fe-Cu-O 50/50	Fe-Cu-O 30/70
BOD_5/COD (6 acids)	0.20	0.17	0.23
BOD_5/COD (7 acids)	0.24	0.18	0.14

IV.4. Conclusions

The interaction between copper and iron oxides in the catalysts showed good results, since in all cases the catalysts comprising both metals showed faster and higher organic charge degradation than Fe-O and/or Cu-O. Comparing the two mother solutions oxidative process, it can be said that the mixture containing more acids is easier to degrade (this was observed in almost all cases) – meaning that the co-oxidation phenomenon is occurring and enhancing the process efficiency. The iron/copper molar ratio of 50/50 can be pointed out as the one that will create more active Fe-Cu-O catalysts, since the TPh and COD abatements for this solid were the best in all cases except one (where the removal difference is only 6 %). Despite the interesting data about organic charge depletion, these catalysts were not tested in what regards the leaching behavior since the biodegradability was reduced in every experiment – especially for the most active solid (Fe-Cu-O 50/50) that most promoted organic matter oxidation.

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V. An analysis of ceramic catalysts comprised by iron and cobalt oxides for the heterogeneous Fenton's reaction[3]

Novel ceramic solids comprising iron and cobalt oxides at different molar proportions were tested and compared as heterogeneous Fenton’s catalysts. The tested cobalt oxide percentage on the solids composition were 30, 50, 70 and 100 %. A solution comprising six phenolic acids commonly found in olive mill wastewaters was used as the simulated effluent. Organic charge removal was followed by COD and TPh. Phenolic content removals were similar and close to 60 % for three of the catalysts (Fe-Co-O 70/30, 50/50 and 30/70). On the other hand, Fe-Co-O 30/70 is pointed out for the higher COD removal: 32 %. Biodegradability was assessed through BOD_5/COD ratio. All solids were able to enhance this parameter (especially Fe-Co-O 30/70, which achieved the value of 0.63 – against the 0.36 of the mother solution).

V.1. Introduction

In the wastewaters treatment area, the Fenton’s process is known for its wide range of applicability and low costs associated with its system – since it requires cheap reactants and works at mild conditions. The homogeneous reaction presents the drawback of generating sludge at the end of the process, creating a gap for investigation on how to overcome this flaw. One of the possible solutions would be to use a heterogeneous catalyst that would be easily separated by simple filtration, avoiding sludge formation and recovering the catalyst (Bautista et al., 2008; Cañizares et al., 2009).

Over the last years, our research group has dedicated part of its efforts to evaluate the feasibility of using ceramic catalysts in the heterogeneous Fenton’s process. For that, we have tested solids comprising paired metal oxides, such as iron-cerium (Martins et al., 2010; Rossi et al., 2012) and iron-copper (Rossi et al., 2014). For this work, we have prepared solids containing iron and cobalt oxides (Fe-Co-O) and tested them as Fenton’s catalysts.

Since olive mill wastewaters (OMW) are an important matter in our country, Portugal, we have tried these catalysts on the treatment of a solution that simulates these effluents – prepared by six phenolic acids commonly found in OMW.

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[3] This chapter is based upon the publication Rossi, A.F.; Martins, R.C.; Quinta-Ferreira, R.M. *Proceedings of the 12th International Chemical and Biological Engineering Conference*, Porto, Portugal, **2014** (4) 29-31.

V.2. Experimental

V.2.1. Catalyst preparation

Catalysts were prepared by co-precipitation, as in Imamura et al. (1985). This methodology starts with the mixture of metal precursor salts in water (iron (III)-9-hydrate nitrate and cobalt (II) nitrate-6-hydrate) at the desired molar proportions. The generated solution has its pH raised to 12 by the addition of NaOH. This provokes the precipitation of the metals, which are filtered, washed, dried overnight at 105 °C and calcinated for two hours at 300 °C – temperature that generates more active solids, according to previous investigation (Rossi et al., 2012). For this work, we have used the proportions iron/cobalt of 70/30, 50/50, 30/70 and 0/100, generating 4 different solids called Fe-Co-O 70/30, Fe-Co-O 50/50, Fe-Co-O 30/70 and Co-O, respectively.

V.2.2. Synthetic solution

In order to simulate OMW, we have prepared solutions containing six phenolic acids that are commonly found on those effluents: 3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid – each at 0.1 mg.L^{-1}. The required amounts of phenolic acids are added to distilled water and forwarded to ultrasounds (Crest Ultrasounds equipment) for 15 minutes to facilitate dissolution. This solution's pH is then set to 3.0 with the aid of a Crison MicropH 2000 probe to obey previously optimized Fenton's parameters of our research group (Martins et al., 2010).

V.2.3. Fenton's reaction

600 mL beakers were used as reactors containing 300 mL of the synthetic solution and magnetic stirring. The catalyst was added at 1.0 g.L^{-1} and 60 minutes were allowed to the media in order to evaluate the organic charge absorbed by the solid phase. Afterwards, hydrogen peroxide was added at 244 mM to start the Fenton's reaction. In the figures, time = -60 minutes corresponds to the catalyst addition and time = 0 to the oxidant agent addition. At certain intervals, samples were withdrawn, filtered to remove the catalyst and, finally, their pH was raised above 10 using NaOH in order to stop the Fenton's reaction.

V.2.4. Organic charge assessment

The total phenolic content (TPh) was measured following the Folin-Ciocalteou procedure (Folin and Ciocalteu, 1927; Silva et al., 2007), with a spectrophotometer (T60 U PG instruments). Standard Method 5220D (Greenberg et al., 1985) was used to measure chemical oxygen demand (COD), using a thermoreactor (WTW CR 3000) and a photometer (WTW MPM 3000). Biochemical oxygen demand in five days (BOD$_5$) was assessed following the standard method 5210B (Greenberg et al., 1985) using garden soil inoculum.

V.3. Results and discussion

Organic charge data was normalized and the profiles were plotted in two figures. On both of them, there is a line at time = 0, indicating the hydrogen peroxide injection and, therefore, the beginning of the Fenton’s reaction.

Figure V.1.A. shows TPh removal profiles. There, we can see that, except for the catalyst comprised only by cobalt oxide, Co-O, all catalysts show a similar trend towards a value close to 60 % TPh removal. Part of the phenolic acids (from 27 to 41 %) are adsorbed to the catalysts at the beginning of the reaction (t = 0, when the peroxide is injected). From that point on, the oxidation begins and these compounds start to be broken by •OH radicals. Fe-Co-O 70/30 stands out with 64 % phenolic content removal at the end of two hours. Yet, Fe-Co-O 50/50 and 30/70 achieve close values, 61 and 58 %.

However, when we look at the COD removal profiles, presented in Figure V.1.B, larger difference between each catalyst oxidative capacity over the time can be seen. Here, the adsorption values are lesser than at the above mentioned picture. Only Fe-Co-O 30/70 and Co-O present 5 % COD removal by adsorption, while the other two catalysts show none. This may suggest that the catalysts are not only adsorbing compounds before the H_2O_2 addition, but some oxidation is occurring due to the catalyst’s superficial oxygen – although only strong enough to destroy the aromatic rings, thus accounting to TPh reduction but slight or null effect on COD values.

Regarding COD removals, Fe-Co-O 50/50 presents the worst result: 8 % after two hours of reaction. Co-O presented a profile close to this one, achieving only 12 % removal, while Fe-Co-O 70/30 could remove 20 % of the chemical oxygen demand. Fe-Co-O 30/70, here, presented the best result, 32 %, being pointed out as the most active solid for the Fenton's process – but still much below a desired value.

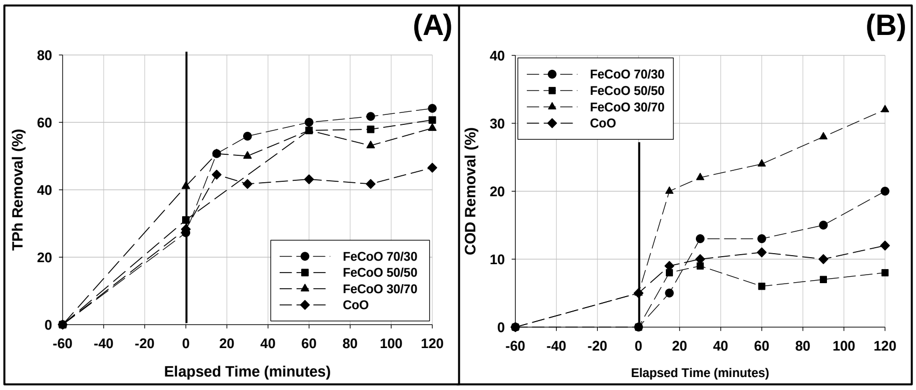

Figure V.1. Organic charge removal profiles along the experiments. **(A)** Total phenolic content; **(B)** Chemical oxygen demand. Reaction conditions: [catalyst] = 1 g.L^{-1}, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C).

The biodegradability of the samples was inferred through the ratio between biochemical oxygen demand in five days (BOD_5) and chemical oxygen demand (COD). This way, we can relate how much of the total organic charge (measured by COD) is oxidizable by the BOD_5 method, in a fraction. The higher this fraction is, the easier it is to bacteria to degrade the sample.

As we can see in Table V.1, this work's mother solution presents a BOD_5/COD ratio of 0.36. Usually, if the sample presents a ratio ≥ 0.40, it can be considered biodegradable – and this is the case of all samples after the Fenton's treatment using the iron-cobalt catalysts. Therefore, we can conclude that all catalysts were able to enhance the mother solution's biodegradability – specially Fe-Co-O 30/70, that presented a ratio of 0.63.

As this catalyst also presented the higher activity (measured by COD removal), the ratio 30/70 is here pointed out as the best one to prepare iron-cobalt ceramic catalysts.

Table V.1. BOD_5 and BOD_5/COD results after each 2h experiment. Reaction conditions: [catalyst] = 1 g.L^{-1}, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C).

Sample	BOD_5	BOD_5/COD
Mother Solution	362	0.36
Fe-Co-O 70/30	351	0.44
Fe-Co-O 50/50	379	0.41
Fe-Co-O 30/70	430	0.63
Co-O	488	0.55

V.4. Conclusions

All iron-cobalt catalysts were able to deplete at least 47 % of the total phenolic content of the mother solution. The maximum removal of this parameter was presented by the Fe-Co-O 70/30 catalyst (64 %), followed by Fe-Co-O 30/70, which removed 58 % of the TPh. This second catalyst was pointed out as the most efficient due to its COD removal: 32 % - the highest value. Although this oxidation level is not high enough for us to consider the preparation of ceramic iron-cobalt for industrial wastewater treatment, the biodegradability enhancement in all cases (especially Fe-Co-O 30/70) pulls attention to further investigation of the cobalt on the Fenton's process.

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Part C. **Low Cost Materials**

In this part of the manuscript, a connection between environmental concerns and the industrial sector's interest is presented to the reader through the use of low cost materials. Waste management was studied to find cheap and effective catalysts, such as the iron sludge resulting from the Fenton's process and iron shavings (zero valent iron, ZVI). All of these wastes were tested in their raw form, after receiving some treatment and even as iron sources. Interesting results were obtained, especially with the ZVI, leading us to present a continuous operation article (chapter IX).

VI. Reuse of homogeneous Fenton's sludge from detergent industry as Fenton's catalyst[4]

Fenton's reaction is an advanced oxidation process where, classically, hydrogen peroxide is the oxidizing agent and an iron catalyst promotes the formation of hydroxyl radicals (•OH). Among the studies that evaluated different metals as Fenton-like catalysts, our group of investigation has recently used cerium-based solids as heterogeneous catalysts in slurry reaction and, in this work, iron sludge coming from an industrial Fenton's reactor used for the wastewater depuration of a detergent production factory is being appraised while treating a synthetic effluent containing 0.1 $g.L^{-1}$ of seven phenolic acids commonly found in olive mill wastewaters – one of our group's major focus. The treatment facility uses a homogeneous Fenton's process and the dried sludge contains approximately 37 % (w/w) iron content. As it comes directly from the plant and it is a pretty raw mud, it is expected to find high amounts of organic matter in the catalyst, because there are no further steps besides baking to enhance its efficiency. This mud was dried, baked and milled to become the catalyst. Calcination temperatures of 300, 400, 500 and 1000 °C were employed and a comparison with the non-baked catalyst was performed. Chemical oxygen demand (COD), total phenolic content (TPh) and total organic carbon (TOC) removals were assessed. Higher calcination temperatures were most-likely to show better organic depletion, although higher levels of iron leaching were detected. Biological oxygen demand in five days (BOD_5) was increased in some cases, what could enable the application of a subsequent biological treatment step. Adsorption tests were carried out in order not to erroneously associate the abatements to oxidation and have proved that TPh, COD, TOC and BOD_5 values did change by chemical reaction rather than single adsorption.

VI.1. Introduction

Fenton's process consists in the oxidation of both organic and inorganic compounds by radicals obtained from the activation of hydrogen peroxide by an iron-containing catalyst. This reaction is much used in wastewater treatment since it is a powerful method considering the low costs involved and the wide range of compounds that can be degraded this way.

When the homogeneous Fenton operation takes place, the iron (usually Fe^{2+}) is dissolved in the bulk to interact with the hydrogen peroxide. Highly oxidative radicals (•OH) are formed, able to react with most compounds. To terminate the reaction, the pH, which is around 3.0 during the procedure, is raised above 10 in order to quench the remaining peroxide and separate the iron by precipitating it as sludge.

This remaining solid waste is one of the major flaws in the homogeneous Fenton's process due to the necessity of extra steps to separate and treat it. Still, there are some

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[4] This chapter is based upon the publication Rossi, A.F.; Martins, R.C.; Quinta-Ferreira, R.M. *J. Adv. Oxid. Technol.* 16 **2013** 298-305.

industries that use this method to handle their effluents, being beneficiated by the associated advantages, such as the low-priced operational costs.

A wastewater treatment plant focused on the treatment of detergent effluents by the homogeneous Fenton's method, previously analyzed by Martins et al. (2010), supplied our research group with samples of the mentioned iron-containing sludge and we tried to recycle this waste by transforming it into a catalyst.

Other methods of Fenton's sludge recycling have already been tested. Cao et al. (2009) prepared catalysts to treat wastewaters from the chemical industry through acidification of the calcinated sludge and observed good efficiency in the organic charge removal.

Costa et al. (2010) developed a new catalyst from a solid waste named red mud that contains mainly Fe_2O_3, Al_2O_3, CaO and TiO_2 obtained from aluminum production. It was reduced at a H_2-controlled atmosphere and showed good performance in both the reduction of Cr(IV) and the degradation of methylene blue dye by Fenton's reaction.

Electric arc furnace dust, an industrial by-product of steel production, was another material that showed interesting results when evaluated by Mecozzi et al. (2006) in the decomposition of pentachlorophenol. As the Fenton's catalyst, it was able to remove almost 50 % of the total organic carbon and 57 % of the chlorine.

The environmental reflexes of these procedures – as well as the present work's catalyst, would reduce industry expenses regarding the treatment of its wastewaters, since they are recycled and demands only simple steps (heating and milling, in this work's case) before being ready for usage. Additionally, valorization of such cumbersome sludges would be much welcome for reducing the negative impact of those wastes in our ecosystems. Plus, recycling is able to save resources by avoiding iron production for this matter.

The central point of this work is to employ this mud as a viable Fenton catalyst, since the only requirement for that is to efficiently be able to activate hydrogen peroxide into hydroxyl radicals in order to enhance its oxidation potential. This was studied through the degradation of the organic charge in an olive mill wastewater simulated solution using the mentioned solid waste as the Fenton's reaction catalyst. Besides organic charge removal, biodegradability was still observed through biochemical oxygen demand in five days and its comparison with chemical oxygen demand.

VI.2. Experimental

VI.2.1. Catalyst preparation

Iron sludge coming from an industrial homogeneous Fenton's reactor used for detergent wastewater treatment was used as catalyst. The mud was completely dried at 105 °C in an oven and was manually crushed into small particles. Four other catalysts were obtained by calcination of the resulting powder from the milling for two hours, one at each temperature: 300, 400, 500 and 1000 °C. This way, five catalysts were prepared: C_{105}, C_{300}, C_{400}, C_{500} and C_{1000}. The calcination step generated different solids with diverse properties, which will be further discussed.

Calcination temperatures were chosen according to a previous study of our investigation group in which the optimum value was 300 °C. As temperatures between 300 and 600 °C had not been tested, the two intermediary values (400 and 500 °C) were also aiming to look if they could generate better results. 1000 °C was the last choice because this temperature generated a Fe-Ce-O catalyst that presented low iron leaching, an important parameter to consider (Rossi et al., 2012).

VI.2.2. Simulated effluent

A phenolic solution simulating olive mill wastewaters was prepared by mixing 0.1 g.L^{-1} of seven phenolic acids: 3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, gallic acid, protocatechuic acid, syringic acid, vanillic acid, veratric acid. The solution was submitted to ultrasounds (Crest ultrasounds equipment) during 10-15 min in order to dissolve the acids and then the pH was adjusted to 3.0 with H_2SO_4. The characteristics of this solution are: chemical oxygen demand of 1280 ± 128 mg O_2.L^{-1}, BOD_5 of 544 ± 109 mg O_2.L^{-1}, BOD_5/COD of 0.42, TOC of 377.2 ± 7.5 ppm, pH (before correction) of 3.5 ± 0.1.

VI.2.3. The Fenton's process

500 mL glass reactors were used to carry the reaction. Inside them, 300 mL of the simulated effluent were poured and the required amount of catalyst was added. Magnetic stirring was employed in order to maintain the bulk as homogeneous as possible. A Crison MicropH 2000 probe was used for pH monitoring (H_2SO_4 and NaOH solutions were employed to apply every necessary correction to keep it at 3.0). After adding the catalyst (time = -60 min), the mixture was left for one hour before the H_2O_2 addition to evaluate contaminants removal by catalyst adsorption. Subsequent to this first period, the desired volume of H_2O_2 to achieve the concentration of 244 mM, as previous studies pointed to be the best dose (Martins et al., 2010) was slowly poured into the reactor and only then the Fenton's reaction started to take place (time = 0 min). At certain time intervals (30, 60, 90 and 120 min), samples were withdrawn to a vacuum filtration system (funnel, kitassato and air pump) using a 0.45 µm pore diameter quantitative filter paper to remove the solid catalyst from the liquid phase. Right after filtration, the pH of the sample was raised above 10 using NaOH 3 M in order to stop the reaction by quenching the remaining hydrogen peroxide. Finally, samples were named and stored at 4 °C until being forwarded to analysis.

Five doses of each catalyst (0.5, 1.0, 1.5, 2.0 and 2.5 g.L^{-1}) were used to assess their efficiency and evaluate which dose/catalyst was more adequate. As there were five catalysts and five doses of each, a total of 25 experiments were carried on.

VI.2.4. Analytical techniques

A Shimadzu 5000 Analyzer was used to assess the total organic carbon (TOC) in all samples. The Folin-Ciocalteu procedure (Folin and Ciocalteu, 1927; Silva et al., 2007) was employed to colorimetrically measure the total phenolic content (TPh) with a T60 U PG instruments spectrophotometer for absorbance detection. The 5220D Standard Method was utilized to analyze the chemical oxygen demand (Greenberg et al., 1985) – for that, a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer were employed. Biochemical oxygen demand in five days (BOD_5) was measured by the method proposed by Greenberg et al. (1985), being the inoculums obtained from garden soil.

The catalysts were analyzed in order to quantify their fixed solids percentage and, furthermore, their iron contents were also measured through acidic digestion, as the baking temperature generated different composition for all catalysts. Both procedures were obtained from Greenberg et al., 1985.

Average values (errors referred below) for each experiment were adopted to plot the final profiles based on the repetitions that were carried out obeying analysis methodology for all parameters. In fact, according to the instrument's calibration method, COD results were obtained from duplicates (error of less than 10 %), TPh from single values and TOC was measured from 5 to 8 times until the error was less than 2 % between the considered measurements. BOD_5 was measured five times (different dilutions of the same sample) and the three closest values had their mean calculated (maximum error was 10 %).

VI.3. Results and discussion

VI.3.1. Catalysts' solid content

In Table VI.1, the percentages of volatile and fixed solids, as well as their respective iron percentages, are shown. As expected, higher calcination temperatures lead to higher fixed solids content. There is an almost linear decrease from 54 to 0 % on the percentage of volatile solids as the calcination increases, while the fixed solids content rises from 46 to 100 %.

Table VI.1. Fixed and volatile solids content in each catalyst.

Catalyst	Volatile Solids (%)	Fixed Solids (%)	Iron Mass Content (%)	Iron Mass Content in the Fixed Solids (%)
C_{105}	54.4	45.6	36.9	76.2
C_{300}	32.3	67.7	43.7	64.9
C_{400}	21.0	79.0	55.0	73.7
C_{500}	12.0	88.0	65.5	77.5
C_{1000}	0.0	100.0	70.8	69.8

As observed in the fixed solids content (and intrinsically related to that), the percentage of iron in the catalyst also increased with the calcination temperature growth. However, the iron percentage in the fixed solids varied with no clear pattern. Values were observed between 65 % (C_{300}) and 77 % (C_{500}), while the others oscillated inside this range.

By knowing the iron content of each catalyst, it was possible to infer the Fe:H_2O_2 ratio that was used in each experiment. These values, expressed in mol Fe:mol H_2O_2, go from 0.014 (C_{105}, dose 1) to 0.130 (C_{1000}, dose 5) (Table VI.2). According to the Fenton's peroxidation review paper published by Neyens and Baeyens (2003), all doses are considered low (initial [Fe^{2+}]:[H_2O_2] << 1), which, as it is explained by the authors, is the ratio range that shows the best H_2O_2 yield regarding radical formation. In the present work, this ratio increases with the catalyst dose augment (from 0.5 to 2.5 g.L^{-1}) and also as a function of the calcination temperature of the catalyst because this affects its solids content. Values for each experiment are presented in Table VI.2.

Table VI.2. Iron/peroxide, in (mol Fe/mol H_2O_2), for each experiment.

Catalyst	C_{105}	C_{300}	C_{400}	C_{500}	C_{1000}
Dose 1 (0.5 g.L^{-1})	0.014	0.016	0.020	0.024	0.026
Dose 2 (1.0 g.L^{-1})	0.027	0.032	0.040	0.048	0.052
Dose 3 (1.5 g.L^{-1})	0.041	0.048	0.061	0.072	0.078
Dose 4 (2.0 g.L^{-1})	0.054	0.064	0.081	0.096	0.104
Dose 5 (2.5 g.L^{-1})	0.068	0.080	0.101	0.120	0.130

An extra experiment was carried out using H_2O_2 alone to infer if it was able to deplete organic charge. While the minimum TPh removal was 61 % for the catalyst C_{105} (dose 1, 0.5 g.L^{-1}), this experiment was able to remove only 49 % of the phenolic content. Plus, no COD abatement was observed. Hence, results show that the hydrogen peroxide alone, at the concentration of 244 mM, is not effective at oxidizing the organic compounds of the synthetic solution. Therefore, catalytic activity plays the major role in the reaction.

VI.3.2. Iron leaching

Almost all experiments presented iron leaching from the catalyst to the bulk. There are only two exceptions that presented zero leaching and they both belong to C_{105}: dose 1 (0.5 g.L^{-1}) and dose 2 (1.0 g.L^{-1}), as reported in Table VI.3.

Table VI.3. Iron leaching, in mg.L^{-1}, and the percentage of the total iron content leached after each experiment.

Catalyst	C_{105}	C_{300}	C_{400}	C_{500}	C_{1000}
Dose 1 (0.5 g.L^{-1})	0.0 (0.00%)	3.1 (1.42 %)	7.4 (2.69 %)	37.6 (11.48 %)	47.8 (13.50 %)
Dose 2 (1.0 g.L^{-1})	0.0 (0.00 %)	4.0 (0.92 %)	18.4 (3.35 %)	46.3 (7.07 %)	101.5 (14.34 %)
Dose 3 (1.5 g.L^{-1})	2.3 (0.42 %)	6.5 (0.99 %)	28.9 (3.50 %)	53.1 (5.40 %)	127.9 (12.04 %)
Dose 4 (2.0 g.L^{-1})	1.2 (0.16 %)	14.0 (1.60 %)	32.9 (2.99 %)	59.1 (4.51 %)	172.0 (12.15 %)
Dose 5 (2.5 g.L^{-1})	2.9 (0.31 %)	10.7 (0.98 %)	34.9 (2.54 %)	56.5 (3.45 %)	100.4 (5.67 %)

For most cases, iron leaching is higher for higher catalyst amounts and the same goes for the calcination temperature, since the metal content in the catalysts is directly related to its calcination temperature, as discussed in the previous section. Superior temperatures presented much higher iron leaching, something that highlights the use of the non-baked catalyst: C_{105}. The fifth dose of this catalyst (2.5 g.L^{-1}) presented only 2.9 mg.L^{-1} iron content in the final treated sample, while the other doses of the same solid presented even less leaching.

