

Universidade de Trás-os-Montes e Alto Douro

# **TREATMENT OF INDUSTRIAL WASTEWATER**

## Application of chemical and biological processes

Dissertation presented for the Doctor of Philosophy degree in  
Chemical and Biological Sciences

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*“O que não aconteceu, nunca esteve para acontecer,  
e o que aconteceu, nunca esteve para não acontecer”*

**Teixeira de Pascoaes**



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## **Abstract**

Agro-industries are the main source of water pollution in industrial sector associated not only to depletion of raw materials, but also to additional products used during processing, thus generating wastewater. When it is released directly into natural watercourses, could be toxic to existing fauna and flora due the wastewater characteristics. Consequently, manufacturers have been challenged to promote the wastewater treatment previous to watercourse discharge. Conventional biological treatment processes, often used for it economic benefits do not always represent satisfactory results since in some cases the wastewater may exhibit resistance to biological oxidation. The use of chemical conventional process and advanced oxidation processes (AOP) have emerged as a promising wastewater treatment technology, mainly to the elimination of toxic and recalcitrant organic pollutants, which consequently allow it discharge into watercourse or their integration with biological processes.

The main objective of this thesis was contribute to the study and development of oxidative technologies for the treatment of industrial wastewaters with high impact in the north of Portugal. The wastewaters generated in the production of olive oil, wine, fruit concentrate juice, crystallized fruit, pulp and paper, and the municipal landfill leachate generated by waste disposal were selected to be assessed.

Structurally, the first part of this work (Chapter 1) is dedicated to the presentation and review of literature in wastewater treatment studied. In this chapter, is presented a brief description of processing, characterization of generated wastewater and a selection of main developed studies in recent years, involving chemical oxidation processes in wastewater treatment and it combination with other treatments (biological and/or chemical). It was found that the combination of processes appears to be the most advantageous for the treatment of effluents in the study. The use of chemical coagulation-flocculation processes as primary treatment plays an essential role in the removal of suspended and colloidal matter, enhancing the efficiency of a complementary treatment. On the other hand, the advanced oxidation processes, used as pre-treatment or final treatment, remove organic matter concentrations in effluents with greater pollutant load to be complemented with biological treatment.

In the second part (Chapters 2 to 7) the experimental work performed for the treatment of wastewater is presented. All studies showed high removal rate of the organic fraction, obtaining in some cases a treated effluent that can be discharged into a watercourse or be sent to an urban municipal treatment plant.

The application of Fenton reagent with solar radiation, applied to the effluent from *pulp mill industry* and already subjected to biological pre-treatment reached removals of COD and total polyphenols above 90%. Solar photo-Fenton reaction presented higher efficiency than the respective dark reaction under identical experimental conditions. Using 20 and 50 mg Fe L<sup>-1</sup> revealed that solar photo-Fenton can reach the same DOC degradation (90%), however, H<sub>2</sub>O<sub>2</sub> concentration and reaction time decreased with higher iron concentration.

In stabilized *landfill leachate* treatment, the combination of coagulation-flocculation process with Fenton reagent allowed to remove 82% of COD. Firstly, from the study of the effect of coagulation/flocculation with different chemicals, was possible to establish the best operational conditions. Thus, using 2 g L<sup>-1</sup> of FeCl<sub>3</sub>·6H<sub>2</sub>O at pH 5, allowed removing 63% of COD, 80% of turbidity and 74% of total polyphenols. Moreover, coagulation/flocculation combined with solar photo-Fenton revealed higher DOC (75%) reductions than single solar photo-Fenton (54%).

The *olive mill wastewater* used in the study was submitted to the combination of Fenton reagent with an anaerobic biological to remove the pollutant load. Using a fixed weight ratio H<sub>2</sub>O<sub>2</sub>/COD of 0.20, a pH = 3.5 and a H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio of 15 defined as optimal initial conditions in Fenton process, there was obtained a reduction of 17.6% in COD and 82.5% in the total polyphenol content. On the other hand, anaerobic biological treatment itself allowed conversions from 52% to 74% of COD using microorganisms immobilized in *Sepiolite* and previously adapted. Both combination allowed COD reductions ranging from 64 to 88% and a yield of methane generation, ranging from 281 cm<sup>3</sup> to 322 cm<sup>3</sup> of CH<sub>4</sub>/g COD removed.

The *candied fruit wastewater* was studied by the combination of Fenton reagent subjected to UV radiation with chemical coagulation-flocculation process. Under the optimal conditions ([H<sub>2</sub>O<sub>2</sub>] = 5459 mg L<sup>-1</sup>; [Fe<sup>3+</sup>] = 286 mg L<sup>-1</sup>; time >180 minutes) previously determined by a Box-Behnken design of Response Surface Methodology allowed to establish a higher treatment efficiency. Thus, it was achieved a COD



removal of 45, 64 and 74% after 360 minutes using an irradiance of 23, 70 and 85 W/m<sup>2</sup> respectively. The combination of UV-A LED photo-Fenton with coagulation-flocculation-decantation reached 80 % of COD removal 95% of total suspended solids, as well as almost total removal of turbidity (99%).