In addition, the leached iron was compared to the total iron content in each experiment. As the calcination temperature rises, also does the iron leaching percentage and this can be noticed by following the leaching percentage for the same dose of any catalyst: the leaching increases for higher calcination temperatures in all cases. This leads us to believe that different iron species with different leaching behaviors are formed as the temperature becomes higher. On the other hand, by following the leaching percentage for different doses of the same catalyst, no pattern that matches more than one catalyst was found.

Previous work from our research group utilized the temperature of 1000 °C to bake a catalyst, Fe-Ce-O, that presented very low iron leaching (Rossi et al., 2012). As the other temperatures were not able to do so in the present study, this one was, then, a further attempt to produce a solid that could last longer without contaminating the effluent with its metal content. However, although this catalyst also presented the best efficiency for COD removal, as discussed below, the iron leaching is too high: from 48 (dose 1) to 172 mg.L^{-1} (dose 4).

VI.3.3. Organic charge depletion – TPh

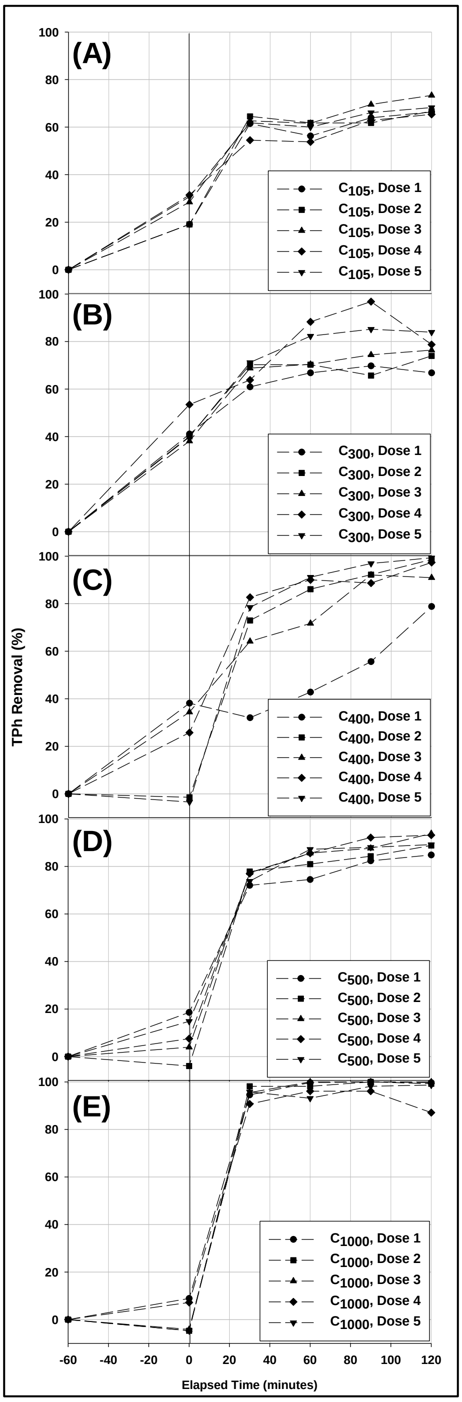

Figure VI.1. Total phenolic content removal (%) profiles along the experiments for all doses of each catalyst: **(A)** C_{105} **(B)** C_{300} **(C)** C_{400} **(D)** C_{500} **(E)** C_{1000}.

C_{105} was not able to completely remove the phenolic compounds from the effluent at any of the five doses and all TPh depletions from Fenton's oxidation are close to 70 % after two hours of reaction – Figure VI.1.A. Adsorption values are from 19 to 31 %. More adsorption can be linked to the higher doses.

C_{300} presents higher removals of TPh than C_{105}, both in adsorption and reaction. Adsorption depletions are between 38 and 54 % and the Fenton's efficiency for TPh starts with 67 % in the first dose (0.5 g.L^{-1}) and raises to 84 % in the last one (2.5 g.L^{-1}) – Figure VI.1.B. Doses 1, 2 and 3 present very similar profiles during all reaction.

Lesser adsorption removals were observed in C_{400}'s experiments. With maximum value of 38 % and a minimum of zero, the Fenton's oxidation was able to remove over 97 % for four of the doses (1.0, 1.5, 2.0 and 2.5 g.L^{-1}) – all with nearly similar profiles over the reaction (except for dose 3, which takes longer to achieve high removals), and 79 % for the first dose (0.5 g.L^{-1}) – Figure VI.1.C.

Adsorption was even lower for C_{500}. The maximum value is 19 % for the first dose (0.5 g.L^{-1}). A small variation in the depletion of the remaining phenolic compounds by Fenton's oxidation was observed. Excluding dose 1 (0.5 g.L^{-1}), which took more time to remove high amounts of phenols, all profiles are very close to each other. Yet, in the end of the reaction, the five depletion values were close to each other – from 85 (dose 1, 0.5 g.L^{-1}) to 94 % (dose 3, 1.5 g.L^{-1}) (Figure VI.1.D).

C_{1000} presented the lowest adsorption results (all under 9 %) and the highest Fenton efficiency for phenolic content removal: from 96 (dose 4, 2.0 g.L^{-1}) to

100 % (dose 3, 1.5 g.L^{-1}) – Figure VI.1.E. Again, the profiles are very similar: all the five of them had above 90 % TPh depletion in the first 30 minutes of reaction and reached complete or almost complete degradation by the end of the second hour.

VI.3.4. Organic charge depletion – COD

C_{105} presented COD depletions by Fenton's reaction from 12 to 22 % (Figure VI.2.A). Before the reaction, the adsorption step of the two first doses (0.5 and 1.0 g.L^{-1}) was able to remove low COD amount, and an increase was noticed in this parameter (2 and 5 %, respectively), which can possibly be explained by the leaching of organic carbon from the catalyst to the bulk. The next dose's (1.5 g.L^{-1}) adsorption step did not remove or contribute to the COD while the other two doses (2.0 and 2.5 g.L^{-1}) were able to remove a small part of the phenolic acids of the synthetic effluent, since these were the only compounds in solution. Regarding the reaction, COD profiles are quite awkward for this catalyst, but, since this catalyst is the one that contains more volatile solids (discussed above in the characterization section, Table VI.1) due to the lower calcination temperature, some organic charge leaching was expected and this can be the reason of such oscillating profiles.

C_{300} presented clearer COD removal profiles when compared to C_{105}, without unexpected oscillations. For this catalyst, the fourth dose (2.0 g.L^{-1}) is highlighted due to its superior efficiency – Figure VI.2.B. This is also observed in the TPh removal for this catalyst in Figure VI.1.B.

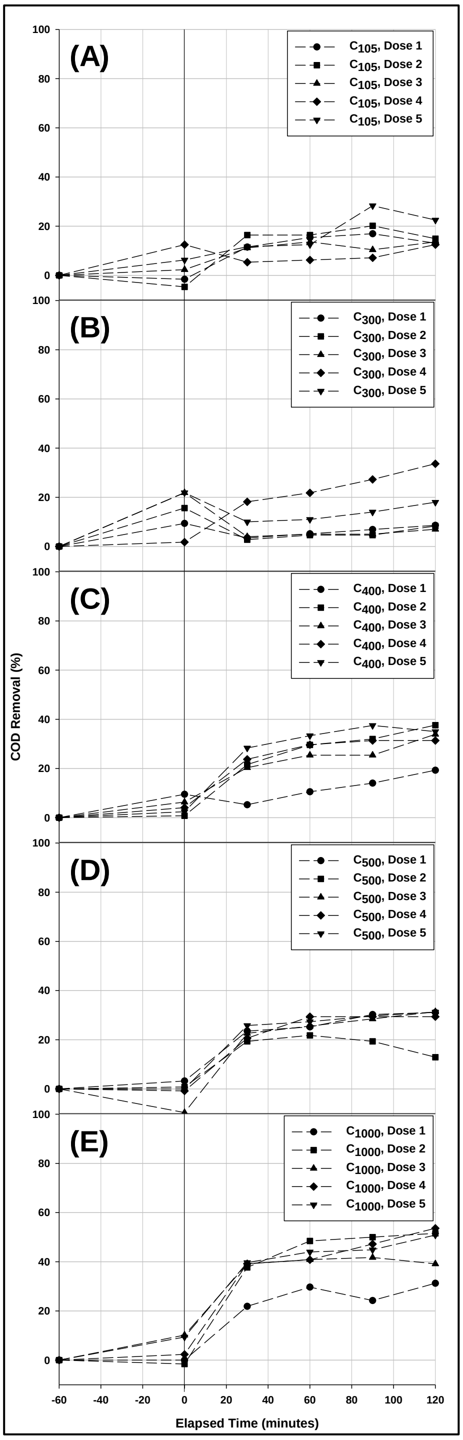

Figure VI.2. Chemical oxygen demand removal (%) profiles along the experiments for all doses of each catalyst: **(A)** C_{105} **(B)** C_{300} **(C)** C_{400} **(D)** C_{500} **(E)** C_{1000}.

%%%%%C_{400} showed oxidation values between those of C_{300} and C_{105} –.%%%%%

Adsorption values for C_{400} are lower: from 1 % to 10 % (Figure VI.2.C). The calcination temperature augment may have started to generate a solid that could adsorb just a small amount of organic compounds, probably due to a decrease in the catalyst surface area. Also, the Fenton's reaction efficiency regarding COD decrease was higher, going from 19 % (dose 1, 0.5 g.L^{-1}) to 37 % (doses 2 and 5, 1.0 and 2.5 g.L^{-1}). As the iron content of this catalyst is also higher than the two first ones, the formation of hydroxyl radicals may be enhanced but the scavenger point probably was not reached yet – these are two factors that would only contribute to assure the oxidation of the organic compounds. The profile of all doses of this catalyst is easier to evaluate and the second dose (1.0 $g.L^{-1}$) seems to be the most indicated due to its low adsorption (1 %) and high organic depletion by Fenton's oxidation (37 %).

The fourth catalyst, C_{500}, was able to reduce the adsorption of organic charge to very low values (dose 1 presented the only significant adsorption value of 3 % while the others did not present any adsorption) but did not reach the same Fenton efficiency as C_{400} – Figure VI.2.D. COD depurations were between 13 % (dose 2) and 31 % (doses 1 and 5). Therefore, there is no reason in utilizing this temperature, expending more energy on the calcination of a catalyst, and gather a less efficient solid regarding Fenton's reaction, unless the objective was to diminish the adsorption step.

The adsorption values for C_{1000} were also low: from 0 % (dose 1) to 10 % (doses 3 and 5). This catalyst presented the highest COD removals at the end of the reaction, going from 31 % (dose 1) to 54 % (dose 4) – Figure VI.2.E.

Regarding COD removal, C_{1000} presented the best results in almost all doses. The mark of 54 % is a great achievement considering the source of this catalyst, which could justify future work to be done with it in order to develop this solid to work with fewer drawbacks – such as the high iron leaching.

VI.3.5. Organic charge depletion – TOC

The first dose (0.5 $g.L^{-1}$) of C_{105} presented a slight increment on the total organic carbon (TOC), 8 %, after the reaction, while the chemical oxygen demand (COD) was depleted by 13 %. This was noticed in several experiments and might be explained by the release of carbon from the catalyst to the bulk (contributing to the TOC) and the oxidation of the organic charge (from both the catalyst and the effluent). As the catalyst activity was not high enough to oxidize the organic charge up to CO_2 but was able to break molecules into smaller ones (as TPh depletions clearly show), an increase in TOC together with a decrease in COD is acceptable. The other doses of this catalyst present TOC depletions from 5 to 9 %.

C_{300} was the only catalyst that in all cases presents TOC increase (values go from 8 to 25 %). Its calcination temperature might have weakened the generated solid, making its organic charge more likely to leach due to the reactor agitation at low pH.

400 °C was the lowest temperature that showed significant TOC depletion. The first dose (0.5 $g.L^{-1}$) was able to reduce 22 % of the TOC. The second (1.0 $g.L^{-1}$), 26 %, and the fifth (2.5 $g.L^{-1}$), 39 %. Yet, only three of the five doses presented good TOC removals, while the other two led, contrarily, to TOC increase. When compared to the simulated effluent TOC instead of the value after the adsorption test, the fourth dose (2.0 $g.L^{-1}$) removed 58 % of the TOC – a good mark for this catalyst.

For C_{500}, again three out of five doses presented positive TOC depletions (doses 2, 3 and 4) but, this time, the two other ones had values not as significant as C_{400}'s and none of the experiments showed higher TOC than the initial simulated effluent.

Again, C_{1000} presented the best results. Adsorption tests demonstrated that this catalyst presented low capacity of adsorbing the phenolic acids and the reaction was able, at all doses, of reducing TOC from 32 (fifth dose, 2.5 g.L^{-1}) to 46 % (second dose, 1.0 g.L^{-1}) – another good mark for a recycled solid.

VI.3.6. Organic charge depletion – BOD_5

In Table VI.4, all BOD_5 values for the last sample of each experiment (after two hours of reaction) are presented. The discussion below will encompass some of those values as well as data from Table VI.5, which shows the BOD_5/COD ratios for the same samples.

Table VI.4. Biochemical oxygen demand in five days (BOD_5), in mg O_2.L^{-1}, for the last sample of each experiment (two hours of reaction).

Catalyst	C_{105}	C_{300}	C_{400}	C_{500}	C_{1000}
Dose 1 (0.5 g.L^{-1})	385	255	246	144	170
Dose 2 (1.0 g.L^{-1})	370	272	185	178	111
Dose 3 (1.5 g.L^{-1})	296	206	183	192	132
Dose 4 (2.0 g.L^{-1})	326	254	190	171	106
Dose 5 (2.5 g.L^{-1})	371	230	159	129	126

C_{1000} was able to deplete about 44 % of the COD in all of its doses. On the other hand, BOD_5 is reduced even more, meaning that the remaining compounds in solution might not be as biodegradable as the initial phenolic acids. Being so, the treatment using this catalyst as it is would not be indicated, since the Fenton's process might be used as a pre-treatment for effluents that will still be sent to biological plants in order to achieve legislation parameters. The BOD_5/COD ratio was diminished to less than half of the initial (0.42 for the simulated effluent and around 0.19 for all C_{1000}'s doses).

Table VI.5. BOD_5/COD ratio for the last sample of each experiment (two hours of reaction).

Catalyst	C_{105}	C_{300}	C_{400}	C_{500}	C_{1000}
Dose 1 (0.5 g.L^{-1})	0.34	0.29	0.27	0.18	0.19
Dose 2 (1.0 g.L^{-1})	0.32	0.34	0.24	0.17	0.18
Dose 3 (1.5 g.L^{-1})	0.27	0.28	0.23	0.20	0.19
Dose 4 (2.0 g.L^{-1})	0.33	0.40	0.23	0.19	0.18
Dose 5 (2.5 g.L^{-1})	0.40	0.29	0.20	0.15	0.22

Similar results were found in C_{500}'s experiments. The COD depletions of four of the five doses were around 30 % but the BOD_5 abatement was even higher, reducing the BOD_5/COD ratio, what would exclude this catalyst from being used in the Fenton pre-treatment for biological processes. Even though the ratio decreased, it did not reach the low values achieved by C_{1000} – the values were slightly higher, which was noticed again in the C_{400}'s analysis.

Regarding C_{300}, almost all doses presented results almost as undesirable as the higher temperatures already discussed, but the fourth dose (2.0 g.L^{-1}) showed a ratio of 0.40, which is very close to the initial value (0.42) – a difference of less than 5 %.

C_{105} showed itself as the catalyst that generated treated samples with the higher BOD_5/COD ratios. The fifth dose of C_{105} (2.5 g.L^{-1}) presented a ratio of 0.40, which is the minimum threshold usually accepted for this parameter so that an effluent can be considered as totally biodegradable.

VI.3.7. Reaction homogeneity

Once this work's catalysts present no solid support to be affixed onto, the reaction will most probably take place in the liquid phase and, to assure this statement, two comparison experiments were carried out. The first one used, as its catalyst concentration, the iron leaching value obtained for C_{105} at the fourth dose (2.0 g.L^{-1}) because this case showed low iron leaching and one of the best BOD_5/COD ratios – 1.2 mg Fe.L^{-1}. The second one used the iron leaching value obtained for C_{1000} at the fourth dose (2.0 g.L^{-1}) as its catalyst concentration – 172.0 mg Fe.L^{-1}. This last experiment was selected due to its iron leaching, which was the highest of all. Since the catalysts' calcination step might oxidize the iron molecules, the catalyst chosen in order to compare the homogeneous process was Fe^{3+} – introduced as $Fe(NO_3)_3.9H_2O$.

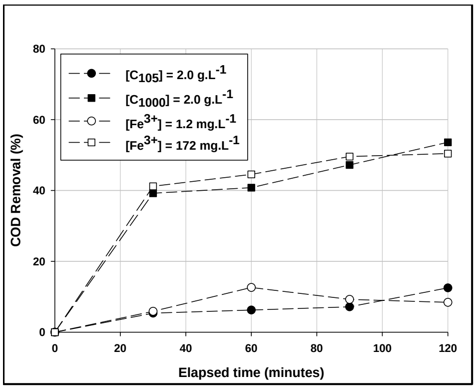

Figure VI.3. Chemical oxygen demand removal (%) profiles along the experiments for comparison between the lowest (C_{105}, dose 4) and highest (C_{1000}, dose 4) iron leaching results with pure homogeneous reaction.

Figure VI.3 shows the COD removal curves along the experiments and the profiles are very similar between both comparisons: (i) C_{105}, dose 4 versus the lowest dose of Fe^{3+} (1.2 mg.L^{-1}) and (ii) C_{1000}, dose 4 versus the highest Fe^{3+} concentration (172.0 mg.L^{-1}), meaning that the reaction using the proposed catalyst is, indeed, almost exclusively homogeneous.

VI.4. Conclusions

Higher baking temperatures generated more active solids (superior TPh, COD and TOC depletions) and less adsorption. Although the catalyst baked at 1000 °C reached very good removals (almost 100 % of TPh, more than 50 % of COD and around 45 % of TOC), the iron leaching was too high (172.0 mg.L^{-1} for the catalyst dose of 2.0 g.L^{-1}). Also, the BOD_5/COD ratio is reduced to less than half of the initial simulated effluent (around 0.19 for the treated samples while the synthetic solution has a 0.42 ratio). Since these two last parameters (iron leaching and BOD_5/COD ratio) are major preoccupations for the Fenton process due to environmental concerns, C_{105}, the non-baked catalyst, is pointed as the best solid in our study. It presents low reaction activity (almost 70 % of TPh removal, approximately 15 % COD abatement and a TOC increment of 8 %), but keeps the biodegradability close to the initial (BOD_5/COD ratio of 0.40). Also, the catalysts baked at the lowest temperatures had the advantage of leaching much less iron. The homogeneity of the process was clearly certificated through two comparative experiments, in which very similar profiles can be observed when Fe^{3+} is used as catalyst at the leached iron concentrations.

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VII. Fenton's sludge as iron precursor for ceramic catalysts preparation[5]

This work had the goal of recycling iron from Fenton's sludge gathered from a detergent industry that uses the homogeneous Fenton's process to treat its effluents. To recover the iron from this waste, the metal was extracted by acidic digestion and employed in the preparation of a new iron catalyst.

Our research group has formerly tested ceramic catalysts prepared by co-precipitation. An iron-cerium oxide presented the best results at the molar proportion of 70/30 between iron and cerium (Fe-Ce-O 70/30). Likewise, the best calcination temperature was studied and found to be 300 °C. The co-precipitation procedure consists on the mixture of precursor salts of both metals (iron and cerium nitrates) that are precipitated by pH augmentation. This work intends to replace the iron nitrate, fundamental reactant in this catalyst preparation, by a solution containing the extracted iron, as referred above.

After the production of the solids using the new procedure, Fenton's activity was compared to discuss the possibility of this novel approach on the catalyst preparation. The assessment took in consideration the chemical oxygen demand (COD) and total phenolic content (TPh) as main parameters and biochemical oxygen demand in five days (BOD_5) as biodegradability indicator.

VII.1. Introduction

Environmental concerns have been growing from many years and are considered a serious matter nowadays. People's needs for new products require each time more and different reactants being handled at factories. Each of these numerous processes generates a specific effluent that requires treatment before disposal to avoid soil and/or water sources contamination.

Our research group has great attention in the depuration of olive mill wastewaters, which are seasonal and present toxicity to bacteria, two factors that inhibit biological treatment. Mediterranean countries are known for the quality of their olive oil. Together with the high amount of oil there produced, comes an elevated wastewater volume that needs treatment before proper disposal. Since the composition of these effluents encompasses phenolic acids, biological systems are not pointed out as the best management process due to the presence of chemical species toxic to activated sludge. Also, this wastewater appears only during a few months of the year and this seasonality is another difficulty about using microorganisms on its remediation.

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[5] This chapter is based upon the publication Rossi, A.F.; Alcoforado, R.A.; Abrantes, T.A.; Martins, R.C.; Quinta-Ferreira, R.M. *Proceedings of the 2nd International Conference on Wastes: Solutions, Treatments and Opportunities*, Braga, Portugal **2013** 427-432.

Advanced oxidation processes (AOPs) are alternatives to treat these kinds of effluents due to their high oxidative power and range of compounds that it can degrade. The Fenton's process is one of the cheapest to implement and use due to the low energy requirements and abundant reactants: hydrogen peroxide is the oxidizing agent and, usually, iron is the catalyst that promotes the formation of hydroxyl radicals (•OH). Nevertheless, this method presents the disadvantage of producing high amounts of sludge, since the iron concentration required is above legislation parameters and its separation is due to precipitation of the metal by pH augment. To overcome this drawback, the heterogeneous reaction became widely studied. Our research group has investigated different solids prepared by co-precipitation, as in Imamura et al. (1985), used as Fenton's catalysts. Amid the tested materials were copper, cobalt, manganese and cerium (all along with iron). This last one presented the best result at the molar proportion of 70/30 (iron/cerium).

The co-precipitation methodology for ceramic catalysts preparation requires, as reactants, the precursor salts of the desired metals (iron and cerium nitrates, for example). This study intended to replace the iron nitrate with a solution containing the same metal extracted from Fenton's sludge coming from a detergent wastewater treatment plant that uses the homogeneous Fenton's process to treat its effluents. In a previous work, this iron sludge was directly evaluated as heterogeneous Fenton's catalyst. Although the mud presented activity in the reaction and good COD removals in some cases, the investigation led us to conclude that it was not recommended for the reaction because it diminished the biodegradability of the treated samples and also the reaction was not heterogeneous (the leached iron was responsible for almost all the efficiency of the catalyst) (Rossi et al., 2013).

After the production of the solid using the new method, Fenton's activity results were compared to discuss the possibility of this novel approach on the catalyst preparation. To assess the Fenton's activity, chemical oxygen demand (COD) and total phenolic content (TPh) were the main parameters. With the new methodology of catalyst preparation, the mud can be recycled and iron would be provided from this waste. Also, the created solid has a lower cost due to the elimination of the iron nitrate reactant from the necessary materials. Thus, economic and environmental advantages may rise from this new methodology, avoiding the waste of iron at the production of ceramic catalysts and reducing the amount of undesired Fenton's sludge.

VII.2. Experimental

VII.2.1. Iron extraction from the sludge

Fenton's sludge collected from detergent's industry that uses the homogeneous Fenton's process to treat its effluents was recently studied by our research group (Rossi et al., 2013). As it contains a high iron load, 37 % (w/w) in the raw mud and 71 % when calcinated at 1000 °C for 2 hours, we have investigated the possibility of recycling this metal to produce a new catalyst. Since the iron leaching was high during the studied Fenton's reaction, we tried a simple methodology to extract the metal: the mud was added to a beaker containing water with previously set pH to the desired value. Magnetic stirring was then initiated and the system was left for 24 hours before filtration and analysis of the iron content in the aqueous media, which was evaluated by atomic absorption. Based on the leaching results of the former study, we have developed a design of experiments (DoE) to optimize the metal extraction. As DoE's parameters, we have chosen pH and sludge concentration – creating, with their interactions, 5 extraction experiments – carried out in duplicates to check the reproducibility of the tests. The parameters, displayed in Table VII.1, were chosen based on former results of iron leaching. The lowest sludge concentration was set equal to the highest dose used on that work: 2.5 g.L^{-1}, and the higher concentration was set to ten times that dose to evaluate if further sludge addition would contribute to more iron leaching. Tested pH values were between 2.0 and 4.0, in order not to set them too far from the Fenton's optimal pH (3.0) and keep an acidic media.

Table VII.1. Design of Experiments low (-), high (+), central (0) values and iron extraction data.

	-	0	+
pH	2.0	3.0	4.0
[Sludge] (g.L^{-1})	2.5	13.7	25.0

Table VII.2 shows the extraction results for each experiment. As one can see, most experiments were not reproducible (see the results attained for the two replicas in the fourth column) and no patterns emerged from them in order to select the best extraction conditions – standard deviations were too high, reaching 81 % in one of the cases (Experiment 1). This disadvantage may be related to the mud composition heterogeneity. Also, the amount of iron extracted was too low in all cases, preventing to proceed to the catalyst preparation with any reasonable efficiency.

Table VII.2. Design of Experiments results.

Experiment #	pH	[Sludge] (g.L^{-1})	$Fe_{extracted,1/2}$ (g.L^{-1})	$Fe_{extracted, average}$ (g.L^{-1})	Standard Deviation (g.L^{-1})	Standard Deviation (%)
1	2.0	2.5	95.2 / 10.2	52.7	42.5	81 %
2	2.0	25.0	7.0 / 40.7	23.8	16.9	71 %
3	4.0	2.5	246.1 / 217.9	232.0	14.1	6 %
4	4.0	25.0	59.7 / 7.5	33.6	26.1	78 %
5	3	13.7	5.3 / 2.5	3.9	1.4	36 %

As the simple method of magnetic stirring in acidic media was not interesting due to the raised discussion, another procedure was implied to extract the iron from the calcinated mud: acidic digestion. It consists on baking the sludge in HCl 6 N before filtration and dilution. With this method, it was possible to predict the obtained iron extraction concentrations because it is capable to completely dissolve the mud's iron content. Nevertheless, samples were still forwarded to atomic absorption analysis so we could be sure of the solution's concentration before the catalyst preparation.

VII.2.2. Catalyst preparation

One of the catalysts was prepared by co-precipitation, as in Imamura et al. (1985). This methodology consists on the precipitation of two metals from their precursor salts (iron and cerium nitrates, in this case). Precursors are added at such concentrations that would match a desired molar proportion between the metals. Since previous work from our research group highlighted the iron/cerium ratio of 70/30 calcinated at 300 °C for 2 hours, these factors were maintained and an innovation was tested: instead of adding iron nitrate, this metal was extracted as explained above, by acidic digestion of Fenton's sludge. The rest of the methodology was maintained and the activity of both solids was compared. Catalysts were named C_1 (normal methodology, original catalyst) and C_2, the new catalyst – which contains recycled iron.

VII.2.3. Synthetic effluent

Since one of our group's major focuses are olive mill wastewaters, we have prepared a synthetic effluent to simulate them. This solution is a mixture of 6 phenolic acids (3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid) at the concentration of 0.1 $g.L^{-1}$ each. As they present low solubility in water, their dissolution is stimulated by 15 minutes of ultrasounds (Crest ultrasounds equipment). To ensure best Fenton's procedure conditions (Martins et al., 2010), the pH of this solution is always set to 3.0 before being forwarded to react.

VII.2.4. The Fenton's process carrying out

Magnetically stirred beckers (500 mL) were used as reactors containing 300 mL of synthetic effluent. The catalyst was added at 1.0 $g.L^{-1}$, 5 minutes was given to the system to homogenize and then the oxidant agent, H_2O_2 at 244 mM, was slowly poured. Right after the catalyst addition, pH started to be monitored and maintained at 3.0 using a Crison MicropH 2000 probe. Time was set to 0 with the peroxide addition. Along the experiment, samples were withdrawn, filtrated (0.45 µm pore diameter filter paper to remove the catalyst) and had their pH raised above 10 in order to quench the reaction. Each sample was then named and reserved to further analysis.

Adsorption tests were carried out in order to evaluate the organic charge removal of phenolic acids by adsorption in the catalysts. These had the same procedure mentioned on the paragraph above but without the peroxide addition. Also, as there was no Fenton reaction on these experiments, there was no need to raise the pH after filtration.

VII.2.5. Organic charge evaluation techniques

The Folin-Ciocalteu procedure (Folin and Ciocalteu, 1927; Silva et al., 2007) was used to assess the total phenolic content (TPh) using a T60 U PG instruments spectrophotometer for absorbance measurement. Chemical oxygen demand (COD) was evaluated by the Standard Method 5220D (Greenberg et al., 1985), using a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer. Standard Method 5210 was employed to measure the biochemical oxygen demand in five days (BOD_5) – using garden soil inoculum.

VII.3. Results and discussion

VII.3.1. First results

Optimal operational conditions aiming organic charge removal and biodegradability enhancement of wastewaters were already determined for the original catalyst, C_1 (Fe-Ce-O 70/30 produced by co-precipitation using iron and cerium nitrates and further calcinated at 300 °C for two hours): [catalyst] = 1.0 g.L^{-1}, [H_2O_2] = 244 mM and pH = 3.0. These conditions were also applied to the reactions involving the new catalyst, C_2, prepared using recycled iron from Fenton’s sludge. Alone, neither of the catalysts presented significant amounts of organic charge adsorption from the synthetic effluent and, likewise, H_2O_2 alone oxidized negligible organic matter. Also, chemical regime was certified, meaning that mass transfer resistances were unimportant (Martins et al., 2009). Afterwards, the activity of both catalysts was compared and will be discussed in the next sections. Their efficiency was measured by COD and TPh depletions, since the first is the most important parameter reported at the legislation for wastewaters disposal and the other is a good way to evaluate the start of the reaction, once the phenolic acids are the first compounds to be broken by the Fenton’s chemical oxidation. Furthermore, the final samples of both treatments were exposed to BOD_5 tests, which can give us an idea about the biodegradability through the BOD_5/COD ratio.

VII.3.2. Total phenolic content

One of the chosen parameters to evaluate the catalysts performances in the Fenton’s oxidation was the phenolic content removal. Since the synthetic solution is exclusively composed by aromatic molecules and those are easily broken by the Fenton’s process, high depletions on this parameter are expected. Also, it is a good way to analyze the initiation of the oxidative process – which is a chain reaction, given that the cleavages generate new radicals that will further react.

As we can see in Figure VII.1, C_2 presents a slightly lower TPh depletion during the process. Even though numeric values did not match, both profiles are very similar: with substantial removals at the beginning of the reaction (approximately 60 % in 20 minutes) and a slower depletion afterwards until the end of the reaction – which is something common regarding the heterogeneous Fenton’s process. Thus, we can affirm that both C_1 and C_2 presented analogous activities towards phenolic cleavage from the synthetic solution at the applied reaction conditions.

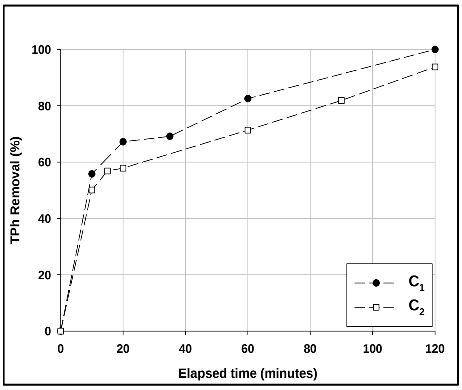

Figure VII.1. Normalized TPh depletion profiles during the Fenton’s process over time for the original catalyst, prepared using iron nitrate (C_1), and the new catalyst, prepared using recycled iron (C_2). Conditions: [catalyst] = 1.0 g.L^{-1}, [H_2O_2] = 244 mM and pH = 3.0.

VII.3.3. Chemical oxygen demand

One of the most important factors regarding wastewater treatments is the COD due to legislation requirements. As one can see in Figure VII.2, C_1 and C_2 also presented similar COD reduction profiles. Although around 15 and 20 minutes of reaction C_2

presented lower depletions, after half an hour the values become very close between both catalysts (as at 10 minutes of reaction) and the final results have a standard deviation of less than 2 % (removals of 49 % for C_1 and 51 % for C_2).

VII.3.4. Biochemical oxygen demand

According to the present legislation, wastewaters direct disposal requires low COD values (below 150 mg.L^{-1}), which are hard to assure using only oxidative processes. Thus, the Fenton's process is commonly used as a pre-treatment for effluents that present some toxicity – it can reduce the organic charge in great amounts and also increase the effluent's biodegradability, allowing further biological processes or even disposal to sewage collection.

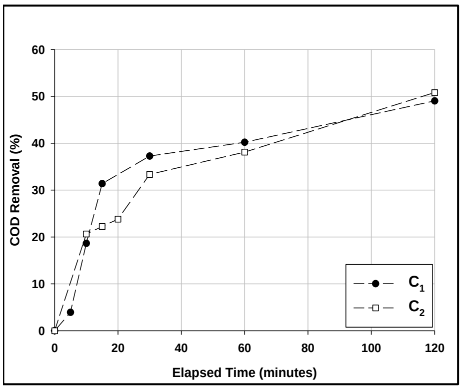

Figure VII.2. Normalized COD depletion profiles during the Fenton's process over time for the original catalyst, prepared using iron nitrate (C_1), and the new catalyst, prepared using recycled iron (C_2). Conditions: [catalyst] = 1.0 g.L^{-1}, [H_2O_2] = 244 mM and pH = 3.0.

One simple way of having an idea about the biodegradability of the treated samples is the BOD_5/COD ratio. Original Fe-Ce-O 70/30 final samples presented a ratio of 0.76, meaning that the remaining compounds are biodegradable. On the other hand, the new catalyst presented a very low ratio (0.22, lower than the initial value, which is 0.40) due to the reduced BOD_5 value: 134 mg.L^{-1} (against 485 mg.L^{-1} for C_1). Thus, as a pre-treatment material, C_2 could not succeed to replace the original catalyst. Even though the new catalyst presented similar organic charge depletions (namely TPh and COD abatements, Figures 1 and 2), somehow the reaction pathways were different and, as a result, the generated molecules at the end of the procedure were much less biodegradable. As the Fenton's process is a chain reaction, it is hard to confirm which compounds are present at the final system and if they are biologically refractory or toxic to the bacteria used in the viability of such methodology.

VII.4. Conclusions

This work raised the possibility of recycling iron from Fenton's sludge coming from detergent and cosmetics industry that handles its effluents by the homogeneous Fenton's process. The recovered metal would be used as a precursor agent to produce a new catalyst with the same properties as a former solid obtained by our investigation group, the Fe-Ce-O 70/30 – as the original material presented great performance as Fenton's catalyst. Regarding TPh and COD removals, two reaction activity indicators, the new catalyst (C_2, produced from recycled iron) presented similar profiles when compared to the original catalyst, C_1. Yet, when it comes to the biodegradability indicator, BOD_5 and the BOD_5/COD ratio, C_2 revealed much worse results: low BOD_5 and a ratio even lower than the initial synthetic effluent. With this argumentation and the abatement values (51 % COD and 93 % of TPh), it can be said that even though the recycled iron can be used for the production of new catalysts aiming organic charge depletion, further biological treatment will be demanded to test if it is suited for effluents remediation.

VII.5. References

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Silva, A.; Nouli, E.; Carmo-Apolinário, A.; Xekoukoulakis, N.; Mantzavinos, D. Sonophotocatalytic/H_2O_2 degradation of phenolic compounds in agro-industrial effluents *Catal. Today* 124 **2007** 232-239.

VIII. Reuse of iron bars from construction sites as Fenton's heterogeneous catalysts[6]

Iron bars from construction sites were converted into iron shavings using a lathe so the resulting solids could be studied as Fenton's catalysts. While treating a synthetic olive mill effluent, this material showed good results regarding COD and TPh removals at concentrations amidst 20 and 60 $g.L^{-1}$ of iron shavings and 35 to 70 mM of hydrogen peroxide. The Design of Experiments methodology was employed to analyze the efficiency of the reactions and optimize the process. Also, it showed good agreement between replicas, meaning that the process is reproducible. Other variables used were pH (between 3.0 and 4.0) and time (10 to 120 minutes). At the best conditions, 65 % COD abatement was observed and 98 % of the TPh was destroyed.

VIII.1. Introduction

Wastewater disposal before proper treatment by the agro-industrial activity can cause severe environmental risks to terrestrial ecosystems and these impacts turn out endangering the surrounding biodiversity. The production of olive oil – a wide field in Portugal, generates effluents with some toxicity guaranteed by its phenolic compounds that are hard to be degraded by regular biological treatment stations, thus, requiring alternative techniques before correct disposal. Also, their production is seasonal, presenting elevated volumes at a certain height of the year and none during the rest of it – a factor that also interferes with biological depuration due to bacterial delays related to adaptation.

The Fenton's process is an advanced oxidation process (AOP) that has been investigated due to the attainment of high mineralization of effluent's compounds and wide range of pollutants capable of treatment. Also, this reaction presents the advantage of being carried out involving low costs to the industry. Parameters such as the pH and the concentrations of iron ions and hydrogen peroxide have been studied to reach better efficiency.

This work investigated the possibility of using zero valent iron (ZVI) gathered from construction site wastes as Fenton's catalysts – more specifically from the iron bars used to enhance building's stability inside its structures: A-400 iron with Ø = 18 mm. These bars are the most commonly used worldwide and were converted into iron shavings using a lathe. The obtained solids were separated into two different categories: the ones extracted from the external part of the bars – containing some rust, and the ones from the internal part of the bars – visibly cleaner and less oxidized.

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[6] This chapter is based upon the publication Rossi, A.F.; Abrantes, T.C.; Martins, R.C.; Quinta-Ferreira, R.M. *Proceedings of the 2nd International Conference on Wastes: Solutions, Treatments and Opportunities*, Braga, Portugal **2013** 769-774.

In this context, the obtained solids were used as Fenton's catalysts tested in the treatment of an olive mill simulated wastewater. The economical factor of this recycling is of great interest to the industry and, by means of sparing other catalyst production, environmental concerns are also inside the advantages. The overall oxidation efficiency was assessed through total phenolic content (TPh) and chemical oxygen demand (COD).

This work was performed using a statistical tool, called design of experiments (DoE), aiding the determination of optimal operational conditions. In this research methodology, a certain number of variables are controlled, such as pH, time and catalyst and hydrogen peroxide concentrations (the independent variables) and their influence on the results, such as TPh and COD (dependent variables) can be calculated. The acquired data, in this case, TPh and COD, are inputted in a software, STATISTICA (StatSoft), able to generate plots and calculate factors that, once interpreted, give us the independent variables' influence on the dependent variables.

VIII.2. Experimental

VIII.2.1. Phenolic solution

A solution containing 0.1 g.L^{-1} of six phenolic acids (3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid) was used to simulate olive mill wastewaters. To assure their dissolution in water, the solution is exposed to ultrasounds (Crest ultrasounds equipment) for 15 minutes. pH is then set to 3.0, 3.5 or 4.0 – according to the DoE, using a Crison MicropH 2000 probe so the reaction can be carried out as our group's used Fenton's parameters (Martins et al., 2010).

VIII.2.2. The Fenton's process carrying out

100 mL sample plastic cups containing 30 mL of the synthetic effluent were used as reactors. The required amounts of catalyst and hydrogen peroxide, according to the DoE, were added to the system and, with the last reagent addition, the cups were closed and the reaction was given as started. At this point, cups were inserted in an orbital stirrer that guaranteed system's homogeneity. The mixture was allowed to react for a certain time interval and, afterwards, it was filtered in 0.45 µm pore diameter filter paper to remove the iron shavings and the pH was raised above 10 with NaOH to stop further oxidation.

VIII.2.3. Organic charge evaluation techniques

The Folin-Ciocalteu procedure (Folin and Ciocalteu, 1927; Silva et al., 2007) was used to assess the total phenolic content (TPh) using a T60 U PG instruments spectrophotometer for absorbance measurement. Chemical oxygen demand (COD) was evaluated by the Standard Method 5220D (Greenberg et al., 1985), using a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer. Standard Method 5210 was employed to measure the biochemical oxygen demand in five days (BOD_5) – using garden soil inoculum.

VIII.2.4. Design of experiments

In a first step, a comparison between the two types of iron shavings (external and internal parts) was performed to evaluate if they presented different activities in the reaction. As the results were close to each other, the entire bar was used without distinction between the inner and outer parts.

This comparison was made through the usage of the ZVI as heterogeneous Fenton's catalyst treating a synthetic olive mill wastewater (a solution used by our research group containing six phenolic acids at 0.1 $g.L^{-1}$ each). Organic charge removal was assessed through the chemical oxygen demand (COD) and total phenolic content (TPh) analysis.

Afterwards, a design of experiments (DoE) was developed to investigate which are the best parameters' values to carry out the reaction. The independent variables were: (1) iron shavings concentration, (2) hydrogen peroxide concentration, (3) pH and (4) reaction time – since the number of experiments will always be equal to (2^n + 2), whereas "n" is the number of independent variables and the constant value of 2 regards the duplicate of a central experiment (central values for all parameters), a total of 18 experiments were performed. Adopted values are presented in Table VIII.1. Usually, this methodology only requires the central experiment to be performed twice, in order to compare results. Yet, since the oxidation pathways use to be very sensitive to operational conditions, all experiments were carried out in duplicates to assure the reproducibility.

Table VIII.1. Variables adopted for the design of experiments: lesser (-), central (0) and higher (+) values.

Parameter	-	0	+
1: pH	3.0	3.5	4.0
2: [iron shavings] [$g.L^{-1}$]	20.0	40.0	60.0
3: [H_2O_2] [mM]	35.0	52.5	70.0
4: Time [minutes]	10	65	120

VIII.3. Results and discussion

VIII.3.1. Design of experiments

After assessing all experiment's COD and TPh reached values after the Fenton's oxidation, the removal percentage of these parameters were calculated and inputted in a computational program (STATISTICA 10, StatSoft) that helps with the statistical analysis. Table VIII.2 displays these results, from which the program extracted all next section's commented data. Good agreement between replicas can be verified, assuring the reproducibility of the performed study.

Table VIII.2. Design of experiments' results for organic charge removals for both duplicates of each experiment.

Experiment #	Factor 1 (pH)	Factor 2 ([iron shavings])	Factor 3 ([H_2O_2])	Factor 4 ([time])	COD removal [%]$_{1/2\ (duplicate)}$	TPh removal [%]$_{1/2\ (duplicate)}$
1	-	-	-	-	47.9 / 44.2	88.4 / 90.7
2	-	-	-	+	57.1 / 53.8	88.1 / 81.9
3	-	-	+	+	66.7 / 64.2	97.6 / 99.0
4	-	+	+	+	65.4 / 62.1	97.9 / 95.5
5	+	+	+	+	68.8 / 68.3	96.4 / 96.7
6	+	-	-	-	12.5 / 13.3	49.3 / 50.7
7	+	-	-	+	46.3 / 49.2	97.9 / 98.4
8	+	-	+	+	45.4 / 47.1	96.9 / 96.6
9	+	+	-	-	23.8 / 29.2	57.8 / 72.9
10	+	+	-	+	54.2 / 57.9	97.6 / 98.4
11	+	+	+	-	25.4 / 26.7	67.8 / 68.8
12	+	-	+	-	12.1 /10.0	47.4 / 48.4
13	-	+	-	+	53.8 / 52.1	87.1 / 90.7
14	-	+	+	-	60.8 / 64.2	97.2 / 97.4
15	-	-	+	-	46.3 / 46.7	95.3 / 89.1
16	-	+	-	-	42.1 / 42.1	86.2 / 85.3
Central	0	0	0	0	11.3 / 14.6	26.4 / 29.0

VIII.3.2. Total phenolic content

In Figure VIII.1, we can see the Pareto chart, which displays the significance level of each considered factor and their interactions (p). When the absolute calculated value is above 0.05, it means that the independent variable has important influence on the regarded system's dependent variable's value.

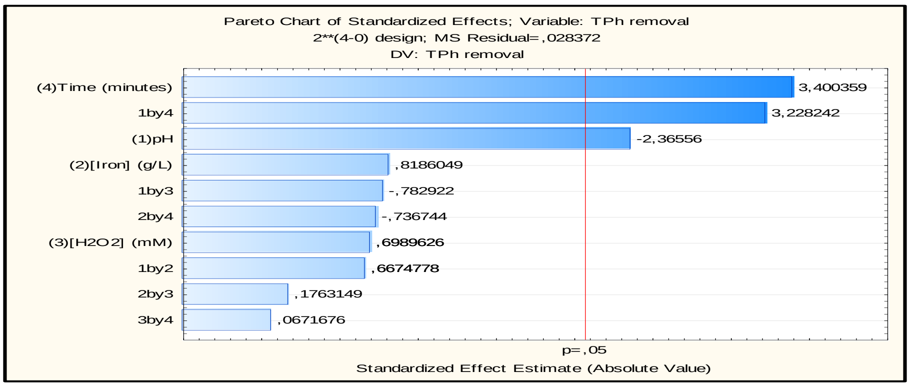

Figure VIII.1. Pareto chart. Independent variables: (1) pH, (2) iron shavings concentration, (3) hydrogen peroxide concentration and (4) reaction time. Dependent variable: TPh removal (%).

In this work's case, the independents variables were: (1) pH, (2) iron shavings concentration, (3) hydrogen peroxide concentration and (4) reaction time. The dependent variable was the TPh removal (%), which, as the chart shows, is mostly influenced by the reaction time, the pH and the interaction of these two parameters. With this in mind, we can conclude that the iron shavings and hydrogen peroxide concentrations, when kept between the two adopted values in this DoE will not interfere in the TPh removal value.

As we can see in Figure VIII.2, comparing the four plots (A, B, C and D), at low pH, the time variable present low interference regarding TPh removal, while at high pH values, this interference becomes much more important – meaning that while increasing the pH we reduce the rate of the phenolic compounds oxidation.

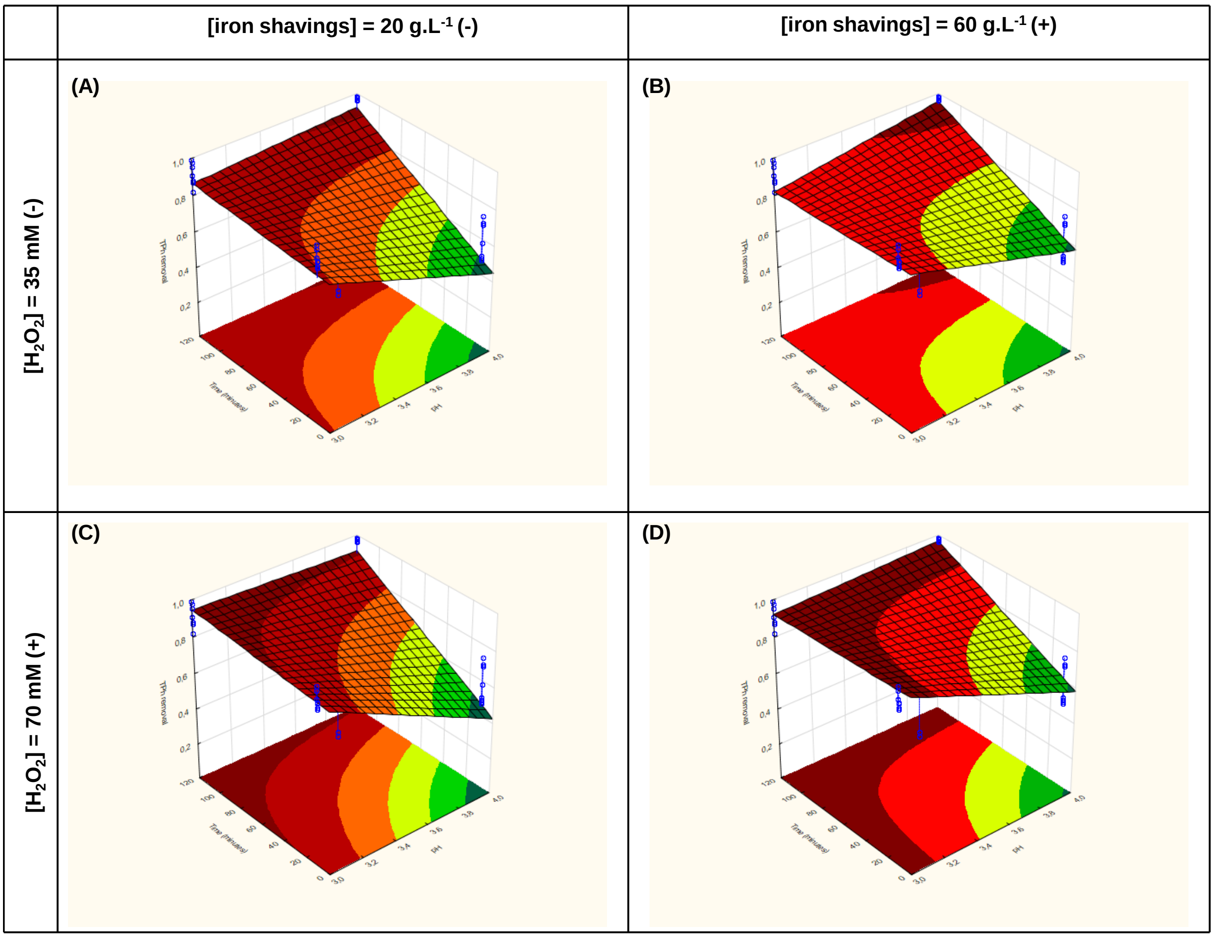

Figure VIII.2. Three-dimensional charts showing pH (X axis) and time (Y axis) interferences on the TPh removal (Z axis). **(A)** [iron shavings]= 20 g.L^{-1} and [H_2O_2] = 35 mM; **(B)** [iron shavings]= 60 g.L^{-1} and [H_2O_2] = 35 mM; **(C)** [iron shavings]= 20 g.L^{-1} and [H_2O_2] = 70 mM; **(D)** [iron shavings]= 60 g.L^{-1} and [H_2O_2] = 70 mM. All experiments took place at room temperature (~25 °C).