The treatment of *winery wastewater* (WW) was studied by the application of oxidative process based on sulfate radicals, catalysed by transition metals and UV radiation. Under determined optimal operational conditions – [HSO<sub>5</sub><sup>-</sup>] = 2.5 mM; [M<sub>2</sub>(SO<sub>4</sub>)<sub>n</sub>] = 1.0 mM; pH = 6.5 and reaction temperature = 323 K – 51%, 42% and 35% of COD removal was achieved using respectively Fe(II), Co(II) and Cu(II) as catalysts. , It was demonstrated that the use of HSO<sub>5</sub><sup>-</sup>/M<sup>n+</sup> in several consecutive doses was more efficient than adding the reagents as a single dose at the beginning of the reaction. The HSO<sub>5</sub><sup>-</sup>/Fe(II)/UV-A LED process demonstrates a high COD and TOC removal efficiency when compared with same conditions conventional photo-Fenton.

Wastewater from an industry of *fruit juice concentrate* was treated by coagulation-flocculation process combined with an aerobic biological process. Firstly in aerobic biological treatment were obtained above 90% of COD removals, in reactors initially loaded with 2 g VSS L<sup>-1</sup> of biomass concentration and 20 g COD L<sup>-1</sup> of organic matter concentration. After determined coagulation-flocculation optimal conditions in a tertiary treatment (0.44 g L<sup>-1</sup> of ferric chloride at pH = 5.5) was achieved 94.4% and 99.6% removal parameters in turbidity and COD, respectively.

The last part (Chapter 8) of this work present the main conclusions that were reached during the various studies conducted, which also suggest improvements and additional ideas to the work already presented.



## **Resumo**

As agroindústrias são um dos setores industriais que causam maior poluição da água, associadas não só ao desperdício de alguma matéria-prima, mas também aos produtos auxiliares adicionados ao longo do processamento que, no seu todo geram as águas residuais. A sua descarga direta nos cursos de água pode, por vezes, apresentar toxicidade para a fauna e flora existente devido às características recalcitrantes dos efluentes gerados. Como consequência, as indústrias têm sido desafiadas para promover um tratamento eficaz previamente à sua descarga. A aplicação de processos biológicos convencionais, frequentemente utilizados pelas vantagens económicas, nem sempre se traduz em resultados satisfatórios, uma vez que em algumas situações as águas residuais podem apresentar resistência à oxidação biológica. A utilização de processos químicos convencionais e em particular de Processos de oxidação avançados (POA) têm surgido como uma tecnologia promissora, de tratamento de águas residuais, principalmente na eliminação de poluentes orgânicos tóxicos/recalcitrantes que, consequentemente, permitem a sua descarga nos cursos de água ou a sua integração com processos biológicos.

O principal objetivo desta tese foi contribuir para o estudo e desenvolvimento de tecnologias oxidativas aplicáveis ao tratamento de águas residuais industriais com potencial impacto na região Norte de Portugal. Foram selecionados os efluentes gerados na produção de azeite, de vinho, de concentrado de sumo de frutas, de frutas cristalizadas, de pasta de papel e celulose, bem como de lixiviados de aterros municipais gerados pela deposição de resíduos sólidos urbanos.

Estruturalmente, a primeira parte do trabalho (capítulo 1) é dedicada à apresentação e revisão da literatura existente para o tratamento das águas residuais alvo de estudo. Neste capítulo, apresenta-se uma breve descrição das etapas envolvidas no processamento, a caracterização das águas residuais geradas e uma seleção de estudos efetuados nos últimos anos, que envolvem processos de oxidação química no tratamento das águas residuais e também quando combinados com outros tratamentos. Dos estudos apresentados verificou-se que a combinação de processos surge como uma proposta muito interessante para o tratamento dos efluentes em estudo. A utilização de processos

de coagulação/floculação química como tratamento primário desempenha uma etapa essencial na remoção de matéria em suspensão e coloidal para, numa etapa complementar, potenciar a eficiência do tratamento aplicado, seja ele biológico ou químico. Por outro lado, os processos de oxidação avançados, utilizados como pré-tratamento ou tratamento final, removem concentrações de matéria orgânica em efluentes com maior carga poluente, podendo ser complementados com um tratamento biológico.

Na segunda parte do trabalho, onde se inserem os capítulos 2 a 7, são apresentados os trabalhos experimentais efetuados para o tratamento das águas residuais. Todos os estudos apresentaram elevadas percentagens de remoção da fração orgânica, sendo que alguns permitem obter um efluente tratado capaz de ser descarregado num curso de água ou então ser enviado para uma estação de tratamento municipal urbana.

A aplicação do reagente de Fenton com radiação solar, aplicado a um efluente de *indústria de pasta de papel*, tratado e submetido a um pré-tratamento biológico permitiu atingir remoções de CQO e polifenóis totais acima de 90%. O tratamento solar com reagente de Fenton (foto-Fenton) apresentou maior eficiência quando comparado com os ensaios realizados na ausência de radiação solar nas mesmas condições experimentais. A aplicação de 20 e 50 mg/L de ferro revelou que a reação foto-Fenton solar pode atingir 90% de redução de COT para as duas situações, no entanto, a concentração de  $H_2O_2$  e o tempo de reação diminuiu com o aumento da concentração de ferro.