VIII.3.3. Chemical oxygen demand

The Pareto chart displayed in Figure VIII.3 has the same independent variables as the one discussed on the section above, but the dependent variable is the COD removal (%). We can see that the “p” values are higher in this chart, meaning that the considered variables have stronger interferences in the COD than in the TPh removals. This is due to the fact that phenolic compounds are easily destroyed by the Fenton’s reaction. Thus, almost all TPh removals are high and much closer to each other when compared with the COD removals. Being the values not far apart, the changes in the reaction parameters did not altered TPh reductions as much as it did with the COD abatements, explaining the higher significance values. Moreover, in the COD removal’s case, one more independent variable is considered important ($p > 0.05$, in absolute values) to the system: the iron shavings concentration.

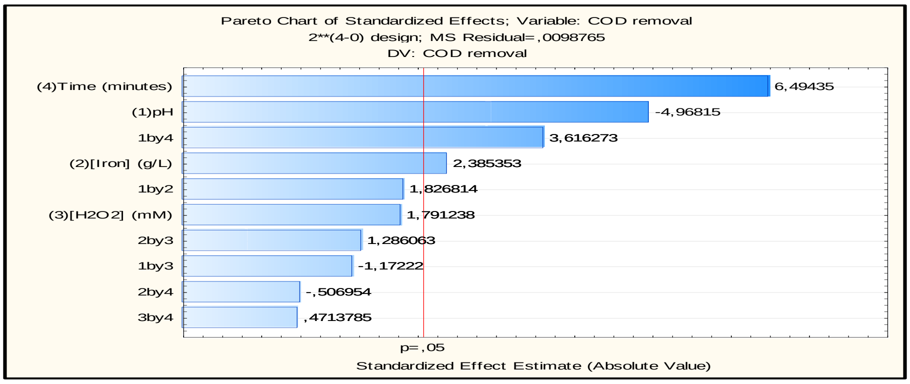

Figure VIII.3. Pareto chart. Independent variables: (1) pH, (2) iron shavings concentration, (3) hydrogen peroxide concentration and (4) reaction time. Dependent variable: COD removal (%).

Comparing the four plots of Figure VIII.4, what was commented at the end of the last section is confirmed (now for COD abatement): at low pH, higher reaction rates are observed. When the high concentrations of iron and peroxide are employed, we have the best COD removals for all pH ranges. The same COD reduction level is attained also for the lower iron concentration and higher peroxide amount. This could be pointed out as the best reaction parameters since the required iron is three times lower than the higher concentration and COD and TPh destruction are close from each other (pH 3.0, 120 minutes of reaction time, 20 g.L^{-1} of iron shavings and 70 mM of hydrogen peroxide).

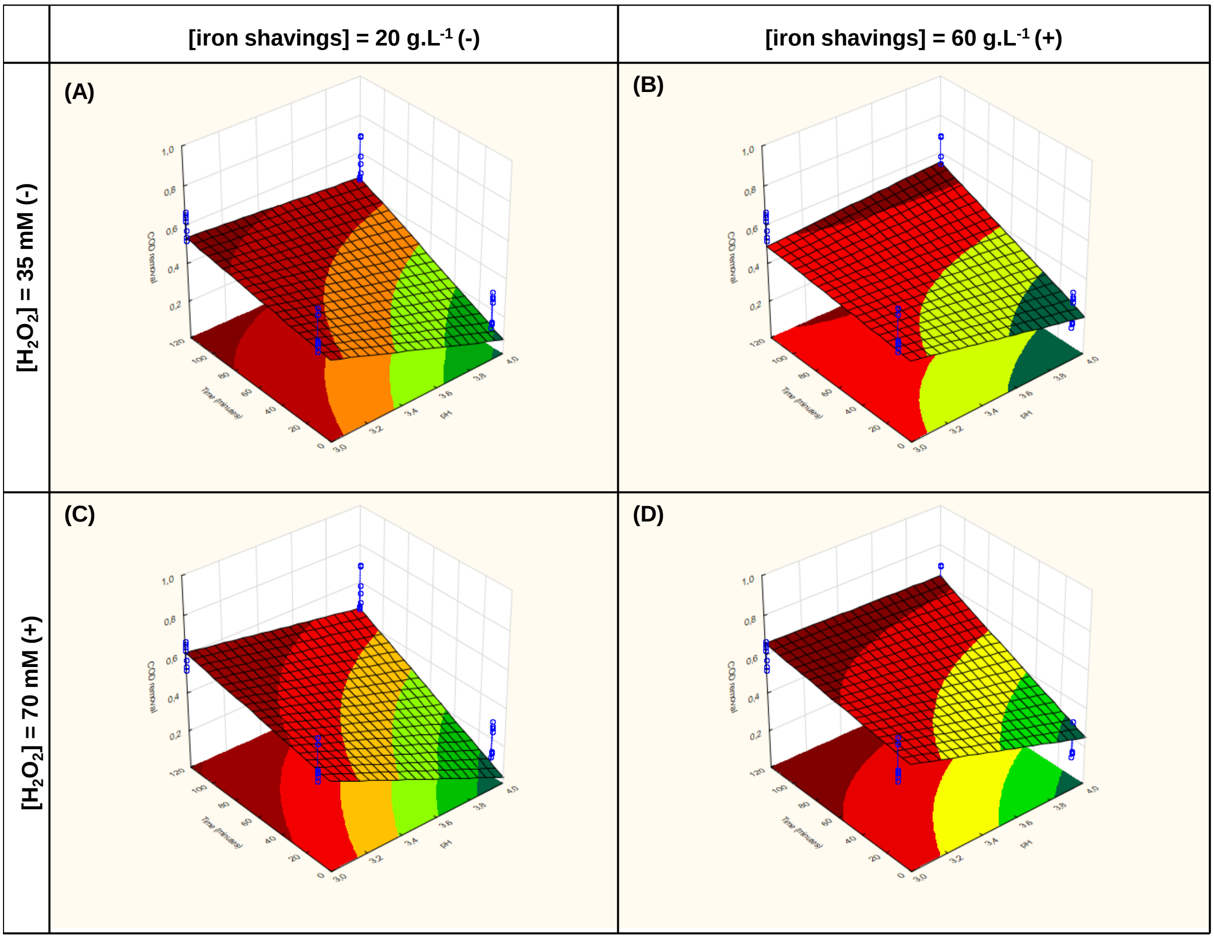

Figure VIII.4. Three-dimensional charts showing pH (X axis) and time (Y axis) interferences on the COD removal (Z axis). **(A)** [iron shavings]= 20 g.L^{-1} and [H_2O_2] = 35 mM; **(B)** [iron shavings]= 60 g.L^{-1} and [H_2O_2] = 35 mM; **(C)** [iron shavings]= 20 g.L^{-1} and [H_2O_2] = 70 mM; **(D)** [iron shavings]= 60 g.L^{-1} and [H_2O_2] = 70 mM. All experiments took place at room temperature (~25 °C).

VIII.4. Conclusions

The utilization of iron shavings from construction site iron bars as Fenton’s heterogeneous catalysts demonstrated good results regarding TPh cleavage and organic charge removal from a synthetic olive mill wastewater. At the optimum conditions (pH 3.0, 120 minutes of reaction time, 20 $g.L^{-1}$ of iron shavings and 70 mM of hydrogen peroxide), COD could be reduced in 65 % and TPh in 98 %. DoE’s results pointed out as important variables, for TPh removal, the reaction time, applied pH and the interaction between these two; while for COD removal the iron shavings concentration was also highlighted as important. As the kind of bars is the most common used worldwide (A-400 steel), the reuse of these solids could bring benefits to the environment and also reduce costs regarding industrial effluents treatment.

VIII.5. References

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IX. Integrating waste management with wastewater treatment: reuse of iron shavings as Fenton's catalysts for continuous operation mode[7]

Amongst low cost materials, the zero-valent iron (ZVI) has been widely studied all over the world - particularly in the iron shavings form, in several applications and processes. For example, pharmaceutical wastewater treatment has been investigated using ZVI as catalysts for the Fenton's oxidation (Segura et al., 2013) and the same process can also be applied to landfill leachates (Martins et al., 2012). Its high reductive power can be employed to reduce 2,4-dinitroanisole producing wastewater as a pre-treatment (Shen et al., 2013) or coking effluents (Lai et al., 2007). The Fenton's process is commonly used as a pre-treatment that enables further biological systems by oxidizing the effluent's organic charge. One of the applications of this process is the remediation of olive mill wastewaters (OMW), as this is one of the greatest concerns in Mediterranean countries regarding residual waters treatment. Therefore, a solution containing phenolic acids was used to simulate the effluent in this work. Iron shavings from two sources were tested as catalysts in a tubular fixed bed reactor in continuous operation mode during up to 6 days and a comparison with a commercial catalyst, N-150, was performed. The first ZVI source is a plate cutting factory located in Marinha Grande, Portugal, and the second kind of shavings was gathered from iron construction bars using a lathe. All ZVI showed higher catalytic activity than the N-150 catalyst – besides presenting stability along the whole process. Washing methodologies for appliance before using the shavings are discussed, as well as the metal leaching from the tested solids. COD and TPh were used as parameters on the discussion about the systems' efficiency and results show that the tested solids present good reactivity as well as stability to be used as Fenton's catalysts. Nevertheless, leaching data pointed out that the metal loss is too high and that homogeneous reactions must be considered and that further studies must be performed before industrial application.

IX.1. Introduction

The preoccupation with our water resources increases more and more as the years go by and industrial pollution holds a great responsibility in this scenario. Understanding the needs of this sector (essential to the modern world's way of life), it is necessary to develop affordable solutions so they can manage their own wastes and effluents without expending massive amounts of money.

In Portugal, as well as in other Mediterranean countries, the olive industry has distinctive importance. Since our research group belongs to this region, our work is focused mainly on olive mill wastewaters (OMW), which are rich in phenolic acids, present high

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[7] This chapter is based upon the submission Rossi, A.F.; Ferrão, J.A.; Martins, R.C.; Quinta-Ferreira, R. M. *J. Hazard. Mater.* **2014**.

organic charge and, therefore, cannot be directly discharged onto soils or rivers. The remaining effluent after oil fabrication presents some difficulties regarding selection of an adequate depuration methodology before disposal, such as the seasonality of its production and the toxicity to bacteria. These two issues, together, discard direct biological treatments, since there is not enough time for the bacteria to adapt to the substrate.

Facing these facts, producers have to recur to alternative treatment processes in order to obey current legislation parameters. Chemical procedures are pointed out, since they can be applied whenever and for how long it is necessary - also ignoring/overcoming the toxicity barriers. Advanced oxidation processes (AOP) are a viable possibility in this matter and encompass a range of options.

Amongst all AOP, the Fenton's process is one of the cheapest (Cañizares et al., 2009; Dulov et al., 2011; Renou et al., 2008), since it involves low cost materials (iron and hydrogen peroxide) and is able to non-selectively deplete a variety of compounds at mild conditions - saving energy costs.

This process accounts as one of the late 19th century's discoveries, by H. J. Fenton (Fenton, 1894). Recently, it has been widely employed as a wastewater treatment and, regarding OMW, its integration with other treatments is viable. In this strategy, the AOP is a pre-treatment, responsible for the effluent's toxicity decrease and biodegradability enhancement. Afterwards, a biological system can be used to meet discharge limits (Oller et al., 2011).

However, the Fenton's process presents the major drawback of producing sludge due to the high amounts of iron required - which is separated by precipitation forced by NaOH addition. To overcome this disadvantage, the scientific community started to research new approaches for this treatment methodology, coming up with the Fenton-like processes - widely studied by many investigators regarding several pollutants (Pera-Titus et al., 2004; Malato et al., 2009; De Laat and Le, 2006; Moffet and Zika, 1987).

Inside our research group, we have already started to study the Fenton-like process in a continuous mode operation and made a comparison with the batch mode (Martins et al., 2013). In the present paper, some of the previous methodology was followed, and it is an attempt to enhance the procedure and keep tracking the continuous operation trail. Since there are huge amounts of this material available, usually squandered by the industry, our interest on it grew after the first glimpses (Martins et al., 2012; Martins et al., 2013; Martins et al., 2014). Regarding this matter and environmental concerns, two wastes were chosen to be tested as catalysts: one from iron industry and another from construction sites, which will be described in details later on. As a result of this study, all iron shavings showed promising results as Fenton's catalysts.

According to Ma et al. (2008), a 60,000 $m^3.day^{-1}$ treatment plant in China used over 900 tons of iron shavings between the years of 2006 and 2008 - demonstrating that huge amounts of this material can be gathered from local industries and at very low expenses (~0.25 $US\$.kg^{-1}$).

One of the iron shavings used in the current work are a result of metallic plates cutting from a factory situated in Marinha Grande, Portugal. After cutting the plates, it is normal to see large amounts of iron shavings covering the ground of the factory, waiting to be swept and dumped. In Portugal, it is not common to apply the iron shavings on remediating systems, as it is in the mentioned Chinese treatment plant.

As a step on the attempt of changing this scenario, the feasibility of using the iron shavings wastes as Fenton's catalysts in a tubular reactor operating in continuous mode was studied. This operation style is still endorsed by scarce literature; however, Mesquita et al. (2012) and Duarte et al. (2013) already presented two examples of packed-bed reactors able to treat azo dye-containing wastewaters and textile effluents, respectively. In the present work, a solution containing a mixture of phenolic acids simulating OMW was treated on the referred Fenton's system. Its efficiency was evaluated through total phenolic content and chemical oxygen demand removals.

Likewise, the system and evaluation parameters have been used for a comparison of the first mentioned iron shavings with another kind of this waste, generated in our laboratory using a lathe to cut construction site's iron bars and gather iron shavings as well. The methodology was refined in order to better assess the system, gathering further results from the experiments and a comparison between all results is presented and discussed.

IX.2. Experimental

IX.2.1. Catalyst acquiring and preparation

The iron shavings were tested in three forms. The first was the raw form, exactly like they came from the ground of the factory. The second form was the iron shavings cleaned with acid. A HCl (Panreac, 37%) solution (10 % v/v) was used to wash the dirt placed on them. The last form involved cleaning with organic solvent, meant to remove greases that may have been placed onto them due to oils used in lubrication of the factory's machinery and that may also be found on the factory's ground. For this, they were treated with kerosene, followed by HCl 10% and 1-butanol to remove residual kerosene - according to a methodology presented by Zara and Weber (2012).

Acquiring these three forms of iron shavings, the necessity of extra steps between the gathering of the waste and its usage as Fenton's catalysts (such as the described cleaning methodologies) could be discussed. Thus, three different experiments were performed and they will be referred as Experiment 1 (raw iron shavings), Experiment 2 (HCl washing) and Experiment 3 (kerosene + HCl + 1-butanol).

IX.2.2. Solids' characterization

The obtained solids were submitted to Brunauer-Emmet-Teller surface area analysis (S_{BET}) determined by nitrogen adsorption at -196 °C in a Micrometrics ASAP 2000; X-ray diffraction (XRD) through a conventional and low angle X-ray diffractometer Philips X-Pert and acidic digestion to acquire data about the iron shavings' composition – procedure obtained from Greenberg et al. (1985).

IX.2.3. Synthetic effluent

Since this study is meant to be applied on OMW in the future, a solution was prepared containing six phenolic acids commonly found on those effluents, each at 0.1 mg.L^{-1} (protocatechuic acid (Acrós Organics, 97 %), 4-hydroxybenzoic acid (Sigma-Aldrich, 99 %), vanillic acid (Sigma-Aldrich, 97%), 3,4,5-trimethoxybenzoic acid (Sigma-Aldrich 99 %), veratric acid (Sigma-Aldrich, 99 %), syringic acid (Fluka, 97 %)). In order to assure the dissolution of those compounds in water, the mixture was submitted to ultrasounds (Crest ultrasounds equipment) for 15 minutes. The pH of the solution was then adjusted to 3.0 (Crison micropH 2000) using H_2SO_4 (Panreac, 96 %), as this is the optimum pH value for the Fenton's reaction to take place, according to previous studies (Martins et al., 2010). At last, the oxidant agent, H_2O_2 (Panreac, 33 % - stabilized QP), was added to the simulated effluent at 35 mM. TPh and Iodometry tests (both described on the next section) were carried out once a day for a whole week to check if the hydrogen peroxide was being decomposed or degrading the mother solution, and none of these effects were taking place - guaranteeing the desired mother solution concentration at the inlet of the reactor.

IX.2.4. The reactor and the continuous Fenton's process

Through the weighting of the water that fit inside the reactor with and without the presence of catalyst, the empty spaces of the reactor (11.5 mL) and its total volume (14.1 mL), respectively, were measured. These values were adopted after 5 measurements, with exclusion of the highest and lowest values and average calculation of the three remaining values. Likewise, the iron shavings' mass that fit the reactor was weighted (6.88 g). A deviation lesser than 2 % was found in all cases. Dividing the empty spaces' volume by the total volume of the reactor, the bed porosity can be found (81.6 %). Since both kinds of iron shavings were very similar, these data were acquired using the construction site iron bars' shavings and adopted to the plate cutting's shavings.

Figure IX.1 shows a simplified diagram (A), along with photographs of the installation (B) and a close-up of the reactor (C). The item number 1 displayed on the diagram consists in a tank that contains the mother solution described in the last section. It is covered by aluminum foil in order to avoid any interference that light may represent. Item number 2 is a peristaltic pump (Ismatec REGLO Analog MS-4/8), used to flow the solution through a darksome rubber tube onto the reactor at a volumetric flow of 1.0 mL.min^{-1}. The flow inside the reactor, marked by number 3, is upwards. Finally, the item number 4 represents the outlet of the reactor, from where samples were withdrawn during the process to be analyzed and assess its efficiency.

Two kinds of samples were taken, with different destinations: organic charge assessment (TPh, COD) and iron leaching evaluation. The first kind of sample was immediately mixed with 3 M sodium hydroxide, prepared from NaOH pellets (Panreac, 98 %), in order to quench the Fenton's activity that may remain due to the leached iron and reminiscent hydrogen peroxide. The second kind of sample received no further treatment, since the iron concentration is not affected by further reactions.

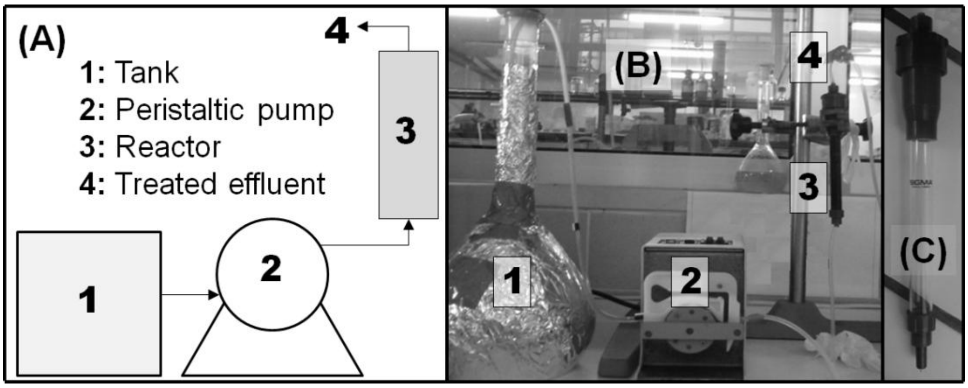

Figure IX.1. Continuous Fenton's process installation: **(A)** Simplified scheme, **(B)** Photograph of the complete system, **(C)** Photograph of the reactor. **1:** Tank containing simulated wastewater with hydrogen peroxide. **2:** Peristaltic pump used to assure a flow of 1 $mL.min^{-1}$ through darksome rubber tubes. **3:** Tubular fixed bed reactor filled with iron shavings. **4:** Reactor's outlet.

IX.2.5. Analytical techniques

The chemical oxygen demand (COD) was measured throughout the closed reflux standard method 5220D (Greenberg et al., 1985) using a thermoreactor (WTW CR 3000) and a photometer (WTW MPM 3000). For the total phenolic content (TPh) assessment, a spectrophotometer (T60 U PG Instruments) was used to measure the absorbance at 765 nm after the procedure presented by Folin and Ciocalteu (1927). Biochemical oxygen demand in five days (BOD_5) was measured according to the method 5210B, described by Greenberg et al. (1985). A spectrometer (Perkin-Elmer 3300) was used to quantify the iron leaching to the liquid phase through atomic absorption. To measure hydrogen peroxide concentrations, we have used the iodometric method as displayed by Brandhuber and Korshin (2009) but basically proposed by Kingzett (1880). It consists on the acidification of the samples (pipetted directly from the reactor to a clean beaker, where the titration would immediately occur to avoid further peroxide decomposition) by 2 M sulphuric acid in the presence of 5 % ammonium molibdate, 1 M potassium iodide and starch solution and posterior titration with sodium thiosulphate.

IX.3. Results and discussion

IX.3.1. Catalyst characterization

Regarding the iron shavings' composition, Ma et al. (2008), reported that its main content is iron (over 95 %), followed by chromium (from 1.3 to 1.6 %), carbon (from 0.3 to 0.4 %), silica (from 0.2 to 0.4 %), and other trace elements, like Mo, S, P, Ni (each at less than 0.03 %).

Through atomic absorption (after acidic digestion) and X-ray diffraction combined analysis of our catalysts, it was possible to conclude that they are mainly composed by ferritic stainless steel - which goes along with the statements of the above results. However, the mentioned work reports a much lower surface area (approximately 2.5×10^{-4} $m^2.g^{-1}$), while our iron shavings presented 1.14 ± 0.04 $m^2.g^{-1}$ - with pore diameters of 4.43×10^{-3} µm (micro/mesoporous structures) (Martins et al., 2013).

Thus, it might be said that, chemically, both samples of iron shavings are similar - but presenting shape and dimensional differences due to the cutting procedure adopted by the factory.

Some experiments were performed using a commercial catalyst (N-150, Süd-Chemie AG, Munich, Germany) - composed by Fe_2O_3 and MnOx in a weight proportion of 60 and 40 %. The received pellets were crushed into smaller particles in order to fit the reactor. BET isotherm and pore size distribution are showed by Martins and Quinta-Ferreira (2011). Meso/macroporous structures were identified with BET area of 133 $m^2.g^{-1}$, pore sizes between 0.01 and 0.1 μm (average of 0.0167 μm) and porosity of 67 %. The bed porosity was not inferred in this case to avoid waste of the catalyst (which has to fill the reactor 5 times and be replaced on each one of them to get precise measurements).

IX.3.2. Organic charge depletion – plate cutting shavings

On the first trials, plate cutting shavings were used. The organic charge depletion was analyzed for all experiments in order to assess and compare the efficiency of each test. All three performances demonstrated catalytic activity and stability during the whole process. In this work, the systems were tested only for 120 hours each to give us an idea about the possible deactivation of the catalysts, and, indeed, under the studied period this phenomenon was not observed - which led us to believe that, for future work, more operation time should be given to systems involving the use of these materials as catalysts. In the next section, another row of tests was performed and more time was given to the systems to operate.

TPh results along the first set of experiments, displayed in Figure IX.2.A, show that the solids present different levels of efficiency. It is clear that the treatment given to the iron shavings somehow interfered on the organic matter oxidation.

Experiment 1 used raw iron shavings and showed the lowest activity (average removal of 69 %), what may be occurring due to eventual dust and grease present in the solids. This dirt could be able to deplete the catalyst's efficiency in two ways: the surface area of the catalyst could be partially blocked and/or organic charge could be added to the synthetic effluent.

The test carried out using iron shavings washed with hydrochloric acid, Experiment 2, already presented much better results than Experiment 1, with an average TPh removal of 83 %. This second profile also did not oscillate as much as the first, suggesting more stability of the solid to be used as a catalyst in this process.

Experiment 3 (iron shavings washed with kerosene, hydrochloric acid and 1-butanol) presented the best results. Besides being even more stable than the catalyst used in Experiment 2, the average TPh removal presented was the highest: 95 %.

The efficiency order between the three experiments can be seen in Figure IX.2.B and was the same considering COD removal: Experiment 3 > Experiment 2 > Experiment 1. However, regarding this parameter, the average was much closer than for TPh removal. Also, Experiment 1 was the only one that presented an increase on COD removal until 30 hours of operation. This may suggest the hypothesis that the solid is adding organic matter to the stream due to the lack of a washing step before use - which was able to diminish the average COD removal (44 %). Also, the superficial dirty material might also decrease after contacting the mixture for hours leading to a higher surface area available for reaction.

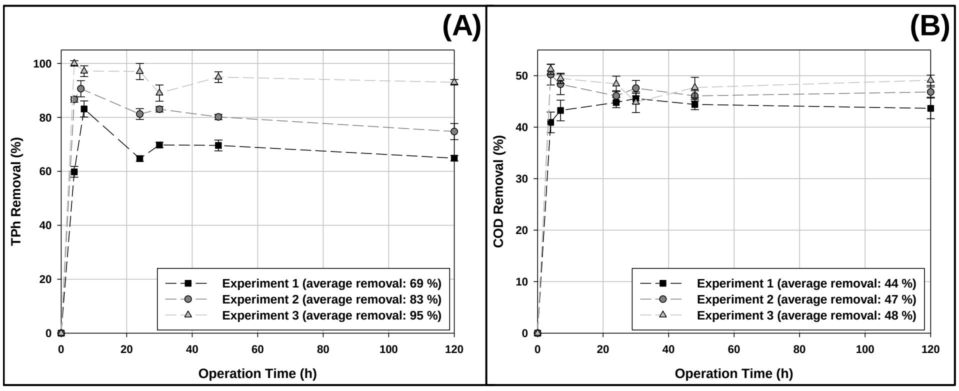

Figure IX.2. Organic charge removal profiles. **(A)** Total phenolic content removal profiles over the continuous Fenton's process; **(B)** chemical oxygen demand removal profiles. Inlet conditions: [H_2O_2] = 35 Mm, pH = 3.0, room temperature (~25 °C).

Experiments 2 and 3 presented very close COD removal values: 47 and 48 %. Almost all experimental data regarding these two tests are inside each other's error bars. With that in mind, the washing methodology must be compared and, since the one employed in the preparation of the catalyst used in Experiment 3 encompasses more costs (such as reactants, steps and, therefore, employed time), Experiment 2 is highlighted as the best one.

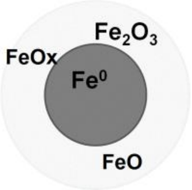

Figure IX.3. Simplified scheme of the outer shell formed around the ZVI, composed by several iron oxides.

Other two hypotheses might explain the efficiency order amongst the tested solids, according to the washing processes: (i) as showed by Singh et al. (2014), the ZVI is able to directly reduce the substrates. (ii) Lai and Lo (2008) discussed that a magnetite (Fe_2O_3) and goethite/hematite (R-FeOOH/R-Fe_2O_3) shell is formed around the ZVI particles and that acid-washing these solids can erase these precipitates from their surfaces – Figure IX.3 presents a scheme of the ZVI surrounded by this outer shell. Therefore, given that the hydroxyl radicals formation strongly depends on the kind and valence of the metal that reduces the hydrogen peroxide molecules (thus generating those radicals), we can say that both of these phenomena would interfere in the Fenton's oxidation, since this reduction, in other words, is the key to the catalyst's efficiency, due to the generation of species as reactive enough to non-selectively break many kinds of substrates - as the Fenton's reaction is well-known for.

IX.3.3. Construction site iron bars' shavings: organic charge depletion

The second row of experiments used iron shavings from construction bars as catalysts. A deeper attention was given to the first 5 hours of operation. This period is indicated by a rectangle on the profiles of Figure IX.4.A and Figure IX.5.A and expansions of those rectangles are presented on Figure IX.4.B and Figure IX.5.B. TPh removal profiles can be seen in Figure IX.4.A. The commercial catalyst, N-150, was used as a comparison amongst all ZVI and showed very poor efficiency on the process which dropped to nearly 0 % for most of the process. These results are plotted against solids gathered from two parts of the same solid: the external and the internal parts. Since the outer part of iron construction bars is visibly rusty, this differentiation was made to evaluate if that metal can be used completely or a "peeling" step is necessary to avoid unwanted effects. Observing the phenolic destruction profiles, we can see that the iron shavings from the internal part of the construction bars present a considerable advantage during the first 30 h of the process: the internal shavings are able to deplete, on average, approximately 10 % more phenolic acids than the external shavings. However, after this first quarter of the evaluated process, the shavings from the external part of the construction bars were able to reach almost the same removals as the others - and with no sign of efficiency drop. Therefore, we can say that, for TPh removal, the iron bars could be used, since more than 80 % of the phenolic acids were decomposed and also that the "peeling" step is not necessary (the bars could be completely used, since the external part is just a thin fraction and no severely unwanted effects were observed).

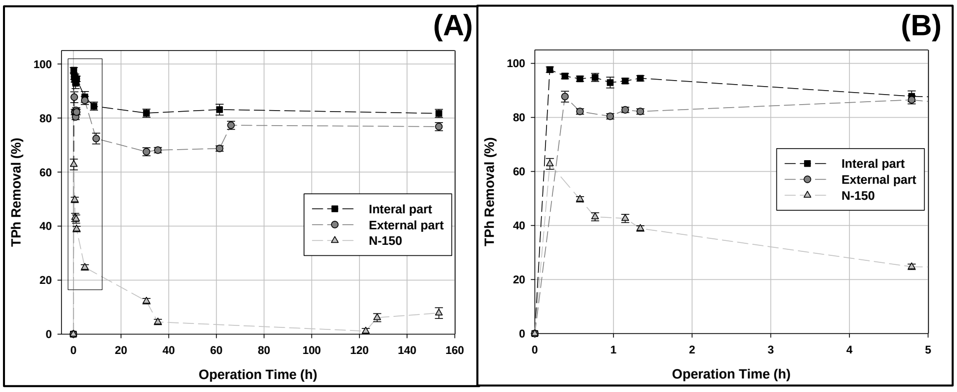

Figure IX.4. Total phenolic content removal profiles over the continuous Fenton's process. **(A)** For the whole process; **(B)** a zoom of the first 5 hours of operation. Inlet conditions: $[H_2O_2]$ = 35 Mm, pH = 3.0, room temperature (~25 °C).

Figure IX.5 presents COD removal profiles, which also highlight the inefficiency of the N-150 catalyst. In fact, N-150's profile suggests that this catalyst may not have been able to reduce the COD by oxidation, but by adsorption - since this parameter was only reduced significantly before 5 hours. After this period (approximately from 40 to 120 hours), the outlet's COD was almost equal to the feed solution's. Negative COD removals, "addition", in other words, can be noticed from this period on (12 % for the last experimental point), indicating that N-150 could be releasing organic charge (or even its own parts, containing adsorbed compounds). Another fact supporting the organic compounds removal by adsorption by the N-150 catalyst is its higher surface area when compared to the ZVI: 133 $m^2.g^{-1}$ against only 1 $m^2.g^{-1}$.

The final comparison between the iron shavings from internal and external parts of construction bars regarding COD removals starts with the first 5 h of the process. The gap discussed about TPh depletions, although still present, is not even nearly as big (on average, approximately 2 %, five times smaller than the TPh removal gap). Nevertheless, afterwards, the COD removal difference increases and becomes as high as the TPh depletion initial gap.

Rust, present on the outside of the construction bars, might be a catalyst poison or a deactivation form, in the ZVI case - explained by the fact that Fe^0 can produce more hydroxyl radicals than Fe^{3+} (encountered on the rust itself, usually Fe_2O_3) which presents slower reaction rates regarding the Fenton's oxidation and also by the fact that Fe^0 can reduce Fe^{3+} to Fe^{2+}, a more reactive specie of iron. Yet, even containing rust and considering the just discussed phenomena, we believe that the external part still presents an activity interesting enough to carry further studies aiming for industrial appliance using iron shavings from the inner and outer parts of the bars indistinctively, i.e., as they are obtained from the construction wastes.

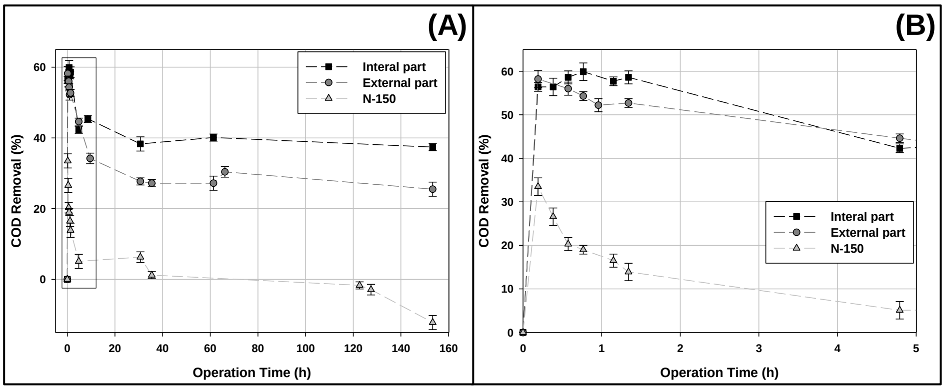

Figure IX.5. Chemical oxygen demand removal profiles over the continuous Fenton's process. **(A)** For the whole process; **(B)** a zoom of the first 5 hours of operation. Inlet conditions: [H_2O_2] = 35 Mm, pH = 3.0, room temperature (~25 °C).

IX.3.4. Construction site iron bars' shavings: metal leaching

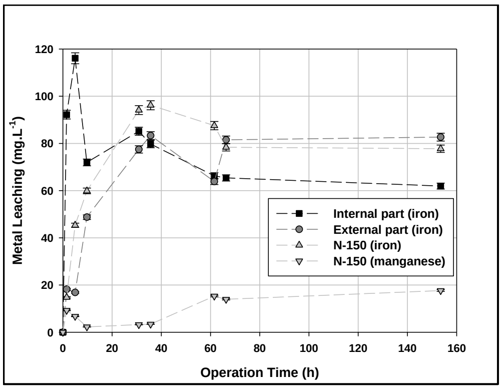

Figure IX.6. Metal leaching (iron and manganese) profiles over the continuous Fenton's process. Inlet conditions: [H_2O_2] = 35 Mm, pH = 3.0, room temperature (~25 °C).

In the heterogeneous catalysis field, one of the most important aspects when evaluating the feasibility of using a specific catalyst is its active species leaching from the solid to the bulk of the liquid phase; in this case, iron and manganese, in the case of the N-150 solid. This loss of reactive phase can alone be responsible for the efficiency reduction and also be a problem regarding its separation after the reactor's outlet.

Figure IX.6 displays the metal leaching profiles for the last row of experiments, where iron shavings from the internal and external part of construction bars and also N-150 were used as catalysts. As we can see, the metal leaching presented by all catalysts is much above legislation parameter (where 2 mg.L^{-1} is the limit).

Another problem is that with those iron concentrations available at the bulk, the allegedly heterogeneous catalysis may have been mistaken for actual homogeneous reaction. Further investigation is required before assumptions are made and conclusions are taken, but we might say in advance that it is likely that good part of the oxidation observed is due to the homogeneous process, since the concentrations levels of leached metal ions are high enough to react.

However, the leached metals percentage can be calculated, i.e., for the internal part shavings case: with the constant flow of 1 mL.min^{-1} and considering an iron leaching average of 75 mg.L^{-1}, at the end of the process there is a total of 711 mg of iron leached through the reactor's outlet. Since that, initially, reactor is filled with 6.88 g of iron shavings composed by > 95 % of iron, the amount of leached iron after 6 days (158 h) of continuous process represents almost 11 % of the initial iron content. Likewise, ≈ 10 % of the iron on the external shavings leached. According to these data, we can say that the iron leaching is too high and that it endangers the suggested catalyst in two ways: the catalyst will soon be deactivated due to lack of active sites and, more importantly, the iron concentration at the outlet of the reactor raises the necessity of a metal ions separation step before this effluent is forwarded to a subsequent treatment (that is usually biological and would not work properly at such iron concentrations).

Besides the low efficiency in removing organic charge from the mother solution, the N-150 catalyst also presented non-desired results regarding metal leaching. This solid is comprised by 60 % of iron oxides (mostly Fe_2O_3, meaning that 21 % of the catalyst's weight corresponds to iron). Even with the low iron content, the leaching of this metal approximates to the external part's shavings. The same leaching calculations, if applied to this solid, would give us the highest result: 46 % of the iron initially present on the catalyst is leached during the whole process. Another aspect of the N-150 catalyst that should be mentioned is the elevated concentration of leached iron allied with the very low catalytic efficiency - since homogeneous reactions could take place instead of the heterogeneous, removing higher levels of organic charge than the ones we can see on the presented profiles. However, we must consider that inside the rusty part of the iron shavings, there are considerable amounts of Fe^0. This ZVI, absent on the N-150 systems, is able to enhance the Fenton's reaction by reducing Fe^{3+} to Fe^{2+}, regenerating, thus, the catalyst sites. Yet, if the iron supply on the N-150 catalyst is already completely oxidized in the form of Fe_2O_3, very low reaction rates are expected and no regeneration would be possible (at least without hydrogen peroxide squandering, which is not desired) due to the lack of reducing agents.

Considering all the mentioned aspects, we may say that, for further studies, the initial pH of the mother solution should not be as acid as 3.0, since lower pH values lead to higher metal leaching. Nevertheless, previous studies have shown that pH values close to 3.0 usually enhance this process' oxidative power (Arnold et al., 2009). Also, at pH levels above 7.0, iron complexes can be generated, giving the Fenton's reagent coagulation capability (which is an undesired effect inside a packed-bed reactor because it could clog the column) (Neyens and Baeyens, 2003).

IX.4. Conclusions

Iron shavings from two sources were tested as Fenton's catalysts in continuous operation mode. The first kind of ZVI was used raw and its efficiency was compared to washed shavings (according to two methodologies), reaching the conclusion that an acid-washing of the solids is beneficial to the process since the TPh and COD removals augmented significantly without adding too much costs with this extra step. The second kind of ZVI was gathered from iron construction bars, the solids were separated according to the internal and external parts of these bars, once the outer part is visibly rusty, and a comparison of both of these parts was made with a commercial catalyst, N-150. Although better results were presented by the ZVI from the internal part of the bars, we concluded that there is no necessity of this differentiation, since the external part corresponds to a thin layer and its mass would represent only a small proportion if both parts are mixed. The acquired data supports that all iron shavings, regardless of source or washing methodology, presented good catalytic activity and stability, being suited for the Fenton's reaction. However, the metal leaching was high in all cases, indicating that homogeneous reactions might play a significant role in the tested systems and also that further studies should consider pH levels above 3.0.

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Part D. **Homogeneous Process and Comparative Studies**

Besides the production and trial of several ceramic catalysts and the investigation on wastes regeneration/management in order to find effective Fenton's catalysts for both batch-wise and continuous operation modes, the homogeneous process was also studied. Since our proposals are always turned to industrial application, reducing the costs and increasing the global efficiency of the treatment were always primary objectives. To perform so, an attempt of finding a new approach for the homogeneous Fenton's process was studied and it is explained on chapter X.

Since the beginning of this work, a constant idea was producing comparable results. Reaction parameters, such as catalysts and oxidizing agent concentrations, process temperatures, pH and oxidation times were carefully chosen in order to generate results that could have common links. Therefore, chapter XI described this development of the work before leading the reader to the end of this manuscript.

X. A new approach of the Fenton's process[8]

A different approach of the classical Fenton's process was analyzed as an attempt to overcome some of its disadvantages. The hydrogen peroxide decomposition has been studied at the ppm/mM ratio of [Fe]:[H_2O_2] = 4.1. Keeping the same ratio and using lower iron concentrations (and proportionally lower H_2O_2 concentrations), a whole set of experiments was carried out. Afterwards, another set was performed using several peroxide injections at each 20 minutes of reaction (time during which the peroxide would be fully decomposed by the Fenton's process). Removals of organic charge were enhanced by this new approach. The experiments that used low concentrations of reactants had their efficiency raised the most. Yields of both iron and hydrogen peroxide were calculated regarding the removed chemical oxygen demand, highlighting the much lower amounts of reactants needed to achieve the same oxidation levels when this methodology is applied. Furthermore, a prolongation of some experiments is quoted as a possible way to use even lower concentrations of reactants.

X.1. Introduction

Numerous applications of H_2O_2 in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, cyanides, and chlorine, are known (Venkatadri and Peters, 1993). Nevertheless, oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low reaction rates at reasonable oxidant agent concentrations. Ozone (Equation X.1), UV-light (Equation X.2) and transition metal salts, such as iron (Equation X.3), are known to activate H_2O_2 to form hydroxyl radicals (•OH), which are strong oxidants:

$$O_3 + H_2O_2 \rightarrow \bullet OH + O_2 + HO_2\bullet \qquad \text{(Eq. X.1)}$$

$$H_2O_2[+UV] \rightarrow 2\ \bullet OH \qquad \text{(Eq. X.2)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad \text{(Eq. X.3)}$$

The third kind of hydroxyl radical formation is called the Fenton's reaction. Hydroxyl radicals are much stronger oxidants than H_2O_2 alone, with an oxidation potential of 2.80 V. With such high potential, it is able to non-selectively oxidize a broad range of compounds at high reaction rates. The reaction was found in 1894 by H.J.H. Fenton (Fenton, 1894), but the process was only turned to wastewaters treatment in the late 1960's (Huang et al., 1993).

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[8] This chapter is based upon the paper in preparation by Rossi, A.F.; Costa, L.; Abrantes, T.C.; Martins, R.C.; Quinta-Ferreira, R. M.

Low installation and maintenance costs, as well as the lack of specificity of the oxidant are some of the main advantages of this system (Bigda, 1995). Furthermore, as the iron ions are dissolved when it comes to homogeneous systems, mass transfer limitations are negligible and the ions are readily available in the reaction medium, efficiently activating the oxidant agent (Pouran et al., 2014). Thus, the Fenton's process is a very interesting alternative for wastewater treatments, motivating many researchers to study it. However, as all other treatment options, this one also presents drawbacks that must be considered. The homogeneous reaction is strongly dependent on the medium's pH, varying from 2.5 to 4.0 (Katsumata et al., 2005); there is difficulty in catalyst recovery (Pariente et al., 2008); the previous acidification and posterior neutralization of the influent/effluent add costs to the system; a final separation step is required to remove the ferric sludge generated above pH 4.0 (Tamimi et al., 2008).

Since those disadvantages limit the industrial application, investigators started to study heterogeneous Fenton's reaction as an attempt to overcome the homogeneous process' deficiencies. Yet, other factors would raise as negative aspects of the process, mostly related to the used catalyst: its production cost augment, metal leaching, lower activity, stirring problems, separation steps for catalyst recover, amongst others.

Although the heterogeneous Fenton's process can be seen as a natural evolution of homogeneous systems, the present work suggests the optimization of the classical methodology as an interesting development alternative and, hereafter, discussion will present our reasons to assure this statement.

This work proposes a new methodology to approach the Fenton's process, which consists in several H_2O_2 additions but, unlike previous studies presented on the related literature, the total peroxide amount is not divided by a number of additions. The presence of this reagent, the oxidant agent, is the conditio sine qua non for the existence of oxidation inside any considered system. Although organic radicals can carry the oxidation further after the hydrogen peroxide and hydroxyl radicals are over, their oxidative power is not as strong. Therefore, we have recently studied the Fenton's reaction with several peroxide additions – each and every one in the same amount of the previously optimized initial (Martins et al., 2010). This way, it is possible to keep the oxidant agent at the most proper and desired concentration, assuring that the organic molecules will still be decomposed.

Since this system keeps the oxidation from stopping, the required concentrations of iron (catalyst) and peroxide, surprisingly, are much lower. This enhances some of the Fenton's advantages and drags along other positive aspects to the process – which will be presented and discussed on further sections.

X.2. Experimental methods

X.2.1. Synthetic effluent

To simulate olive mill wastewaters, a synthetic effluent was produced. It comprises six phenolic acids, commonly found in those residues, at the concentration of 0.1 mg.L^{-1} each: protocatechuic acid, 4-hydroxibenzoic acid, vanillic acid, 3,4,5-trimetoxybenzoic acid, veratric acid, syringic acid. The mixture is treated with ultrasounds (Crest ultrasounds equipment) during 15 minutes to assure complete dilution of all acids.

X.2.2. Analytical techniques

To assess the organic charge evolution over the experiments, COD was measured according to the 5220D Standard Method (Greenberg et al., 1985) – in which a WTW MPM 3000 photometer and a WTW CR 3000 thermo-reactor were employed. Folin-Ciocalteou procedure was used to colorimetrically infer the TPh through a T60 U PG Instruments spectrophotometer (Folin and Ciocalteu, 1927; Silva et al., 2007). Duplicates were performed in all analysis to confirm values.

The hydrogen peroxide concentration was measured following the iodometric method. Samples were pipetted directly from the reactor to a clean beaker (where the titration would immediately occur to avoid further peroxide decomposition), acidified by 2 M sulphuric acid in the presence of 5 % ammonium molibdate, 1 M potassium iodide and starch solution. Titration with sodium thiosulphate, along with the 1:2 stoichiometric ratio between hydrogen peroxide and this reactant will give the necessary data to calculate the peroxide concentration through Equation X.4. Samples were analyzed after 1, 5, 10, 15, 20, 25, 35, 60, 90 and 120 minutes of reaction.

$$[\mathrm{H_2O_2}](g.L^{-1}) = \frac{1}{2} \times \frac{[\mathrm{Na_2S_2O_3}] \times V_{\mathrm{Na_2S_2O_3}}}{V_{sample}} \times 34 \qquad \text{(Eq. X.4)}$$

X.2.3. The oxidative reaction and parameters' definition

The Fenton's process was carried out in beakers containing 500 mL of the previously described synthetic solution. pH was set to 3.0 (Crison MicropH 2000 probe) to assure best Fenton's efficiency, according to former studies of our group (Martins et al., 2010). Iron(II) sulphate was added as catalyst precursor. Magnetic stirring was used to homogenize the solution for about 5 minutes and, afterwards, the reaction was started with the addition of hydrogen peroxide.

Several metal and peroxide concentrations were tested and those can be seen in Table X.1. EXP 1's conditions were the first doses to be tested ([Fe] = 1000 ppm and [H_2O_2] = 244 mM), using parameters gathered previously optimized (Martins et al., 2010). As this study regarded heterogeneous Fenton using an iron-cerium catalyst, we supposed that the homogeneous process could reach the same efficiency using lower concentrations of reactants due to enhanced mass transfer of the dissolved iron ions in the medium.

Thus, reduced iron concentrations were also tested: half of the first experiment (500 ppm, EXP 2) one tenth of the initial (100 ppm, EXP 3), the European Economic Council limit of iron discharge (2 ppm, EXP 6) (EEC, 1982), another value above but close to this limit (10 ppm, EXP 5) and an intermediate value, important for comparison (20 ppm, EXP 4). Keeping the [Fe]:[H_2O_2] ratio always at 4.1, the respective hydrogen peroxide concentrations were calculated, a procedure adopted for future comparison amongst experiments.

Table X.1. Iron and hydrogen peroxide concentrations, as well as their ratio, for each experiment.

Experiment	[Fe^{2+}] (ppm)	[H_2O_2] (mM)	[Fe]:[H_2O_2]
EXP 1	1000	244.0	4.1
EXP 2	500	122.0	4.1
EXP 3	100	24.4	4.1
EXP 4	20	4.9	4.1
EXP 5	10	2.4	4.1
EXP 6	2	0.5	4.1

The first set of experiments was carried out as the classical Fenton's process: one single peroxide injection to begin the reaction. Magnetic stirring was applied to the synthetic solution at pH 3.0, room temperature followed by catalyst addition before H_2O_2 pouring. Samples were gathered for organic charge removal assessment by chemical oxygen demand (COD) and total phenolic content (TPh) at each 5 minutes until 30 minutes of reaction (5, 10, 15, 20, 25, 30 minutes), then at larger intervals: 45, 60, 90 and 120 minutes – methodologies described on the next paragraph. For these tests, the following denomination for each experiment was used: EXP 1, EXP 2, and so on.

The second set of experiments served to gather information about hydrogen peroxide decomposition instead of supplying organic charge evolution information. Experiments had their temperature controlled with a hot water bath to assess this parameter effect on the oxidant agent concentration decay (20, 25, 30, 35 and 40 °C). Each experiment was carried out in duplicate to assure data consistency and the metal and peroxide concentrations were always as in EXP 1 (see Table X.1).

After gathering information about the hydrogen peroxide decomposition, we proceeded to the third set of experiments, where a different approach was given regarding the hydrogen peroxide injection. It consisted on several doses of the oxidant agent – the reasons of this modification, based on the second set of experiments results, will be pointed out and explained in section X.3, along with the data discussion. The third set was two hours long and its samples served for organic charge removal assessment (COD and TPh). Since the peroxide was being replenished, samples were gathered at each 5 minutes during the whole experiment (assuming that the oxidation would go further and need closer attention to observe COD and TPh changes). The nomenclature used for this set was the same as for the first set, but with an asterisk to inform the difference on the peroxide injection: EXP 1*, ..., EXP 6*.

Table X.2 presents information about all sets of tests for a better understanding of the present work. There, the reader can see how many runs were performed in each set, as well as the nomenclatures, the reaction time, the number of peroxide injections and the sampling intervals.

Table X.2. Information about all sets of experiments.