No tratamento de um *lixiviado de um aterro* sanitário estabilizado, a combinação do processo de coagulação/floculação química com reagente de Fenton, permitiu remover 82% de CQO. Inicialmente, a partir do estudo do efeito do processo de coagulação-floculação para diferentes reagentes, foi possível estabelecer as melhores condições operacionais. Assim, a aplicação de 2,0 g/L de  $FeCl_3 \cdot 6H_2O$  a pH 5, permitiu remover 63% da CQO, 80% de turvação e 74% dos polifenóis totais. Além disso, a combinação do processo de coagulação/floculação seguido do processo foto-Fenton solar revelou maior remoção de COT (75%) quando comparadas com as verificadas apenas no processo foto-Fenton solar (54%).

As águas residuais provenientes de um *lagar de azeite* foram submetidas ao processo de oxidação por reagente de Fenton combinado com um processo biológico anaeróbio, o que permitiu uma remoção de 58% de CQO. Para as seguintes condições ótimas,  $\text{H}_2\text{O}_2/\text{CQO}$  de 0.20, um valor de  $\text{pH} = 3,5$  e razão molar de  $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$ , o reagente de Fenton traduziu-se numa redução de 17,6% de CQO e 82,5% de polifenóis totais. Por outro lado, o processo biológico anaeróbio por si só, atingiu entre 52% e 74% de redução de CQO, com utilização de microrganismos inoculados em *Sepiolite*, previamente adaptados. A combinação dos dois processos permitiu obter reduções de CQO entre 64% e 88% e gerar valores de metano entre  $281 \text{ cm}^3$  e  $322 \text{ cm}^3$  de  $\text{CH}_4/\text{g}$  de CQO removido.

As águas residuais resultantes de uma *indústria de fruta cristalizada* foram submetidas ao processo reagente de Fenton com radiação em combinação com o processo de coagulação/floculação química. Para as condições ótimas ( $[\text{H}_2\text{O}_2] = 5459 \text{ mg/L}$ ;  $[\text{Fe}^{3+}] = 286 \text{ mg/L}$ ; tempo  $> 180 \text{ min}$ ) previamente determinadas, através da metodologia RSM do modelo de *Box-Behnken*, foi possível estabelecer a maior eficiência de tratamento. Assim, as condições definidas atingiram 45, 64 e 74% de remoção de CQO após 360 minutos, para uma irradiância de 23, 70 e  $85 \text{ W/m}^2$ , respetivamente. A combinação do processo UV-A LED foto-Fenton com o processo de coagulação/floculação atingiu 80% de remoção de CQO, 95% de sólidos suspensos, bem como a 99% de turvação.

O tratamento de *efluentes vinícolas* foi efetuado através da aplicação de um processo oxidativo com base na utilização de reagentes que geram radicais sulfato, catalisados por metais de transição e radiação solar. A aplicação das condições ótimas, previamente determinadas ( $[\text{HSO}_5^-] = 2,5 \text{ mM}$ ;  $[\text{M}_2(\text{SO}_4)^n] = 1,0 \text{ mM}$ ;  $\text{pH} = 6.5$  e temperatura da reação  $= 323 \text{ K}$ ) permitiu obter reduções de CQO de 51, 42 e 35% com aplicação de Fe(II), Co(II) e Cu(II), respetivamente, como catalisadores. Verificou-se que a aplicação de  $\text{HSO}_5^-/\text{M}^{n+}$  em várias doses consecutivas apresenta maior eficiência no início da reação. O processo  $\text{HSO}_5^-/\text{Fe(II)}/\text{UV-A LED}$  demonstrou maior capacidade de remoção de CQO e TOC quando comparado com o processo convencional foto-Fenton.

As águas residuais de uma empresa de *concentrados de sumo de frutas* foram submetidas a um processo biológico aeróbio seguido do processo de

coagulação/floculação química. Na primeira fase, o processo biológico atingiu remoções de CQO acima de 90%, nos reatores em que se adicionaram 2 g/L de biomassa e 20 g/L de matéria orgânica. Após determinação do coagulante ótimo e respectivas condições operacionais (0,44 g/L de  $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$  e  $\text{pH} = 5,5$ ) atingiram-se 94,4% e 99,6% de remoção de CQO e turvação, respetivamente.

Na última parte deste trabalho (Capítulo 8), são apresentadas as principais conclusões que se alcançaram ao longo dos vários estudos efetuados, onde se sugerem também melhorias e ideias complementares ao trabalho já apresentado.

## **Nomenclature**

AOP – Advanced Oxidation Processes

AOS – Average oxidation state

BOD<sub>5</sub> – Biochemical oxygen demand, gO<sub>2</sub> L<sup>-1</sup>

CDEO – Conductive diamond electro-oxidation

CFD – Coagulation flocculation decantation

COD – Chemical oxygen demand, gO<sub>2</sub> L<sup>-1</sup>

COD<sub>o</sub> – Initial chemical oxygen demand

COD<sub>f</sub> – Final chemical oxygen demand

CPC – Compound parabolic collectors

CWAPPO – Catalytic wet air peroxide oxidation

DOC – Dissolved organic carbon

E<sub>EO</sub> – Electric energy per order

EPA – Environmental Protection Agency

EU – European Union

FJW – Fruit juice wastewater

FN-i – Anaerobic biological experiments previous submitted to Fenton treatment

GDP – Gross domestic product

IC – Inorganic cations

INE – Statistical national institute (Instituto Nacional de Estadística)

HDPE – High density polyethylene

HRT – Hydraulic retention time

k<sub>FN</sub> – Kinetic constant of OMW anaerobic digestion process pre-treated with Fenton's reagent, h<sup>-1</sup>

k<sub>N</sub> – Kinetic constant of OMW anaerobic digestion process, h<sup>-1</sup>

$k_s$  – Kinetic constant, gCOD L<sup>-1</sup>

$K_S$  – Monod constant saturation, gCOD L<sup>-1</sup>

LED – Light emitting diode

M – Molecular weight, g mol<sup>-1</sup>

M<sup>n+</sup> – Metal ion

MWWTP – Municipal wastewater treatment plant

N-i – Anaerobic biological experiments

NTU – Nephelometric Turbidity Units

OMW – Olive mill wastewater

OUR<sub>max</sub> – Oxygen uptake rate

PMS – Peroxymonosulphate

PMW – Pulp mill wastewater

PWM – Pulse with modulation

PSA – Plataforma Solar de Almeria

P&P – Pulp and Paper

Q<sub>UV</sub> – Accumulated ultraviolet energy, kJ L<sup>-1</sup>

rb<sub>COD/COD</sub> – biodegradability rate

RSM – Response surface methodology

S – Substrate concentration

S<sub>0</sub> – Biodegradable substrate concentration at the beginning of experiments

S\* – Substrate concentrations

SPSS – Statistical package for the social sciences

SR-AOPs – Advanced oxidation processes using sulphate radicals

TKN – Total Kjeldahl Nitrogen, gL<sup>-1</sup>

TOC – Total Organic Carbon, gL<sup>-1</sup>



TP – Total polyphenols,  $\text{mgL}^{-1}$

TP<sub>0</sub> – Initial value of TP,  $\text{mgL}^{-1}$

TP<sub>f</sub> – Final value of TP,  $\text{mgL}^{-1}$

TSS – Total suspended solids,  $\text{gL}^{-1}$

TVS – Total volatile solids,  $\text{gL}^{-1}$

USA – United States of America

UV – Ultraviolet radiation

V – Volume of the anaerobic bioreactor

VSS – Volatile suspend solids

X – Biomass concentration

X<sub>COD</sub> – Chemical oxygen demand conversion

X<sub>TP</sub> – Total polyphenols conversion

Y<sub>CH<sub>4</sub></sub> – Methane generation coefficient

Y<sub>X/s</sub> – Cell yield (g microorganisms/g of substrate)

WTP – Wastewater treatment plant

WW – Winery wastewater

### **Greek letters**

$\nu$  – Specific growth rate

$\nu^*$  – Maximum real specific degradation rate

$\nu_{\text{max}}$  – Maximum specific substrate utilization rate

$\mu$  – Specific growth rate of biomass

$\mu_{\text{max}}$  – Maximum specific growth of microorganisms

$\chi^2$  – Chi square statistic test



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# **1. TREATMENT OF RECALCITRANT INDUSTRIAL WASTEWATER**

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# **1. TREATMENT OF RECALCITRANT INDUSTRIAL WASTEWATER**

## **1.1. Introduction**

One of the greatest challenges of the twenty-first century is to have an incessant supply of safe drinking water for the millions of persons all over the world. Nowadays, much attention is given to the treatment of industrial wastewaters due to their growing pollution potential arising out of the rapid industrialization and multiple anthropogenic activities. Uncontrolled discharge of wastewaters into the environment will pose detrimental effects to humans, animals and plants.

Depending on the type of discharge of the effluents and the nature of the constituents present in it, most of the treatments are based on conventional technologies, involving physical, biological and chemical methods. The selection of a particular treatment process depends on the self-purification capacity of streams, permissible levels of pollutants in water bodies and the economic interests of industries. In addition to classical processes we may also use advanced techniques, like membrane separation processes, reverse osmosis, ultrafiltration and advanced oxidation processes, which are being increasingly tried upon for wastewater treatments.

In Mediterranean countries, olive oil and wine manufactures are among the most important agro-industrial activities due to their economic impact. A relevant environmental problem arises concerning the wastewater generated along the different production steps. These wastewaters are characterized by their large pollutant load which represents a real problem to surrounding environment when discharged without appropriate treatment. For instance, improper disposal of these wastewaters on the soil is a common situation which poses a potential risk to groundwater contamination. In order to prevent environment pollution, olive mill wastewater (OMW) and winery wastewater (WW) should be properly treated aiming at either the recovery, valorisation or the removal of compounds from the discharging effluents.

Biological treatment processes can be a suitable option, however some issues like toxicity, low biodegradability and seasonal production affect the treatment efficiency and is not possible to achieve the legal limits of discharge for this kind of effluents.

In this way some chemical processes have been studied and among these advanced oxidation processes. AOPs, which involve the generation of highly reactive radicals (especially hydroxyl radicals (HO<sup>•</sup>)) in sufficient quantity to influence water purification, have been productively explored for the elimination of a wide variety of recalcitrant and toxic compounds with the purpose of reducing toxicity and increasing biodegradability<sup>[1, 2]</sup>. HO<sup>•</sup> radicals are extremely reactive species that attack most of the organic molecules. These processes have shown great potential in the treatment of pollutants, either in high or low concentrations.

Accordingly, this work addresses some novel treatment perspectives covering a wide range of wastewaters generated from different processing industries (such as olive mill, winery, pulp mill, crystallized fruit, fruit juice and also landfill leachate) using advanced oxidation processes (AOPs) and, sometimes, its combination with conventional treatment methods. Along these different case studies a broad range of methods and reactors (chemical and biological) were used.