Set	Number of Experiments	Nomenclature	Reaction time (min)	Peroxide injections	Sample intervals (min)
1	6	EXP 1, ..., EXP 6	120	Single	From 5 to 30
2	5	20 °C, ..., 40 °C	120	Single	From 1 to 30
3	6	EXP 1*, ..., EXP 6*	120	Several	From 5 to 30

X.3. Results and discussion

X.3.1. Process efficiency assessment

First set of experiments: classical Fenton's process. This work's starting point is EXP 1, using 1000 ppm of iron and 244 mM of hydrogen peroxide, which presented good COD and TPh removals for the studied effluent: 78 and 95 %, respectively. Figure X.1 shows these results, along with others. Although the second experiment used half of the iron and peroxide concentrations of EXP 1, both COD and TPh removal profiles are very close to each other, meaning that there is no need to use as much reactants as in EXP 1. When we look at EXP 3 profiles, we begin to notice that COD and TPh reduction values are not as good as for the two first runs. We also notice that this drop becomes drastic when EXP 3 (43 and 77 % COD and TPh removals using one tenth of the initial quantities) and EXP 4 (16 and 39 %, which used amounts 50 times lesser) are compared. EXP 5 is very close to EXP 4, presenting only 1 % less COD removal and 2 % less TPh removal. EXP 6's results, where the legal iron threshold amount (2 ppm) was used are much below: merely 4 % and 20 % COD and TPh removals, respectively, presenting, thus, the lowest degradation levels.

If, on one hand, we can clearly see the efficiency decay with the reactants concentration reduction, on the other we have a similarity for all experiments of this first set: the great majority of the oxidation happened on the first minutes of reaction. To evaluate how to enhance the classical Fenton's procedure, we performed other groups of laboratorial tests.

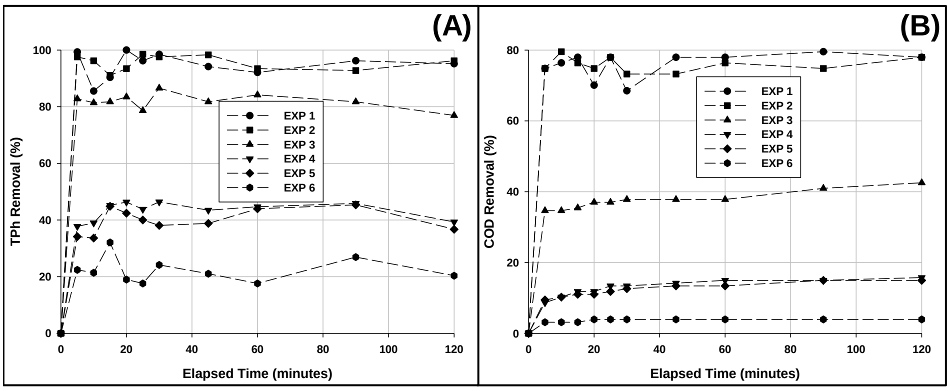

Figure X.1. TPh **(A)** and COD **(B)** removal profiles for the first set of experiments.

The second set of experiments was carried out to evaluate the hydrogen peroxide decomposition in reactions where its concentration (and also the iron concentration) was equal to EXP 1. Several temperatures were adopted to infer about its interference on this part of the process. As we can see in Figure X.2, at all temperatures the process decomposes the peroxide to the same stable level, somewhere not far but below 10 mM. The only profile that stands out from the others belongs to the reaction that took place at 20 °C – it is the slowest and takes about one hour to reach the low level stabilization. Although it is hard to differentiate the other four profiles due to their very close proximity, we can assure that the temperature augment, inside the studied range, is capable of making the reaction faster in all cases. Yet, as the peroxide decomposition enhancement is not significant for the higher temperatures, we chose to work with 25 °C from here on, since the decomposition is good and energy costs are reasonable.

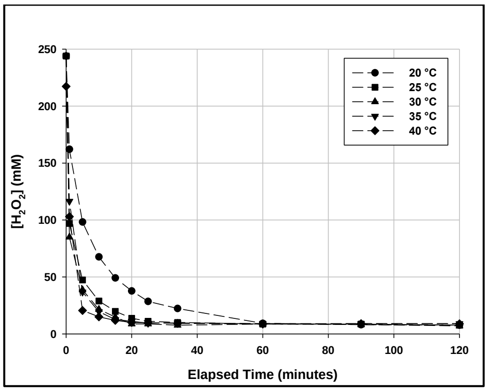

Figure X.2. Hydrogen peroxide decomposition profiles for the second set of experiments. $[Fe^{2+}]$ = 1000 ppm; $[H_2O_2]_0$ = 244 mM; pH = 3.0.

With the second set of experiments' results, we can explain what may be causing the oxidation to stop after the first minutes of reaction on the first set of experiments: the lack of oxidant agent. We could see that after 20 minutes of reaction we had only a very low concentration of peroxide available (below 10 mM, less than 6 % of the initial dose) for all temperatures from 25 to 40 °C.

If our previous assumption about the oxidant agent is correct, we might have what is a simple solution for the oxidation quench after the first minutes of reaction: peroxide refueling. Mixing this idea with the second set of experiments given know-how, we have come up with the third set of experiments, which had peroxide refueled at each 20 minutes. The literature and even previous studies of our research group (Martins et al., 2010) have tried to enhance the Fenton's oxidation by dividing the initial peroxide dose along the reaction. The difference, here, is that our refueling was completely done at each interval, and not divided by the number of injections. It means that the peroxide concentration was considered to be zero a moment before the injection and, therefore, was injected again in order to sustain the reaction. The six following runs were designated with an asterisk (EXP 1*, …, EXP 6*) to differentiate them from the initial ones.

Although EXP 1* and EXP 2* (Figure X.3) present similar COD and TPh removal profiles to EXP 1 and EXP 2 (Figure X.1), the third set of experiment's results are still in agreement with the previous statements. For the two just-mentioned experiments, the maximum Fenton's efficiency for this effluent was already reached with one peroxide injection – which is why the profiles do not differ significantly. The other experiments are examples proving our statements: EXP 3* presented a COD removal of 41 % after two hours of reaction and 6 peroxide injections (25 % more than with a single

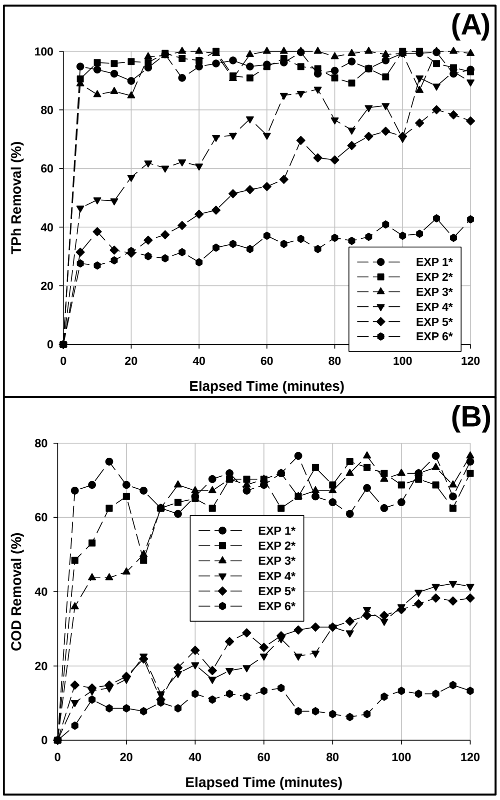

Figure X.3. TPh **(A)** and COD **(B)** removal profiles for the third set of experiments.

injection). Regarding TPh removal, EXP 3* presented 93 % removal – against the previous 77 %. EXP 4* reached 41 % COD removal (against 16 %) and 90 % TPh removal (against 39 %). EXP 5* removed 38 % of the initial COD (against 15 %) and 76 % TPh (against 37 %). Those two last experiments, EXP 4* and EXP 5*, were the most interesting for further studies. Their profiles pointed that the reaction could further oxidize the phenolic mixture if more time and refuels were given for the oxidation to continue. Therefore, these two experiments were selected for the third set of experiments, where more (and peroxide refuels) time was given to the reaction. EXP 6*, which had only 4 % COD removal on the previous relative experiment (EXP 6), had this rate increased to 13 % and the TPh removal grew from 20 to 43 %. Yet, we believe that these values are still too low to be considered attractive for the industry – reaction would have to be too long to reach interesting removals if more time and refuels were given.

In the last paragraph, 12 experiments were considered. Each with COD and TPh analysis, in a total of 24 values to read and memorize. Thus, for a better understanding of what was described, all the given information was summarized in Table X.3.

Table X.3. Data comparison between first and third sets of experiments (EXP n, EXP n*). All values relate to 120 minutes of reaction.

Experiment	COD removal (%)	TPh removal (%)	$COD_{EXP\ n*}$ - $COD_{EXP\ n}$ removal (%)	$TPh_{EXP\ n*}$ - $TPh_{EXP\ n}$ removal (%)
EXP 1 / EXP 1*	78 / 75	95 / 94	- 3	- 1
EXP 2 / EXP 2*	78 / 72	96 / 93	- 6	- 3
EXP 3 / EXP 3*	42 / 77	77 / 99	35	22
EXP 4 / EXP 4*	16 / 41	39 / 90	25	51
EXP 5 / EXP 5*	15 / 38	37 / 76	23	39
EXP 6 / EXP 6*	4 / 13	20 / 43	9	23

Since this work is about a process intended to be expanded to industrial scale, the reactants amounts employed in each experiment is an aspect of great significance, regarding costs, since there are large variations between experiments – EXP 1 uses 500 times more peroxide and iron than EXP 6, for example (see Table X.1). And, due to the subsequent injections, the amount of oxidant agent is even more important. Table X.4 sums these references. The given data still in concentration units (mM), but the reader may understand that the project is yet to be scaled upwards and the reactor's volume is still a variable.

Table X.4. Total hydrogen peroxide amount used after each injection for the third set of experiments, in mM.

Experiment	$[H_2O_2]$ summed concentration after each injection (mM)					
	1st injection	2nd injection	3rd injection	4th injection	5th injection	6th injection
EXP 1*	244.0	488.0	732.0	976.0	1220.0	1464.0
EXP 2*	122.0	244.0	366.0	488.0	610.0	732.0
EXP 3*	24.4	48.8	73.2	97.6	122.0	146.4
EXP 4*	4.9	9.8	14.6	19.5	24.4	29.3
EXP 5*	2.4	4.9	7.3	9.8	12.2	14.6
EXP 6*	0.5	1.0	1.5	2.0	2.4	2.9

Besides the reduction of costs regarding reactants (H_2O_2 and iron sulphate), other big advantages of the methodology here presented are: (i) By using much lesser iron concentrations, there is a proportional, therefore, significant, decrease on the amount of generated sludge and even the possibility of sending the treated effluent directly to biological plants (without pH augment beyond neutralization for iron separation), depending on the chosen iron concentration to be scaled up. (ii) If the treated effluent is directly sent to a biological plant, the costs with strong basis (the industry usually uses CaO in this case) will be lesser, since the neutralization is much closer from the Fenton’s pH than the pH required for iron separation (no sludge formation, in this case). (iii) The excess hydrogen peroxide will be decomposed into water and oxygen after neutralization/alkalinization with CaO, forming bubbles and preventing the treated effluent to set and precipitate. Using lesser concentrations of H_2O_2 would prevent this to happen, meaning time saving on the process overall.

X.3.2. Reactants’ yield

The results of this overall analysis were reorganized in order to highlight their great expression through the calculation of two new parameters: COD removal in what regards the used amounts of catalyst and oxidant, which were therefore designated as Fe yield and H_2O_2 yield. The equations (X.5 and X.6) considered then the removed COD and the reactants’ concentrations, as following:

$$Yield_{\,Fe}\left(\frac{mg\ O_2}{mg\ Fe}\right) = \frac{Removed\ COD\ (mg\ O_2.L^{-1})}{[Fe]\ (mg\ Fe.L^{-1})} \qquad \text{(Eq. X.5)}$$

$$Yield_{\,H_2O_2}\left(\frac{mg\ O_2}{mmol\ H_2O_2}\right) = \frac{Removed\ COD\ (mg\ O_2.L^{-1})}{[H_2O_2]\ (mmol\ H_2O_2.L^{-1})} \qquad \text{(Eq. X.6)}$$

All parameters and results concerning the first and third sets of experiments are presented in Table X.5. This table also encompasses the experiments’ yields, plotted in Figure X.4. The second column of the table displays the number of hydrogen peroxide injections, which were chosen according to the oxidative step of each experiment (injections that did not represent further oxidation were not considered). The removed COD, displayed on the fourth column, was calculated using the initial COD value (1270 mg $O_2.L^{-1}$) and the final value after the considered peroxide injections (to which were given 20 minutes for the H_2O_2 dose to react).

Table X.5. Experiments’ reaction parameters and results that supplied iron and hydrogen peroxide yields.

Experiment	H_2O_2 injections	$[Fe^{2+}]$ (ppm)	Total H_2O_2[1] (mM)	Removed COD (mg $O_2.L^{-1}$)	$Yield_{Fe}$[2]	$Yield_{H_2O_2}$[3]
EXP 1	1	1000	244	990	1	4
EXP 2	1	500	122	990	2	8
EXP 3	1	100	24.4	540	5	22
EXP 4	1	20	4.9	200	10	41
EXP 5	1	10	2.4	190	19	78
EXP 6	1	2	0.5	50	25	102
EXP 1*	1	1000	244	880	1	4
EXP 2*	1	500	122	840	2	7
EXP 3*	3	100	73.2	980	10	13
EXP 4*	6	20	29.3	530	26	18
EXP 5*	6	10	14.6	490	49	33
EXP 6*	6	2	2.9	170	85	58

[1] Total amount of hydrogen peroxide after the number of injections presented on the second column.

[2] Calculated by dividing the removed COD, in mg $O_2.L^{-1}$ (fifth row), by the iron amount, in ppm (third column).

[3] Calculated by dividing the removed COD by the total hydrogen peroxide, in mM (fourth column).

As we can see, some of the experiments were not able to oxidize considerable organic matter amounts under the studied reaction times, such as EXP 4, EXP 5, EXP 6, and EXP 6* (all COD removal values below 200 mg $O_2.L^{-1}$). However, considering the two different approaches of experiments that used 20 ppm of iron (EXP 4 and EXP 4*) and 10 ppm of iron (EXP 5 and EXP 5*) and their COD removal profiles, it is possible to see that they presented fairly increasing COD removal profiles with several peroxide injections were performed, which is interesting considering the amount of reactants used. Their iron yields raised from 10 to 26 mg $O_2.(mg\ Fe^{2+})^{-1}$ (EXP 4 and EXP 4*) and from 19 to 49 mg $O_2.(mg\ Fe^{2+})^{-1}$ (EXP 5 and EXP 5*), meaning that the same iron concentration could oxidize much more organic charge when 6 H_2O_2 doses were injected. In our point of view, this is an extremely interesting result when confronting the Fenton´s drawback of final sludge generation provoked by the use of high iron concentrations. In fact, a quite simple management of the hydrogen peroxide addition can overcome the main negative reasons that are generally associated to this attractive Fenton’s AOP in what concerns its in-situ application.

On the other hand, for the same cases, the H_2O_2 yields drop considerably when there are six hydrogen peroxide injections: 41 to 18 mg $O_2.(mmol\ H_2O_2)^{-1}$ for EXP 4 (with 4.9 mM of H_2O_2) and EXP 4* (29.3 mM of H_2O_2) and 78 to 33 mg $O_2.(mmol\ H_2O_2)^{-1}$, for EXP 5 (2.4 mM) and EXP 5* (14.6 mM) which indicates that the sequential doses of the oxidant agent suffer sequential yields decay – what implies that there will be a point after which more peroxide injections will not increase the organic charge depletion and this might be related to compounds refractory to the oxidative power of the solution at the considered concentrations. Another factor accounting for the advantages of using more peroxide injections is the very low reaction yields presented by EXP 1 and EXP 2, which are much below the other experiments’ yields.

The previous results can be highlighted by their representation in Figure X.4, where the final removed COD yields regarding iron (in black) and H_2O_2 (in gray) show the relevance of the oxidant mechanism addition targeting a good efficiency under amenable conditions guided by environmental sustainable iron sludge formation. For a better understanding of the overall process, Figure X.5 was built to put in parallel the COD removal in the same situations.

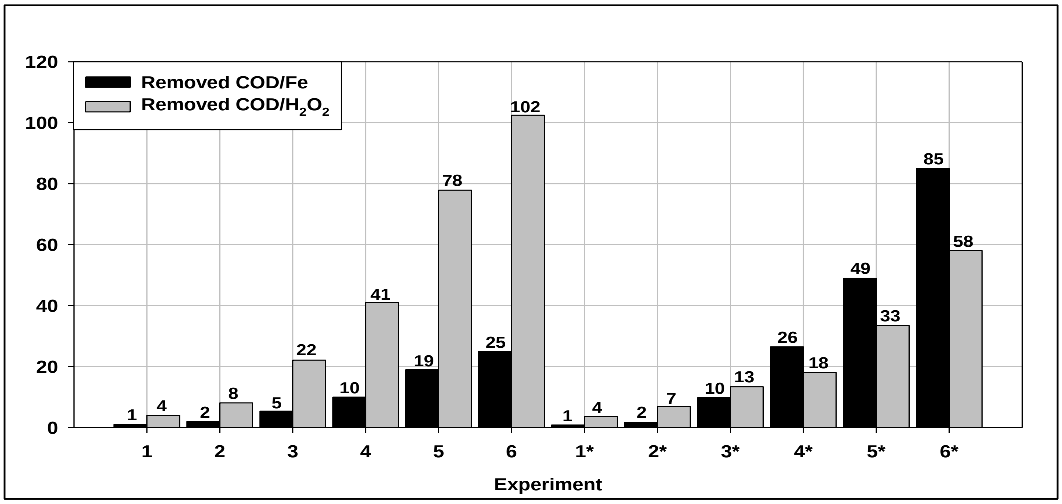

Figure X.4. Iron and hydrogen peroxide yields regarding COD removals for all performed experiments (EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6, EXP 1*, EXP2*, EXP 3*, EXP 4*, EXP 5* and EXP 6*).

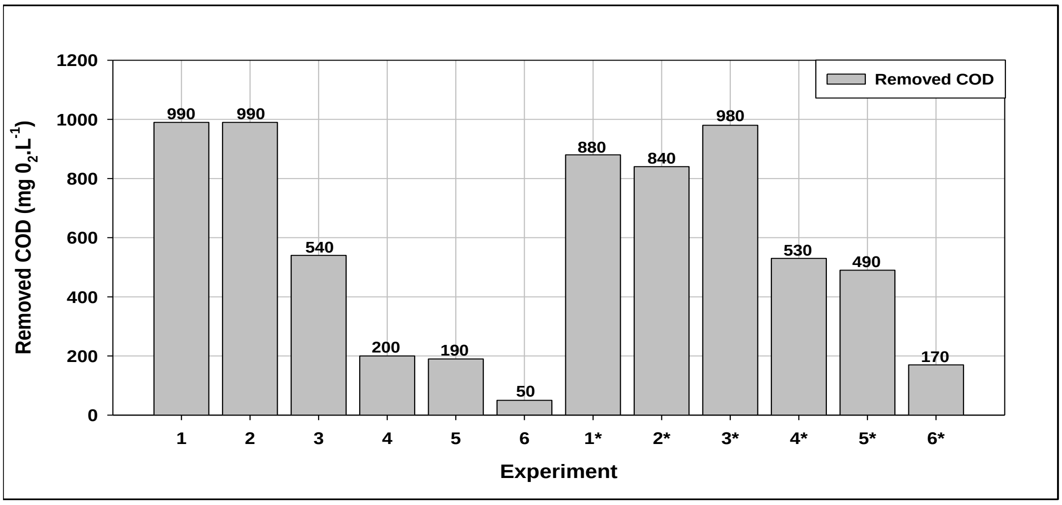

Figure X.5. COD removals for all performed experiments (EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6, EXP 1*, EXP2*, EXP 3*, EXP 4*, EXP 5* and EXP 6*).

Although the mentioned experiments' iron and peroxide yields were the greatest, along with EXP 6 and EXP 6*, they were not able to attain interesting COD removals. Yet, a more attractive COD removal was attained by the new approach with EXP 3* in comparison with EXP 3. Section X.3.1, through Table X.3's discussion (presented on page 133), already mentioned the COD removal evolution: 42 to 77 %. The iron yield with one peroxide injection is 5 mg O_2.mg Fe^{2+}, while after 3 peroxide injections this value is raised to 10 mg O_2.mg Fe^{2+}. Since more H_2O_2 injections did not lead to further oxidation, only to peroxide yield decay, this excluded such experiment's concentrations from the previous analysis of the last paragraph. However, as referred before, EXP 3* achieved good COD removal. This fact, allied to the low iron and peroxide concentrations used, brings attention to the experiment. Further work will pursue with the industrial scaling up of EXP 3*, together with the extension experiments EXP 4*, EXP 5* and EXP 6* - that might bring other great results regarding Fenton's efficiency with extremely low sludge formation, since very small iron concentrations are used.

X.4. Conclusions

The H_2O_2 complete decomposition time was found to be 20 minutes for the following reaction conditions: $[Fe^{2+}]$ = 1000 ppm, $[H_2O_2]$ = 244 mM, room temperature and pH 3.0. Therefore, a new approach was given to the classical Fenton's process: injecting several H_2O_2 doses at each 20 minutes in order to keep its concentration high enough for the oxidation to occur. This scheme was tested for several iron concentrations while the $[Fe^{2+}]$:$[H_2O_2]$ ratio was kept at 4.1 for comparison purposes. The reactions that received more peroxide injections were able to further oxidize the organic matter. Since low iron and peroxide concentrations were used on some of the experiments that presented good results, this new approach could overcome important deficiencies of the homogeneous Fenton's process, mainly associated to the final iron the sludge formation. Results of using lower iron and peroxide concentrations showed that this methodology is promising and could be a new alternative to the industry, especially considering the reactant's yields – calculated through the ratio between the removed COD and iron/peroxide used concentrations, in mg O_2.(mg $Fe^{2+})^{-1}$ and mg O_2.(mmol $H_2O_2)^{-1}$. For instance, using $[Fe^{2+}]$ = 100 ppm and $[H_2O_2]$ = 24.4 mM with three injections (EXP 3*), the same TPh and COD removals were observed when compared to the use of reactants' concentrations 10 times higher and a single peroxide injection (EXP 1). Moreover, experiments EXP 4* ([Fe^{2+}] = 20 ppm and [H_2O_2] = 4.88 mM) and EXP 5* ([Fe^{2+}] = 10 ppm and [H_2O_2] = 2.44 mM) showed interesting organic load removal profiles and reactants yields, pointing that the oxidation could occur even further, after more than 6 peroxide injections. However, these experiments' prolongation was not yet studied, being future work to be done.

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XI. Comparative studies between homogeneous and heterogeneous Fenton's process[9]

XI.1. Introduction

Before the closing part of this document, an overall comparison of several results reached along the work will be addressed. Along the acquiring of all data presented below, many links have been found between different experiments and this chapter will encompass the raised questions about some of them. The efficiency of three ceramic catalysts (Fe-Ce-O, Fe-Cu-O and Fe-Co-O), three low cost materials (ZVI from both iron bars and iron cutting shavings and Fenton's sludge) and the homogeneous Fenton's process will be put side to side to give the reader a closer look and share some of our findings. Likewise, batch experiments will be compared to continuous mode operation, indicating the best conditions for each and highlighting the most interesting points. Being the center of this discussion, the Fenton's oxidative capacities on the remediation of a phenolic synthetic wastewater will be exposed.

XI.2. Comparisons information and experimental methods

Although all experimental methods here presented were already mentioned in previous chapters, they'll be stated again in this section in a summarized form.

XI.2.1. Ceramic catalysts production and characterization

All ceramic catalysts were produced through co-precipitation (Imamura et al., 1985). This procedure consists on the precipitation of a solution containing 15 g of precursor salts (metal nitrates at the desired molar proportion) by the addition of NaOH solution (Panreac 98 %). The resulting mixture is filtrated and washed with 2.5 L of ultrapure water (Milli-Q^{50}, Millipore). Afterwards, it is dried overnight at 105 °C, calcinated (all selected catalysts were calcinated at 300 °C for 2 h, according to chapter III's results). Table XI.1 presents each selected catalyst for this comparison and the used salts to produce them.

Table XI.1. Information about selected ceramic catalysts' production.

Catalyst	Primary metal precursor salt	Secondary metal precursor salt
Fe-Ce-O 70/30	Iron nitrate (Panreac 98.0 %)	Cerium nitrate (Acrós 99.5 %)
Fe-Cu-O 50/50	Iron nitrate (Panreac 98.0 %)	Copper nitrate (Riedel-de-Haën 99.0 %)
Fe-Co-O 30/70	Iron nitrate (Panreac 98.0 %)	Cobalt nitrate (Riedel-de-Haën 98.0 %)

A fourth element was added to the ceramic catalysts comparison: Fe-Ce-O 70/30 produced with iron extracted from Fenton's sludge, the solid studied in chapter VII. The iron used in the production of this catalyst was extracted by baking iron-rich mud in 6 N HCl

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[9] This chapter is based upon the paper in preparation by Rossi, A.F.; Martins, R.C.; Quinta-Ferreira, R. M.

before filtration and dilution and, afterwards, used to substitute the iron nitrate on the co-precipitation methodology. At the discussion below, this solid will be presented as Fe-Ce-O 70/30* in order to differentiate it from the Fe-Ce-O 70/30.