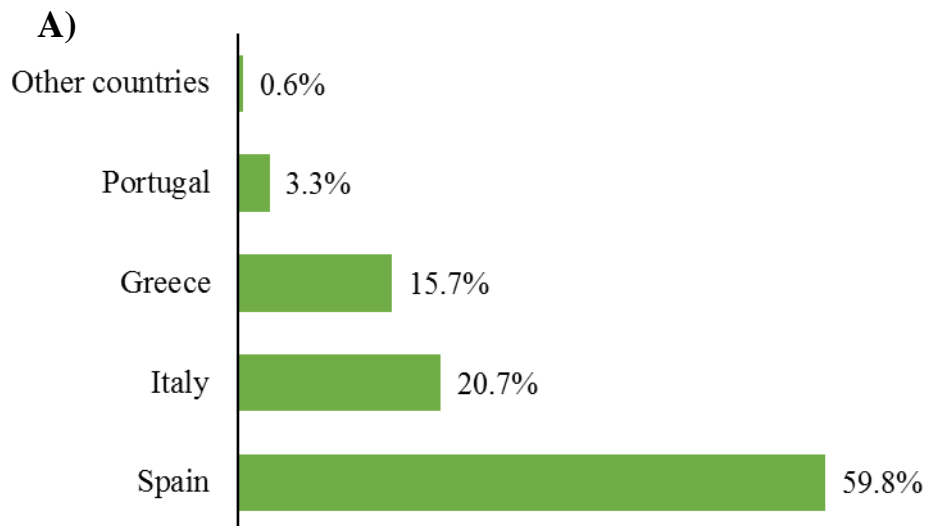
## **1.2. Olive mill industry**

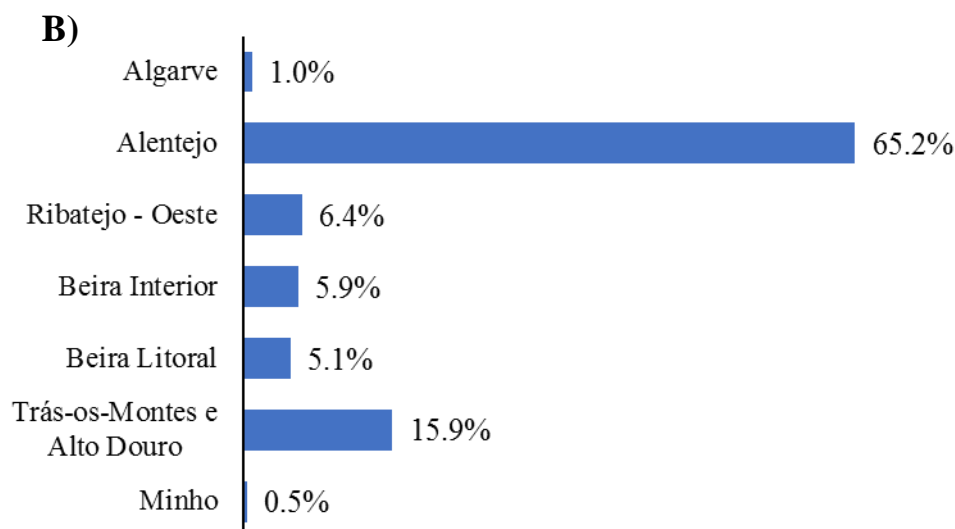
Olive oil production (Figure 1.1) is one of the major important agronomic activities in the Mediterranean region and it is economically significant for several countries<sup>[3]</sup>. According to Brenes *et al.*<sup>[4]</sup> annual world production of olive oil was estimated in  $25 \times 10^6$  hectolitres, with Spain, Italy, Greece and Portugal being the major producers in last years (Figure 1.2 A). High production of olive oil results in the generation of large amount of olive mill wastewaters (OMWs). In Portugal, olive oil production is one of the most traditional industries.



**Figure 1.1** - Olive oil production.

According to data obtained from statistical national institute (INE), between 2011 and 2013 around  $2.5 \times 10^6$  hectolitres of olive oil was produced in Portugal. Water used in this activity is about the quadruple of the amount of oil produced, suggesting that Portugal produces more than  $3.3 \times 10^5$  tonnes/year of OMW.

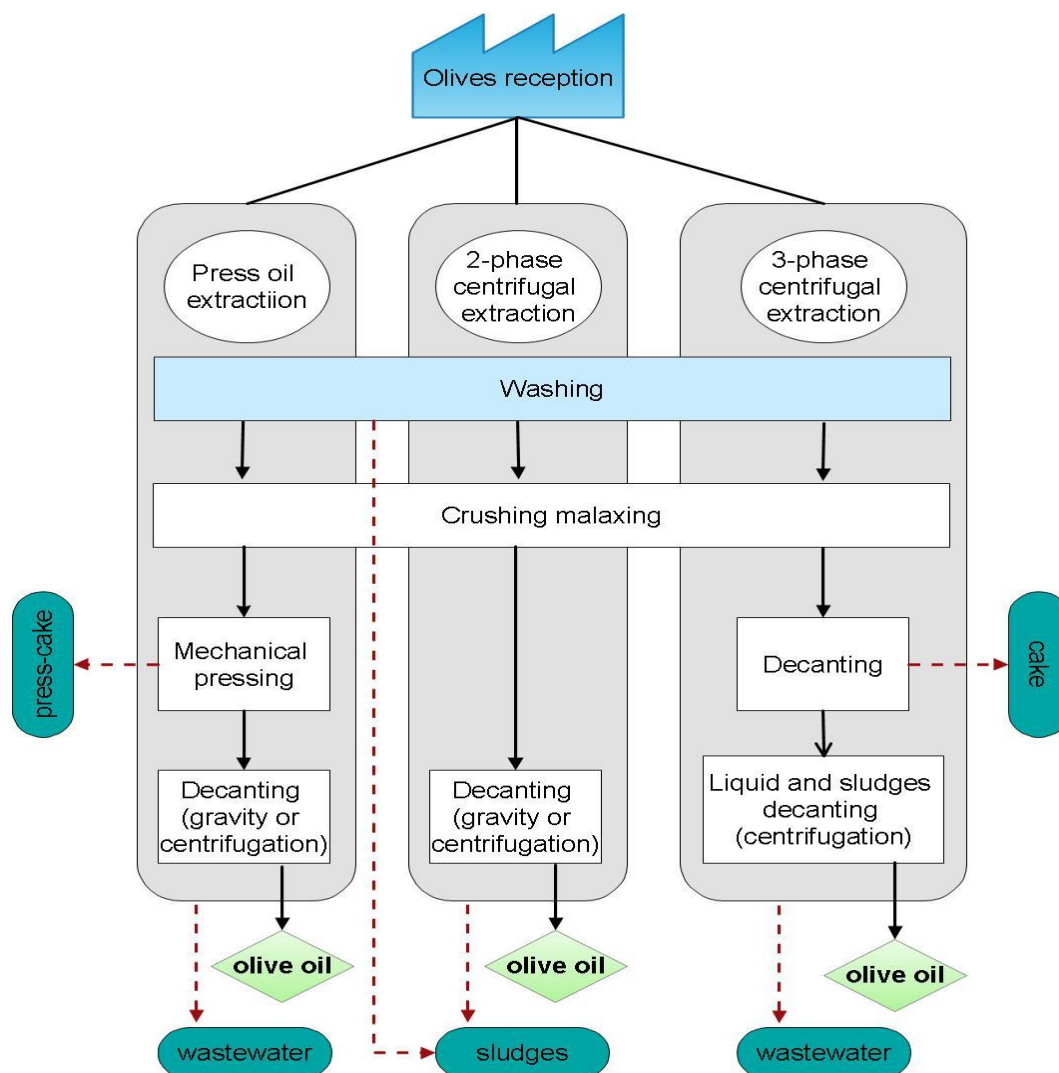




**Figure 1.2** - Olive oil top producers between 2011-2013: (A) in European Union (EU)<sup>[5]</sup> and (B) in the different areas of Portugal<sup>[6]</sup>.

### ***1.2.1. Process of olive oil production***

Olive oil production (Figure 1.3) is typically conducted with the following extraction processes: (1) a traditional discontinuous press process, (2) three-phase centrifugal or (3) two-phase centrifugal extraction systems<sup>[7]</sup>. This waste stream is generated in several forms and compositions following the particular characteristics of the used extraction equipment, olive variety, season and maturity of the fruit. Discontinuous press and three-phase centrifugation processes, although in different volume, produce considerably more liquid effluent than two-phase centrifugal extraction system<sup>[8]</sup>.



**Figure 1.3** - Olive oil extraction methods (adapted from Vlyssides *et al.*<sup>[9]</sup>).

Traditional pressure extraction process results in 0.5 - 0.8 m<sup>3</sup> of wastewater per ton of olives and the waste stream volume in three-phase centrifugal process increases to 1.18 - 1.68 m<sup>3</sup> per ton of olives. This fact is verified due to the constant washing of the olive paste with water at high temperatures prior to oil separation from the paste<sup>[10]</sup>. The volume of wastewater is reduced in the two-phase centrifugal extraction system, however, large amounts of semisolid or slurry waste area also discharged<sup>[8]</sup>. The annual world OMW production is estimated from 10 to over 30 million of m<sup>3</sup>.

### **1.2.2. Olive mill wastewater**

Two main liquid effluents can be identified during olive oil production. The first effluent is generated during the olives washing procedure, and another one arises from the olive oil extraction process (Figure 1.4), which is composed by humidity of fruit coupled with some water used in manufacture<sup>[11]</sup>. As already stated, generation of OMWs depends on several factors yielding an unpredictable effluent<sup>[7]</sup>. The characteristics and composition of OMWs are not constant, and varies according to (i) Composition of vegetation water; (ii) Olive oil extraction process; (iii) Storage time.

- i. The composition of vegetation water ranges according to factors like olive variety, maturity of the olives, olive's water content, cultivation soil, harvesting time, presence of pesticides and fertilizers and climatic conditions.
- ii. Water used in the mills varies widely, both because of equipment requirements (the centrifugal mill needs substantially greater quantities of water) and local operational conditions and practices. The water used in different stages of oil production plus olive washing water reduce the concentration of the various components already in the vegetation water.
- iii. Storage gives rise to substantial changes in composition caused by the anaerobic fermentation of several organic compounds with consequent emission of volatiles, increase of the acidity, precipitation of suspended solids, etc.