The catalysts Fe-Ce-O 70/30 and Fe-Cu-O 50/50 were characterized through the following analysis: Brunauer-Emmet-Teller surface area (S_{BET}) determined by nitrogen adsorption at -196 °C in a Micrometrics ASAP 2000, X-ray diffraction (XRD) in a mercury porosimetry and pore size distribution measurement at a Micrometrics Poresizer 9320 (penetrometer constant 10.683 µL.pF^{-1}, penetrometer weight 70.84 g, penetrometer volume 5.3905 mL, stem volume 0.392 mL, maximum head pressure 4.45 psia, room temperature) and gas picnometry at a Micrometrics AccuPyc 1330 (cell volume 12.2169 cm^3, equilibration rate: 0.0500 psig.min^{-1}, expansion volume 8.2518 cm^3, room temperature). The random errors associated with Micrometrics ASAP 2000 analysis (B.E.T. Surface Area, Average Pore Diameter and Single Point Total Pore Volume) are in the range of ± 0.1 %; for Micrometrics Poresizer (Porosity), ± 1.0 %, and, for Micrometrics AccuPyc 1330 (Average Density), ± 0.03 %.

XI.2.2. Low cost materials preparation

In a more global context based on environmental sustainability, the subsequent studies tried to explore the possibility of jointing solid wastes to the treatment of liquid wastes. As a final goal, the process costs reduction, by using non-expensive materials, would mutually target solid wastes valorization by using non-wanted leftovers. The first low cost material considered to be used as Fenton's catalyst was iron sludge from an industrial homogeneous Fenton's reactor used for detergent wastewater treatment. The mud was dried overnight (105 °C) and manually crushed into small particles. Calcination at several temperatures supplied 4 solids to be compared to the non-calcinated mud. Since the higher activity regarding organic charge removal by the Fenton's process was obtained by the sludge calcinated at 1000 °C, this solid was chosen to be part of this comparison. A homogeneous Fenton's process was inserted in this evaluation due to the high leaching presented by the studied solids. Once the Fenton's procedure, as well as the calcination procedure, elevates the oxidation state of the iron (Fe^0 or Fe^{2+} to Fe^{3+}), ferric iron was used as catalyst instead of ferrous iron. The concentration of these ions were chosen according to the highest leaching value observed during the study presented on chapter VI (172 mg.L^{-1}).

Afterwards, the efficiency of zero valent iron (ZVI) gathered from construction site wastes (A-400 iron bars with Ø = 18 mm) as Fenton's catalysts was compared. These bars were converted into iron shavings using a lathe and the obtained solids were directly used as Fenton's catalysts.

Finally, besides the ZVI from those construction bars, ZVI from iron plate cutting industry were used in continuous operation. An acid cleaning simple process was applied to this material in order to wash its dirt, since it came directly from the industry's floor. To do so, a HCl (Panreac, 37%) solution (10 % v/v) was used.

A commercial catalyst, N-150, was also tested under continuous operation. Before being inserted into the tubular reactor, it was crushed into smaller pieces (the parts that were transformed into powder were excluded in order to avoid the clog of the column).

XI.2.3. Synthetic effluent

All solids mentioned in sections XI.2.1 and XI.2.2 were compared through their catalytic activity on the treatment of a synthetic olive mill wastewater (OMW). This simulated effluent was prepared through the addition of 0.1 $g.L^{-1}$ of six phenolic acids commonly found in OMW (3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid). To assure their dissolution in water, the solution is exposed to ultrasounds (Crest ultrasounds equipment) for 15 minutes. PH is then set to 3.0 (Crison MicropH 2000) to obey previously optimized parameters (Martins et al., 2010).

XI.2.4. Batch oxidative procedure

In the case of all ceramic catalysts and the Fenton's sludge, a 500 mL beaker was used to carry out the experiments containing 300 mL of the simulated olive mill wastewater. PH was checked with a Crison MicropH 2000 probe and corrected to 3.0 with NaOH (Panreac 98%) or H_2SO_4 (Panreac, 96 %), whenever necessary. The catalyst was introduced at the concentration of 1.0 $g.L^{-1}$ and magnetic stirring was started. In the cases of the Fe-Co-O 30/70 catalyst, one hour was given without pH correction to evaluate the adsorption of the phenolic acids onto the catalyst and a first sample was withdrawn in order to evaluate if the catalyst had adsorbed any organic charge. Hydrogen peroxide (Panreac, 33 % - stabilized QP) was then poured at the concentration of 244 mM. At certain time intervals, samples were withdrawn by pipetting from the reactor to a filtration system (Buchner funnel, kitassato and air pump) using a 0.45 µm pore diameter quantitative filter paper to remove the solid catalyst from the liquid phase. Sample's pH were immediately raised to 10 in order to quench the remaining H_2O_2 and •OH.

The ZVI process was carried out differently. 100 mL sample cups containing 30 mL of the synthetic effluent were used as reactors. 20 $g.L^{-1}$ of ZVI and 35 mM of H_2O_2 were added to the reactors and the system's mixture was induced by an orbital stirrer. The mixture was allowed to react for 120 minutes and, afterwards, was filtered in 0.45 µm pore diameter filter paper to remove the iron shavings and the pH was raised above 10 with NaOH to stop further oxidation.

The homogeneous Fenton's processes were carried out in beakers containing 500 mL of the previously described synthetic solution. pH was set to 3.0 (Crison MicropH 2000 probe) and iron sulphate was added as catalyst precursor. Magnetic stirring was used to homogenize the solution and the reaction was started with hydrogen peroxide addition. $[Fe^{2+}]$ = 500 ppm were used, as well as $[H_2O_2]$ = 122 mM were used in the classical reaction, while $[Fe^{2+}]$ = 100 ppm and $[H_2O_2]$ = 24.4 mM for each injection were used when three peroxide injections were performed (total $[H_2O_2]$ = 73.2 mM). Each of these injections took place with a 20 minutes interval and there were no division of the reactants for each injection (the iron was placed before the reaction beginning and the hydrogen peroxide was completely refilled at each mentioned interval).

XI.2.5. Continuous operations

All experiments were carried out in the reactor described in chapter IX, section IX.2.4. The efficiency of ZVI from two different sources was compared to a commercial catalyst, N-150.

A peristaltic pump (Ismatec REGLO Analog MS-4/8) was used to push the solution through a darksome rubber tube onto the reactor at a volumetric upwards flow of 1.0 mL.min^{-1}. Samples were taken at the outlet of the reactor to be analyzed and assess the process' efficiency. They were immediately mixed with 3 M sodium hydroxide, prepared from NaOH pellets (Panreac, 98 %), in order to quench the reaction.

XI.2.6. Analytical techniques

All system's efficiencies were compared through the abatements of chemical oxygen demand (COD) and total phenolic content (TPh). COD was measured throughout the closed reflux standard method 5220D (Greenberg et al., 1985) using a thermoreactor (WTW CR 3000) and a photometer (WTW MPM 3000). Total phenolic content was assessed with a spectrophotometer (T60 U PG Instruments) measuring the absorbance at 765 nm of samples treated following the procedure presented by Folin and Ciocalteu (1927).

XI.3. Results and Discussion

XI.3.1. Characterization of the ceramic catalysts

In this section, Fe-Ce-O 70/30 and Fe-Cu-O 50/50 ceramic catalysts are going to be compared. Gas adsorption isotherms are displayed in Figure XI.1.A. As we can see, both catalysts present a type IV isotherm type, characterized by the hysteresis phenomenon and the presence of an elbow. Solids that present this kind of isotherm usually have mesopores – sizes between 5 and 50 nm (Figueiredo and Ribeiro, 1989).

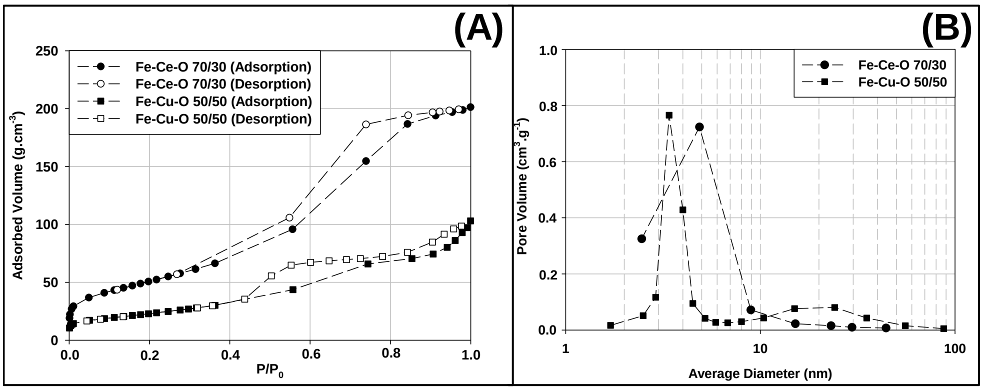

Figure XI.1. (A) Gas adsorption isotherms (adsorbed volume versus relative pressure) of two ceramic catalysts (Fe-Ce-O 70/30 and Fe-Cu-O 50/50). **(B)** Pore size versus pore volume profiles for the same solids.

Table XI.2 presents the numeric values extracted from this analysis and we can see that Fe-Cu-O 50/50 has pores ~13 % larger than Fe-Ce-O 70/30 (7.5 nm and 6.6 nm, respectively). However, when the pore sizes profiles are plotted against their average diameters (Figure XI.1.B), we can see that Fe-Ce-O 70/30 presents most of its pores close to the size of 5.0 nm, while Fe-Cu-O 50/50 presents a lesser value: ~3.5 nm (and a small peak indicates that there are also pores close to 20 nm, an absent characteristic on the other solid).

Table XI.2. Catalysts characterization.

Catalyst	Fe-Ce-O 70/30	Fe-Cu-O 50/50
B.E.T. Surface Area ($m^2.g^{-1}$)	188	85
Average Pore Diameter (nm)	6.6	7.5
Single Point Total Pore Volume ($cm^3.g^{-1}$)	0.311	0.160
Average Density ($g.cm^{-3}$)	3.99	4.45
Porosity (%)	58	45

Regarding the BET surface areas, the cerium-composed solid presents a much higher value: 188 $m^2.g^{-1}$ when compared to the 85 $m^2.g^{-1}$ presented by Fe-Cu-O 50/50, a difference of more than 120 %. This could be pointed out as the reason of the higher Fenton's activity observed for Fe-Ce-O 70/30 (see section XI.3.2), since the surface area is one of the most important characteristics of a good catalyst. This solid also presented higher porosity (58 % compared to 45 %), which leads to lesser density (3.99 $g.cm^{-3}$ against 4.45 $g.cm^{-3}$). More voluminous, the Fe-Ce-O 70/30 solid would become more available for reactions, being easier to reach by the hydrogen peroxide and the organic compounds that need to be oxidized.

Although the solid Fe-Co-O 30/70 has also been selected for reaction efficiency comparison, it has not been characterized since the cobalt-containing solids resulted as poor Fenton's catalysts and attracted no further interest.

XI.3.2. Ceramic catalysts performance

Even though all ceramic catalysts were prepared in several molar proportions between iron and another metal (e.g. 30/70, 50/50 and 70/30, as in Fe/Ce, Fe/Cu or Fe/Co), for the comparison discussed in this section, only the best resulting solid of each metal couple was selected (Fe-Ce-O 70/30, Fe-Cu-O 50/50 and Fe-Co-O 30/70). To complete this deliberation, solid produced similarly to Fe-Ce-O-70/30, using iron extracted from Fenton's sludge, was also added to the comparison and named Fe-Ce-O 70/30*.

Table XI.3 displays the reaction conditions used for all experiments carried out using ceramic catalysts and discussed in this section, as well as TPh and COD removals. Temperature and pH were excluded because all runs were carried out at room temperature (~25 °C) and pH 3.0.

Table XI.3. Reaction conditions for ceramic catalysts.

Catalyst	[catalyst] ($g.L^{-1}$)	[H_2O_2] (mM)	Reaction time (minutes)	pH	Temperature (°C)	TPh removal (%)	COD removal (%)
Fe-Ce-O 70/30	1.0	244	120	3.0	~25	100	49
Fe-Cu-O 50/50	1.0	244	120	3.0	~25	100	36
Fe-Co-O 30/70	1.0	244	120	3.0	~25	58	32
Fe-Ce-O 70/30*	1.0	244	120	3.0	~25	94	51

Figure XI.2.A displays all four TPh removal profiles during the Fenton's process, in which we can see the higher efficiency presented by the cerium-containing solids (Fe-Ce-O 70/30 and Fe-Ce-O 70/30*), followed by the Fe-Cu-O 50/50, which was also capable of completely removing the phenolic compounds from the simulated wastewater. Fe-Co-O 30/70, on the other hand, was able to degrading less than 60 % TPh (most of it, ~40 %, by adsorption, since this removal was observed after one hour of contact between the solid and the phenolic mixture, before H_2O_2 addition).

COD depletion profiles can be seen in Figure XI.2.B, where we can see the repeated efficiency pattern: Fe-Ce-O 70/30 (and the similar solid produced with extracted iron, Fe-Ce-O 70/30*) > Fe-Cu-O 50/50 > Fe-Co-O 30/70, highlighting the cerium as the best metal inside our screening to be coupled with iron to produce Fenton's ceramic catalysts.

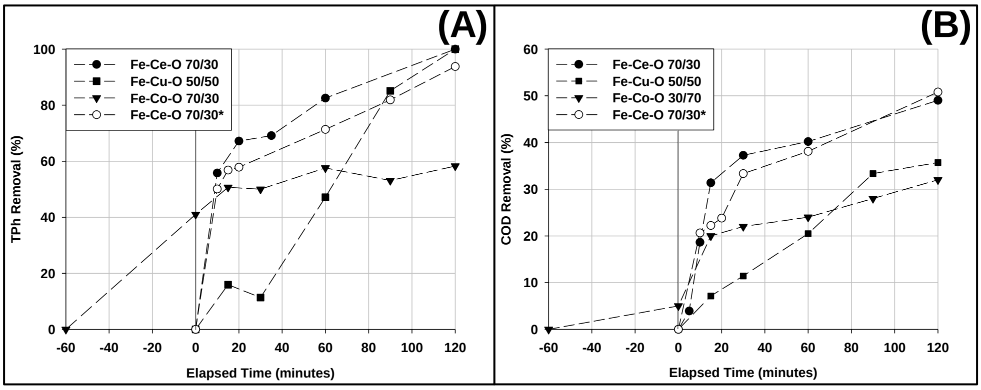

Figure XI.2. Organic charge removal profiles. **(A)** Total phenolic content removals. **(B)** Chemical oxygen demand removals. Experiments' conditions: [catalyst] = 1 g.L^{-1}, [H_2O_2] = 244 mM, pH = 3.0, room temperature (~25 °C).

Moreover, it might be said that the resources for ceramic catalysts production does not have to be the metal nitrates, since both TPh and COD removal profiles (activity indicators) for Fe-Ce-O 70/30 and Fe-Ce-O 70/30* were so close to each other.

XI.3.3. Low cost materials

Two low cost materials were chosen to be compared regarding their catalytic activity. The first solid was Fenton's sludge dried and calcinated at 1000 °C. Since the study of the related solids revealed that high iron leaching is expected when these kinds of solids are exposed to low pH solutions and a homogeneous comparison using Fe^{3+} as homogeneous catalyst was performed, this metal was also included in the current discussion. The third solid is ZVI gathered from iron bars in the shape of shavings. Information regarding these experiments' conditions are displayed in Table XI.4, along with their organic charge depletions.

Table XI.4. Reaction conditions for low cost materials.

Catalyst	[catalyst] (g.L^{-1})	[H_2O_2] (mM)	Reaction time (minutes)	pH	Temperature (°C)	TPh removal (%)	COD removal (%)
Fenton's sludge	1.0	244	120	3.0	~25	99	51
Fe^{3+}	0.172	244	120	3.0	~25	N.C.*	50
ZVI	2.0	35	120	3.0	~25	98	65

*N.C.: not calculated.

Figure XI.3 displays TPh and COD removals, in percentage, after 120 minutes of reaction time. Due to the close value presented for both Fenton's sludge and Fe^{3+}, we believe that all sludge's activity is from the leached metals (identical reaction parameters), indicating homogeneous processes in both cases.

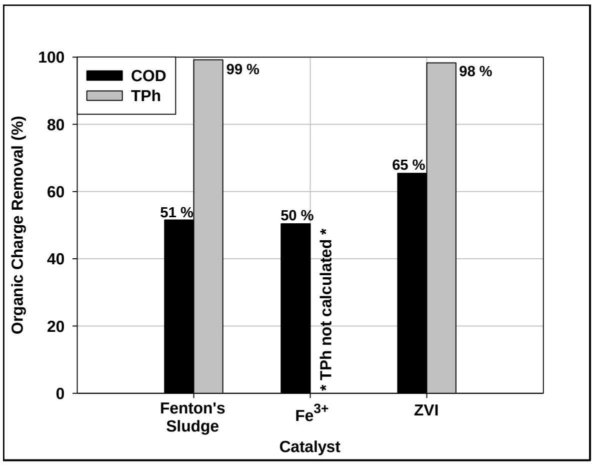

Figure XI.3. Organic charge removal results after 120 minutes of reaction. For the Fenton's Sludge catalyst, the calcination temperature was 1000 °C and the Fenton's reaction parameters were the following: [sludge] = 1 $g.L^{-1}$, $[H_2O_2]$ = 244 mM, pH = 3.0, room temperature (~25 °C); for the homogeneous case (Fe^{3+}), same conditions were applied, but the catalyst concentration was 172 ppm (0.127 $g.L^{-1}$) of ferric iron; and the ZVI conditions were: [ZVI] = 20 $g.L^{-1}$, $[H_2O_2]$ = 35 mM (also at room temperature and pH 3.0).

Although ZVI presents 1 % lesser TPh removal than Fenton's sludge, it must be considered the H_2O_2 concentration great difference: 35 mM against 244 mM (lesser dose corresponding to less than 15 % of the higher dose). Even using a much lower peroxide concentration, ZVI was able to deplete the COD value in 65 %, a much better result compared to Fenton's sludge. This way, it can be concluded that ZVI is a much more promising low cost material due to the highest catalytic activity and H_2O_2 yield.

XI.3.4. Best results and homogeneous process consideration

The last comparison regarding batch mode operation encompasses the best solids pointed out in the previous two sections (XI.3.2 and XI.3.3): Fe-Ce-O 70/30 (ceramic catalyst), ZVI (low cost material) and two approaches of the homogeneous Fenton's reaction: the classical and another one considering several hydrogen peroxide injections. Information regarding these experiments' conditions are displayed in Table XI.5, along with their organic charge depletions.

Table XI.5. Reaction conditions for low cost materials.

Catalyst	[catalyst] ($g.L^{-1}$)	$[H_2O_2]$ (mM)	Reaction time (minutes)	pH	Temperature (°C)	TPh removal (%)	COD removal (%)
Fe-Ce-O 70/30	1.0	244	120	3.0	~25	100	49
ZVI	20.0	35	120	3.0	~25	98	65
Classical Fenton	0.5	122	120	3.0	~25	96	78
Several Injections	0.1	24.4 (x3)	60	3.0	~25	100	70

While the first two bar groups displayed on Figure XI.4 represent the heterogeneous Fenton's process, the two last bar groups regard reactions purely homogeneous. By a first look, the homogeneous sets can already be pointed out as much more efficient in this oxidative process.

Regarding COD abatement, ZVI, the low cost material considered in this discussion, presented a better result, 65 %, than Fe-Ce-O 70/30's: 49 % - especially if the costs concerning hydrogen peroxide and catalyst acquisition are taken into consideration.

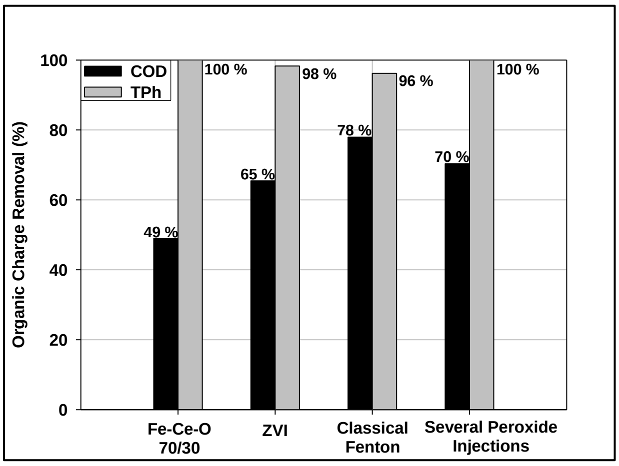

Figure XI.4. Best organic charge removal results for each kind of procedure. For the Fe-Ce-O 70/30 catalyst, the Fenton's reaction parameters were the following: [Fe-Ce-O 70/30] = 1 g.L^{-1}, [H_2O_2] = 244 mM and 120 minutes of reaction time; for the ZVI case, same reaction time was used, but with [ZVI] = 20 g.L^{-1} and [H_2O_2] = 35 mM; the classical Fenton's process used [Fe^{2+}] = 500 ppm (0.5 g.L^{-1}) and [H_2O_2] = 122 mM; and the Fenton with several injections used [Fe^{2+}] = 100 ppm (0.1 g.L^{-1}) and [H_2O_2] = 24.4 mM (the results presented on this figure regard organic charge removals after 3 peroxide injections, or 60 minutes of reaction time). All experiments were carried out at room temperature (~25 °C) and pH = 3.0.

However, even ZVI could not reach the homogeneous process' achievements: 78 % COD removal. Once the hydrogen peroxide doses are different for the two compared reactions, it must be said that, according to chapter X, the use of a higher peroxide dose did increase COD abatement by ZVI.

The classical Fenton's process discussed on the last paragraph reached the best COD abatement amongst all experiments. Nevertheless, alternatives that could overcome the familiar disadvantages of this process were studied in chapter X and the closest of them was also presented in Figure XI.4. In the mentioned example, three injections of hydrogen peroxide were done, separated by 20 minutes each. Close COD removals and best TPh depletion were attained through an experiment that employed lesser reactant amounts: [Fe^{2+}] = 100 ppm and [H_2O_2] = 24.4 mM (compared to 500 ppm and 122 mM on the classical Fenton's process). Even when the three peroxide injections are considered, the total amount sums 73.2 mM, which corresponds to a dose 27 % lesser than the classical Fenton's dose.

The advantages found through the carrying out of experiments employing several H_2O_2 injections not only encompass lower costs due to reactants reduction. Importantly, by using much lower iron amounts, the sludge generation at the end of the process will be proportionally reduced (5 times, in this case), which is a substantial factor when it comes to environmental concerns.

XI.3.5. Continuous operation mode

The good results presented by the iron shavings as Fenton's catalysts and the availability of this metal at low prices, with the fact that a joint goal of simultaneously tackling solid wastes recycling and waste waters remediation, led our research group to investigate this solid's efficiency on continuous operation mode. The main goal was to address the stability characteristics of these materials along the time. The ZVI samples were gathered from two different sources, being the first type from plate cutting industry. Since these shavings were picked from the industry's floor, two washing methodologies were applied and compared to the raw material. This comparison showed that an acidic washing was able to enhance the metal's properties related to the Fenton's process activity. The second type of iron shaving was iron bars from construction sites. The inner and outer parts of the bars were separated and their activity as Fenton's catalysts were compared, showing a lesser efficiency by the external part, probably due to the oxidized state of the rusty iron.

Thus, two solids were brought to this new comparison: ZVI from plate cutting industry washed with acidic solution and the internal part of iron bars. A commercial catalyst, N-150, comprised by iron and manganese, was also considered in this discussion. Two operation times were selected: 4 and 120 h. TPh depletions by all catalysts at the mentioned periods are displayed in Figure XI.5. As we can see, the two sources of ZVI were able to achieve high phenolic abatement both at 4 and 120 h. Although there is a decay on the ZVIs' oxidative processes (-12 % for the plate cutting ZVI and -13 % for the iron bars), it is not so large as N-150's. Moreover, we can mention the very poor oxidizing capability of the commercial catalyst, which, at an operation time of 4 h, could merely degrade 50 % TPh and only 1 % at 120 h.

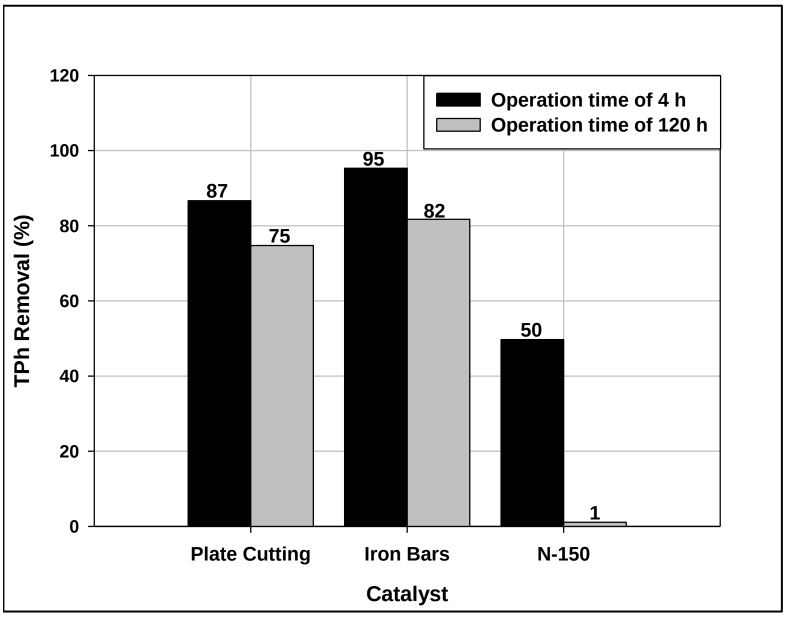

Figure XI.5. TPh removal results after two operation times for one catalyst of each kind (iron shavings from plate cutting industry, iron shavings from construction site's bars and the commercial catalyst N-150): 4 and 120 hours. Reaction parameters: pH = 3.0, [H_2O_2] = 35 mM, flow rate of 1.0 mL.min^{-1}, room temperature (~25 °C).

Likewise, the COD removals presented by N-150 were low: 27 % at 4 h operation time and -2 % at 120 h, which can be seen in Figure XI.6. This negative removal shows that the organic charge concentration on the outlet of the reactor is higher than on the inlet – meaning that the catalyst released organic species onto the bulk. This suggests that, at an initial operation time, the catalyst was not oxidizing all the organic charge referred as 27 % COD removal, but only adsorbing it and, at longer operation times, the catalyst would then start to release these species – thus increasing the inlet's COD.

On the other hand, both ZVI presented good COD removals during the process. Although the iron bars' shavings were able to achieve the highest COD removal value at 4 h operation time, 56 %, its efficiency was reduced in 19 % at 120 h. This activity loss could be associated to the formation of a shell, comprised by iron oxides, outside the ZVI, that would reduce its activity. This phenomenon was presented and discussed on section IX.3, page 117. The best overall results were presented by the plate cutting shavings after acidic washing. While the first value (50 % COD removal) is lesser than the iron bars' results (for both TPh and COD removals), the higher stability of this material brings more interest, since it can be used for longer operation times: at 120 h of operation time, the COD removal value dropped only 3 % (as opposed to the 19 % of the iron bars' shavings).

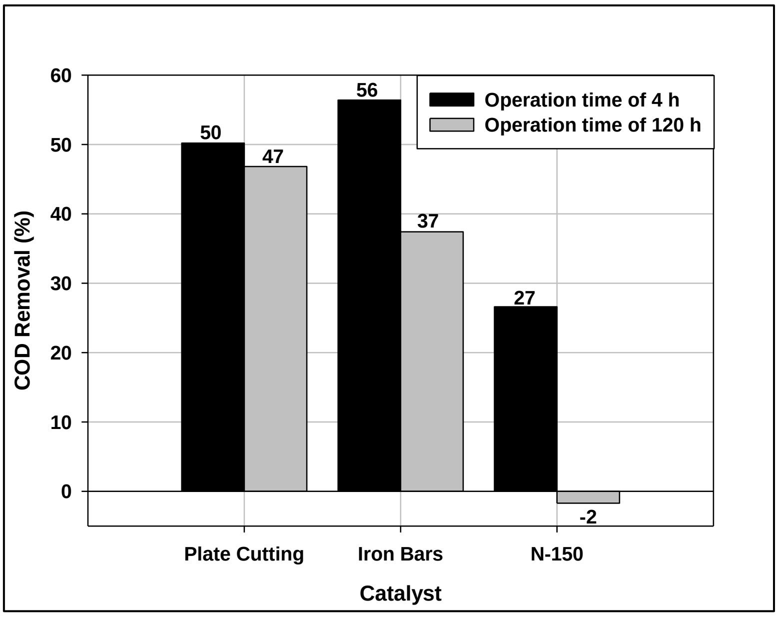

Figure XI.6. COD removal results after two operation times for one catalyst of each kind (iron shavings from plate cutting industry, iron shavings from construction site's bars and the commercial catalyst N-150): 4 and 120 hours. Reaction parameters: pH = 3.0, [H_2O_2] = 35 mM, flow rate of 1.0 mL.min^{-1}, room temperature (~25 °C).

XI.4. Conclusions

Amongst all ceramic catalysts, Fe-Ce-O 70/30 calcinated at 300 °C for two hours presented the best results as Fenton's catalyst: TPh and COD removals of 100 % and 49 %, respectively. The higher surface area and porosity presented by this solid (188 m^2.g^{-1} and 58 %) might explain its greater efficiency. The broader valence range of the secondary metal, cerium, compared to the other two secondary metals (copper and cobalt), would allow further electron exchanges with the ferric ions (thus reducing to ferrous ions), enhancing the hydroxyl radicals formation and leading to higher organic matter oxidation. Moreover, the solid produced using iron extracted from Fenton's sludge presented similar TPh and COD profiles, showing that it is possible to recover metal from the mud and produce a catalyst as active as the one produced using iron nitrate.

Regarding all low cost materials, ZVI can be pointed out as the best: even using much less hydrogen peroxide (35 mM) then the Fenton's sludge (244 mM), ZVI removed 61 % COD, while 51 % COD was removed by Fenton's sludge.

The comparison between the homogeneous and heterogeneous processes shows that the solid catalysts evaluated in our facilities (ZVI and Fe-Ce-O 70/30) are not as active as dissolved Fe^{2+}. Even presenting the closest results, ZVI's COD removal is still 13 % lesser than the homogeneous process using optimized conditions for the classical Fenton's operation. However, the use of several peroxide injections reached organic charge abatements close to the best ones, but using much lesser reactants concentrations – which would overcome some of the process' disadvantages, mainly those associated to final unwanted iron sludge production.

The outstanding results achieved by ZVI led our research group to test it in continuous operation mode, where the iron shavings from plate cutting industry washed with acidic solution showed the best results. At 4 h of operation time, 50 % COD removal was observed, while at 120 h this value dropped only 3 % – showing that the solid is stable enough to be used in this kind of systems.

XI.5. References

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Part E. Conclusions and Forthcoming Work

A recollection of the most relevant results start the last part of the manuscript. One chapter will summarize all this information and show some interesting comparison among some of the results obtained. Finally, closing the document, there is a section dedicated to the discussion of possible continuations of this work, explaining pertinent ideas that could not be thoroughly performed during this research period but that may be the starting ground of a next one.

XII. Conclusions and forthcoming work

The Fenton's process is well known for representing a cheap alternative for the industry. Low energy requirements, as well as installation and maintenance costs are very attractive characteristics of the systems based on this kind of oxidation. Nevertheless, there are some disadvantages that still limit its application. The main goal of this thesis was to extend the investigations over the Fenton's theme trying to find alternatives that overcome its drawbacks.

As a model solution, an olive mill synthetic effluent comprising six phenolic acids was used. The efficiency of several systems on oxidizing this mixture was evaluated, generally, through organic charge depletion and biodegradability enhancement. The related cost-benefits were taken into account, such as the reactants used and their yields or the pros and cons of the production and employing of certain catalysts.

The next sections will be a bit more than a glimpse throughout all results previously discussed. The most important conclusions will be pointed out before the future work is mentioned as the closure of this document (chapter XII.5).

XII.1. Ceramic catalysts

XII.1.1. Iron-cerium solids

Presented on chapter III, the first ceramic catalyst to be introduced was comprised by iron and cerium oxides. This study evaluated the best calcination temperature of the produced solids amongst the values of 300, 600 and 1000 °C. Organic charge removal from a synthetic wastewater through the Fenton-like heterogeneous process, assessed through TPh, COD and TOC removals, was the primary parameter on the evaluation of the generated solid.

In this regard, the augment on the calcination temperature seemed to generate less active solids, since the highest temperature produced the only solid that could not completely degrade the phenolic acids in the solution. Its COD removal was also the lowest, approximately 20 %, and no TOC removal was observed in 2 h of reaction. This low activity might be related to the reduced surface area (5 $m^2.g^{-1}$) and the elevated oxidation state of the iron species presented on the solid's surface (since Fe^{3+} is less active than Fe^{2+} on the generation of hydroxyl radicals).

The intermediate temperature, 600 °C, generated an intermediate solid regarding all physical characteristics, such as BET area (86 $m^2.g^{-1}$), average pore diameter (87 Å), single point total pore volume (0.189 $cm^3.g^{-1}$) and average density (5.41 $g.cm^3$). Likewise, this solid's activity was between the other 2 catalysts: although the TPh degradation was complete, it removes 20 % less COD and 10 % TOC when compared to the solid produced at 300 °C – the one highlighted in this chapter.

Fe-Ce-O 70/30 calcinated at 300 °C showed the highest efficiency related to organic matter oxidation. When the biological parameters of the treated samples, such as BOD_5,

EC_{20}, EC_{50} and respirometry, are addressed, the best calcination temperature is 300 °C: elevated BOD_5/COD ratio (0.76) and respirometry results, where the toxicity was reduced from 67 to 0 % and the biodegradability was raised from 2 to 70 %.

On the other hand, the solid calcinated at the lowest temperature was the less stable. Its iron leaching reached the value of 36 ppm, while the others achieved better results: 29 ppm (600 °C) and 11 (1000 °C).

XII.1.2. Iron-copper solids

The following chapter regards iron-copper based solids prepared by co-precipitation and their efficiency when used as Fenton-like heterogeneous catalysts. Chemical oxygen demand, total phenolic content, and biochemical oxygen demand in five days were the parameters used for the evaluation of the oxidation of a synthetic olive mill wastewater, simulated by two solutions: one comprising six phenolic acids and another containing one extra model compound (gallic acid). The objective of adding this extra acid was evaluating if there is any synergistic effect created that would increase the radicals in the bulk after the beginning of the oxidation and hence the solution's oxidation/reduction potential (ORP). According to previous results, 300 °C was the calcination temperature of all solids. Nevertheless, since another metal couple was being studied, different molar proportions between them were adopted to assess the best one.

The interaction between copper and iron showed good results, since in all cases the catalysts comprised by two metals achieved faster and higher oxidations of the mother solutions than iron oxide and/or copper oxide under the same conditions. Fe-Cu-O 50/50 is pointed out as the most active solid – TPh and COD abatements for this solid were the best in all cases except one (where the removal difference is low, 6 %). As in the case of iron-cerium solids, for Fe-Cu-O, the most active solid also presents the highest surface area: 85 $m^2.g^{-1}$, against the 62 and 15 $m^2.g^{-1}$ of Fe-Cu-O 30/70 and 70/30, respectively. Despite the interesting data about organic charge depletion, these catalysts were not tested in what regards the leaching behavior since the biodegradability was reduced in every experiment.

Comparing the oxidative reaction of the two prepared solutions, it was observed in almost all cases that the mixture containing more acids can be more easily degraded. The co-oxidation phenomenon was pointed out, enhancing thus the process efficiency. The Fe-Cu-O 70/30 catalyst presented the most discrepant values when the TPh reductions from both solutions are compared: 95 % of the phenolic acids were removed from the solution containing seven phenolic acids when only 31 % were removed from the other solution – what might indicate a strong participation of the free radicals in solution, especially in this last case. Another hypothesis that may support the increased degradation of the solution containing seven phenolic acids is the reducing power of the gallic acid, which could reduce Fe^{3+} to Fe^{2+} and Cu^{2+} to Cu^{+} (ions that are more suited to activate the hydrogen peroxide into hydroxyl radicals). Still, it is important to mention that the concentrations of the literature studies benefiting oxidative processes with gallic acid as a reducing agent are much higher than the ones used in this document. Therefore, this second explanation would be responsible for only a small part of the oxidation increase when the solution containing seven acids was compared to the one containing six acids.

Although good organic depletions were achieved, the BOD_5/COD ratio was reduced from 0.45 to less than 0.25, indicating that the biodegradability was somehow affected by the use of these solids as catalysts. We believe that the presence of leached copper species cannot be pointed out as the cause of biodegradability loss because the Fe-O catalyst presented similar BOD_5 results. Organic intermediate compounds, however, might be refractory to biological decomposition and, since the composition of all catalysts is qualitatively the same (copper and iron oxides), the oxidation pathways might have been similar and this would explain the biodegradability loss for all cases.

XII.1.3. Iron-cobalt solids

The last catalyst screening using co-precipitation technique comprised solids containing iron and cobalt oxides. Different molar proportions were tested and compared as heterogeneous Fenton's catalysts. The tested cobalt oxide percentages on the solids composition were 30, 50, 70 and 100 %. The usual solution comprising six phenolic acids was employed as olive mill wastewaters simulated effluent.

All iron-cobalt catalysts were able to deplete at least 47 % of the total phenolic content of the mother solution, and the maximum TPh abatement was presented by Fe-Co-O 70/30: 64 %. However, Fe-Co-O 50/50 and Fe-Co-O 30/70 achieved close values (61 and 58 %, respectively). On the other hand, when COD removal is taken into account, 30/70 is highlighted as the best molar proportion since Fe-Co-O 30/70 presented the highest COD removal: 32 %. Biodegradability was assessed through BOD_5/COD ratio. All solids were able to enhance this parameter (especially Fe-Co-O 30/70, which achieved the value of 0.63 – against the 0.36 of the mother solution).

Although the organic charge depletion values are not high enough for these solids to be considered for industrial wastewater treatment, the biodegradability enhancement in all cases (especially Fe-Co-O 30/70) pulls attention to further investigation of the cobalt on the Fenton's process.

XII.1.4. Extracted iron from Fenton's sludge and cerium solids

Since the best results presented by ceramic catalysts was achieved by Fe-Ce-O 70/30, the reproduction of this solid using recycled material was studied. This work had the goal of recycling iron from Fenton's sludge gathered from a detergent industry that uses the homogeneous Fenton's process to treat its effluents. The metal was extracted by acidic digestion and employed in the preparation of a new iron catalyst.

After the production of the solids using the new procedure, Fenton's activity was compared to discuss the possibility of this novel approach on the catalyst preparation. The assessment took in consideration the chemical oxygen demand and total phenolic content as main parameters and biochemical oxygen demand in five days as biodegradability indicator.

Regarding TPh and COD removals the new catalyst presented similar profiles when compared to the original catalyst. Yet, when it comes to the biodegradability indicator, BOD_5 and the BOD_5/COD ratio, it revealed much worse results: low BOD_5 and a ratio even lower than the initial synthetic effluent. With this argumentation and the abatement values (50 % COD and 93 % of TPh), it can be said that both present the same activity but, somehow, the catalyst produced using recycled iron affected the effluent's biodegradability – what discards further studies in this regard.

XII.2. Low cost materials

XII.2.1. Fenton's sludge

Sludge from a detergent industry that uses the homogeneous Fenton's process to treat its effluents was evaluated as catalyst in this work. This residue was appraised on the treatment of a synthetic effluent containing seven phenolic acids commonly found in olive mill wastewaters. The transformation of the raw mud into a useful catalyst was intended to involve as lower costs as possible; therefore, it was only dried and milled before being tested. Since these muds come directly from the treatment plant, it is expected to find organic matter in the solids, because there are no further steps besides baking to enhance its efficiency. The dried sludge's efficiency was compared with other dried muds, calcinated at 4 temperatures: 300, 400, 500 and 1000 °C. The iron content rose with the temperature augment, from the value of 37 % (w/w) for the dried sludge, to 44, 55, 65 and 71 % for the subsequent higher temperatures. Regarding organic charge depletion through the Fenton's process, this work's results were that greater calcination temperatures were most-likely to show more catalytic activity and lower adsorption of the model compounds, although higher levels of iron leaching were detected (accounted in both iron percentage of the catalyst and total leached amount). Although the catalyst baked at 1000 °C reached very good removals (almost complete TPh destruction, more than 50 % COD removal and around 45 % TOC abatement), the iron leaching was too high (172.0 mg.L^{-1} at a catalyst dose of 2.0 g.L^{-1}). Also, the BOD$_5$/COD ratio is reduced to less than half of the initial simulated effluent (around 0.19 for the treated samples while the synthetic solution has a 0.42 ratio). Since these two last parameters (iron leaching and BOD$_5$/COD ratio) are major preoccupation for the Fenton catalysts due to environmental concerns, C$_{105}$, the non-baked catalyst, is pointed as the best solid in our study. It presents low reaction activity (less than 70 % TPh removal, approximately 15 % of COD abatement and an increment of 8 % of the TOC), but keeping the biodegradability close to the initial (BOD$_5$/COD ratio = 0.40). Also, the catalysts baked at the lowest temperatures, had the advantage of leaching much less iron. The homogeneity of the process was clearly certificated through two comparative experiments, in which very similar profiles can be observed when Fe^{3+} is used as catalyst at the leached iron concentrations.

XII.2.2. Zero valent iron

Construction site's residues, iron bars, were transformed into shavings with a lathe and tested as Fenton's heterogeneous catalysts. This material showed good results regarding COD and TPh removals on the treatment of a synthetic olive mill effluent. To assess the process efficiency and study the best conditions for the reaction, the Design of Experiments methodology was employed. DoE's independent variables were (1) iron concentration, in the range of 20 and 60 g.L^{-1}, (2) hydrogen peroxide concentration, from 35 to 70 mM, (3) pH, values of 3.0 and 4.0 and (4) reaction time, from 10 to 120 minutes. At the best conditions ([ZVI] = 20 $g.L^{-1}$, [H_2O_2] = 70 mM, pH = 3.0 and time = 120 min), 65 % COD abatement and 98 % TPh destruction was observed. Agreement between replicas was verified, proving the process as reproducible. DoE's results pointed out as important variables, for TPh removal, the reaction time, applied pH and the interaction between these two; while for COD removal the iron shavings concentration was also highlighted as important.

As the kind of bars is the most common used worldwide (A-400 steel), the reuse of these solids could bring benefits to the environment and also reduce costs regarding industrial effluents treatment. Moreover, due to the high activity presented through these results, ZVI can be pointed out as the best low cost material discussed in this document.

XII.3. Continuous operation

The results achieved by the batch-wise systems using ZVI motivated the study of the iron shavings in continuous operation in a tubular fixed bed reactor. Shavings from two sources were tested and evaluated. The first one was gathered from a plate cutting industry. It was used in its raw form and its efficiency was compared to washed shavings (according to two methodologies), reaching the conclusion that an acidic washing of the solids is beneficial to the process, since TPh and COD removals augmented significantly without adding too much costs with this extra step. With a flow rate of the simulated effluent at 1 $mL.min^{-1}$, pH 3.0, hydrogen peroxide concentration of 35 mM and 11.5 min of residence time, the referred iron shavings were able to deplete, on average, 83 % TPh and 47 % COD during the 120 hours of operation studied at room temperature.

The second kind of ZVI was gathered from iron construction bars, the solids were separated according to the internal and external parts of these bars, once the outer part is visibly rusty, and a comparison of both of these parts was made with a commercial catalyst, N-150. At the tested conditions (longer trials of 158 hours using the same parameters presented on the last paragraph), the best results for this kind of shavings were presented by the ZVI from the internal part of the bars (TPh removals stabilized slightly above 80 %, while the COD removal was close to 40 %). Therefore, it was concluded that there is no necessity of making this differentiation, since the external part corresponds to a thin layer and its mass would represent only a small proportion if both parts are mixed, besides presenting the interesting organic charge removal results. When N-150 was employed as Fenton's catalyst, very poor oxidative power was observed, excluding this solid of further studies.

The acquired data supports that all iron shavings, regardless of source or washing methodology, presented good catalytic activity and stability, being suited for the Fenton's reaction. However, the metal leaching was high in all cases, indicating that homogeneous reactions might play a significant role in the tested systems and also that further studies should consider pH levels above 3.0.

XII.4. Classical Fenton's process

Close attention was given to a topic not approached before: the classical Fenton's process. Conditions that were used to most reactions discussed before chapter X were applied to a homogeneous reaction using iron sulphate as Fe^{2+} precursor. This first run had its $[Fe^{2+}]$:$[H_2O_2]$ ratio of 4.1 kept and a whole set of experiments was carried out using lower iron concentrations (dropping from 1000 to 500, 100, 20, 10 and 2 ppm). Due to the great range of these reactants' concentrations, the organic charge depletion substantially varied too: when $[Fe^{2+}]$ = 1000 ppm and $[H_2O_2]$ = 244 mM were used, 95 % TPh destruction and 78 % COD depletion was observed, while this removals dropped to 20 % TPh abatement and 4 % COD reduction when reactants' concentrations were diminished 500 times.

To assess the hydrogen peroxide decomposition, the experiment using the highest iron and peroxide concentrations was performed at the controlled temperatures of 20, 25, 30, 35 and 40 °C – at all temperatures, except 20 °C, the process was able to stimulate nearly complete H_2O_2 decomposition in 20 minutes. Since the Fenton's process depends on H_2O_2 to produce oxidizing hydroxyl species, a new set of experiments was performed with several peroxide additions, one at each 20 minutes, considering that at each interval the concentration of the reactant would decrease to insignificant levels.

The organic charge depletions were enhanced by this new approach – specially in experiments that used low concentrations of reactants. Yields of both iron and hydrogen peroxide were calculated regarding the removed chemical oxygen demand, highlighting the much lower amounts of reactants needed to achieve the same oxidation levels when this methodology is applied. EXP 3* was pointed out as the best inside the screening performed, achieving almost complete TPh depletion and removing almost as much COD as EXP 1 but with the very important advantage of using only one tenth of its iron concentration and less than one third of the hydrogen peroxide quantity. This advantage would mean, besides cost reduction for the industry, a substantial benefit to the environment due to the generation of much lower iron sludge amounts.

Moreover, a prolongation of the experiments using lower concentrations is quoted as a possible way to further enhance the reactants yields and diminish the mud formation. However, these experiments' prolongation was not yet studied, being future work to be done.

XII.5. Forthcoming work

The use of solutions comprised by model compounds is very common when it comes to the AOPs investigative area due to the uniformity of the initial pollutant mixture, which facilitates results comparison to be reached more directly, highlighting the process differences resulting from various approaches. This was the reason why the same synthetic effluent was the basis for the studies carried out along this work. In fact, our main goal was focused on a comparative analysis of different types of Fenton's operations, in what concerns batch and continuous modes, with an important focus on different solid materials for the heterogeneous system and a specific relevance to the homogeneous process by tackling various addition ways of the hydrogen peroxide oxidant aiming to overcome the principal environmental sludge formation drawback. This said, the below points can be considered as the continuation of the present research.

- The first point to be addressed in future work is the application of the most important findings of this document to real wastewaters. Indeed, since the aim of all Fenton's catalysts, methodologies and parameters studied, is to handle new alternatives to the industry, the remediation of real effluents should be further tested.

- The calcination temperature is a very important factor when ceramic catalysts are in discussion, as mentioned on the first experimental study presented on this thesis. Yet, besides the temperature, the atmosphere composition during the calcination process also plays an important role on the properties of the generated solid due to the oxidative reactions that might take place on the presence of oxygen. Once the activity of most Fenton's catalysts rely on the species oxidation state, which present better catalytic performance when are in their reduced forms, the valence state of the reactive species becomes an important issue. The Fe-Ce-O 70/30 calcinated at 1000 °C, for example, presented low iron leaching but poor reactivity. If the air oxidation of the solid was avoided by the use of helium or nitrogen controlled atmosphere during calcination, maybe the resulting catalyst could achieve acceptable catalytic properties. The same happens with the catalysts calcinated at lower temperatures, that could present even higher reactivity if controlled atmosphere was used.

- Another research yet to be done is the conformation of ceramic catalysts to be used in continuous packed bed reactors.

- Amongst the low cost materials evaluated, water from barbed wire washing is another industrial waste that could be integrated to wastewater treatment as Fenton's catalyst (as homogeneous process or precursor to produce ceramic catalyst), since this residue presents high iron concentrations and acidic pH, which would contribute to the pH reduction pre-Fenton's reaction (reducing costs with acidification).

- Iron removing systems, such as membranes, could upgrade Fenton's continuous technologies, reducing this metal's concentration on the outer stream of the ZVI-containing continuous reactors. The usage of such structure might be able to prepare the treated effluent for biological depuration, as well as retaining the metals that could be integrated on other systems or receive new applications.

- Regarding the homogeneous studies, a closer look on the organic charge profiles and hydrogen peroxide evolution for more than one $[Fe^{2+}]:[H_2O_2]$ ratio could provide interesting results. Besides, kinetics could be calculated based on those new profiles, serving as basis for future scaling up of the optimized conditions. The chapter also raised one hypothesis: the possibility of further increasing the oxidation by performing more H_2O_2 injections (which would require longer reaction times), raising the iron yields of experiments EXP 4* and EXP 5* to even greater values and maybe achieving charge removals similar to EXP 3*. Biodegradability assessment, using BOD_5, respirometry and eco-toxicity analysis, should also be performed, in order to evaluate if the several peroxide additions lead to more biodegradable samples. After finding the optimal conditions, the continuous operation could be tackled and, finally, industrial scaling up might be achieved.