**Figure 1.4** - Olive mill oil and wastewater generation.



Considering all these factors and taking into account that olive oil manufactures operate seasonally, OMWs have fluctuations on their characteristics and produced amount. Report the type and origin of OMWs samples is not a common practice. Thus, it cannot be determined if the characteristics reflected total plant waste or a partial waste stream. However, it is possible to estimate each parameter according to OMWs already studied (Table 1.1) from press phase and three-phase olive oil extraction methods.

**Table 1.1-** OMW characteristics (from Vlyssides *et al.*<sup>[9]</sup>).

Parameter	Press	3-phase
pH	4.50 ± 0.60	4.8 ± 0.8
COD (g/L)	158.18 ± 32.63	92.5 ± 17.5
BOD <sub>5</sub> (g/L)	68.71 ± 12.64	45.5 ± 8.2
TOC (g/L)	64.11 ± 10.79	39.82 ± 6.47
TSS (g/L)	4.51 ± 3.27	2.8 ± 2.2
TVS (g/L)	87.20 ± 27.57	57.37 ± 21.96
TKN (g/L)	1.15 ± 0.21	0.76 ± 0.13
Total phosphorus (as P <sub>2</sub> O <sub>5</sub> ) (g/L)	0.87 ± 0.14	0.53 ± 0.084
Total sugars (g/L)	25.86 ± 8.30	16.06 ± 5.92
Fats and oils (g/L)	2.80 ± 1.03	1.64 ± 0.64
Polyalcohols (g/L)	4.75 ± 1.77	3.19 ± 1.22
Total proteins (g/L)	28.30 ± 9.95	17.91 ± 6.88
Organic acids (g/L)	4.88 ± 2.41	3.21 ± 1.23
Total phenols (g/L)	17.15 ± 4.55	10.65 ± 4.08

The OMWs look as high turbidity, dense, intensive violet-dark brown up to black colour and strong smell (specific of olive oil). Typically, this wastewater is acidic, with a high organic matter (COD can be 100 times higher compared to urban wastewaters one) and suspended solids content. The organic matter mainly consists of polysaccharides, sugars, polyalcohols, proteins, organic acids, long-chain fatty acids and oil. Most importantly, OMWs contain phenolic compounds, which are well known for their exclusive antioxidant properties for human health. However, these compounds

are toxic to microorganisms and plants becoming necessary a suitable OMWs treatment in order to minimize the environmental impact of their discharge.

### ***1.2.3. Olive mill wastewater treatment by AOPs***

The application of advanced remediation strategies are required either to fulfil legal requirements for direct disposal or, when economically wiser, to reduce toxicity and improve biodegradability to allow a subsequent inexpensive biological process<sup>[12]</sup>. A conventional biological process on OMW becomes an inefficient process. The high phenols concentrations present on OMW results in phytotoxicity and toxicity to microorganisms used in biological wastewater treatment plants<sup>[13-15]</sup>.

Additionally, turbidity and suspended solids can affect in different ways the processes used for OMWs treatment (e.g., filtration, adsorption, membranes, advanced oxidation processes). Thus, a pre-treatment could be essential to increase the efficiency of following treatment steps<sup>[10]</sup>.

Due the environmental concern related to this type of wastewater, in recent years, OMW treatment using advanced oxidation processes (AOPs) has been extensively studied.

In Table 1.2 are presented some studies using AOPs and summarized the principal and most relevant results. Processes such as electrochemical oxidation, Fenton oxidation and ozonation can only reach partial decontamination even after extended retention/reaction time, thus making OMW treatment by AOPs an expensive process. On the other hand, processes such as TiO<sub>2</sub> photocatalysis, may be not effective at all.

In order to obtain affordable treatments, the strategy adopted is the application of AOPs as pre-treatment to improve the biodegradability of OMW<sup>[16,17]</sup>, prior to subsequent cheapest biological treatment.

Despite the improved treatment efficiency on combined processes, adverse effects have been related. Andreozzi *et al.*<sup>[18]</sup> investigated the possibility of coupling chemical oxidation by ozone with anaerobic digestion. First step showed a longer lag phase and a lower methane production. These effects can be explained by formation of oxidation intermediates compounds, more biorecalcitrant or toxic than initials<sup>[19,20]</sup>.

Specifically, AOPs based on ozone oxidation, applied to assess the possibility to decrease phytotoxicity of OMW, remained toxic to algal growth (*Pseudokirchneriella subcapitata*), and germination index of *Raphanus sativus* L., *Cucumis sativus* L. and *Lactuca sativa* L. did not significantly decrease<sup>[21]</sup>. Furthermore, the long-term storage of OMW coupled with solar irradiation without or with Fe(III) ions in continuous aeration was less efficient than ozonation, and the combined action of the two former treatments did not significantly contribute to enhance germination index.

**Table 1.2** - OMW treatment by AOPs.

Wastewater	Treatment	Remarks	Reference
OMW from continuous processing plant (pH 5.09; 26.7 g TSS/L; 121.8 g COD/L; 6.2 g polyphenols/L)	Ozonation followed by anaerobic digestion	About 50% reduction of total phenols and unsaturated lipids after 3h O <sub>3</sub> treatment; COD remained almost unvaried. O <sub>3</sub> treated OMW showed a longer lag phase and a lower ethane production compared to untreated OMW	[18]
OMW from an olive oil production plant located in Extremadura, southwestern Spain (pH 4.8; BOD 52 g/L; COD 112 g/L; total phenols 2.20 g as caffeic acid/L; TSS 5.14 g/L)	Ozonation and aerobic processes alone, O <sub>3</sub> /aerobic, aerobic/O <sub>3</sub>	The two combined processes resulted in higher COD removal (82%) than either single stage treatment under similar operating conditions	[22]
OMW from a factory located in Navalvillar de Pela, southwestern Spain (pH 4.85; BOD 89 g/L; COD 165 g/L; polyphenols 5.78 g/L)	Fenton process on 10 times diluted OMW samples	COD removal was 85-90% after 3-4 h treatment with 0.01 M of Fe(II), 1 M of H <sub>2</sub> O <sub>2</sub> and pH 2.8	[23]
OMW from a continuous three-phase mill located in Salerno province southern Italy (pH 4.3, COD 53.1 g/L, TSS 6.7 g/L)	Comparison among Fenton, photo-Fenton and TiO <sub>2</sub> photocatalysis on coagulated/ diluted OMW samples	The best COD removal was achieved with photo-Fenton process (93%) after 1.0 h treatment. TiO <sub>2</sub> photocatalysis did not significantly decrease COD	[24]
OMW from a stepwise extraction procedure (3-phase process) in the North of Portugal	Biological process (with fungi)/Fenton oxidation, and Fenton/biological	Toxicity was quite high also after biological process/photo-Fenton oxidation.	[25]
OMW from the homogenization tank of an olive mill plant with a daily olive processing capacity of 100 tonnes in Bursa City, Turkey (pH 4.65-5.50, SS 65 g/L, COD 185.6 g/L, total phenols 9.68 g/L)	Acidification (pH 2) /coagulation/ AOPs (H <sub>2</sub> O <sub>2</sub> /UV and O <sub>3</sub> /UV)	Both H <sub>2</sub> O <sub>2</sub> /UV (pH 2) and O <sub>3</sub> /UV (pH 7) were found to give practically same COD and total phenol removal efficiencies (over 99%)	[10]

OMW from an olive oil processing plant near El-Asamalia in the East of Egypt, operating with a continuous three-phase centrifugation process (TSS 8.5 g/L, COD 117.9 g/L, BOD <sub>5</sub> 22.5 g/L, phenols 6.3 g/L)	photo-Fenton and heterogeneous photocatalysis (TiO <sub>2</sub> , ZrO <sub>2</sub> and FAZA)	At the optimum conditions, photo-Fenton process and TiO <sub>2</sub> photocatalysis (after 8 h treatment) achieved COD and total phenolic compounds removals of 87%, 97%, and 69%, 40% respectively. BOD <sub>5</sub> /COD ratios of both pre-treated photo-Fenton and TiO <sub>2</sub> photocatalysis increased from 0.19 to 0.8 and 0.66, respectively	[16]
OMW from an olive oil mill in Jaén, Spain (COD 3.0 g/L, TOC 840 mg/L, pH around 6)	Conductive diamond electro-oxidation (CDEO), ozonation and Fenton oxidation	Only CDEO allowed achieving the complete mineralization of OMW. Both ozonation at alkaline pH and Fenton oxidation lead to the generation of high concentration of intermediates (mainly carboxylic acids)	[26]
OME from two olive mills (W1 and W2) located in the region of Chania, Crete, Greece (pH, TSS, TP, COD of W1 and W2 were 5.3, 36.7, 3.5 and 61.1 g/L and 5.1, 52.7, 2.5 and 29.3 g/L, respectively)	Coagulation and Fenton oxidation	Fenton reaction increased COD reduction to about 60%	[27]
Settled and diluted OMW from a three-phase olive oil plant located in Sfax (Tunisia) (pH 5.2, COD 19 g/L, TP 672 mg/L)	Fenton Oxidation with zero-valent iron	With a pH value within 2 and 4 the maximum COD removal was 92%	[17]
OMW from a three-phase mill from Nicosia, Cyprus (pH 5.3; COD 43.3 g/L; TP 1.67 g/L)	Sequential coagulation – flocculation <sup>(A)</sup> , solvent extraction <sup>(B)</sup> and photo-Fenton oxidation <sup>(C)</sup>	A) Addition of 6.67 g/L of FeSO <sub>4</sub> ·7H <sub>2</sub> O and 0.287 g/L Floccan23 led to removal of COD (72%) and TP (40%) B) Extraction for 15 min with ethyl acetate at a solvent to sample ratio of 2:1 (v/v) led to 36% TP recovery. C) Oxidation for 240 min at 0.2 g/L Fe <sup>2+</sup> , 5 g/L H <sub>2</sub> O <sub>2</sub> and pH=3 reduced the remaining COD and TP by 73% and 87%, respectively	[28]
OMW was supplied by a three-phase olive mill located in Larnaca, Cyprus (pH 5.7; COD 13.5 g/L; TP 3.1 g caffeic acid/L)	Solar Fenton combined with previous coagulation-flocculation	Coagulation-flocculation with 6.67 g/L of FeSO <sub>4</sub> ·7H <sub>2</sub> O and 0.287 g/L Floccan23 and solar Fenton in a compound parabolic collector pilot plant using concentrations ([Fe <sup>2+</sup> ]=0.08 g/L; [H <sub>2</sub> O <sub>2</sub> ]=1 g/L), led to a high COD removal (87%), while the polyphenolic fraction was eliminated	[29]

OMW was obtained from an olive mill company located in Badajoz, Extremadura, Spain (pH 4.8; COD 92.5 g/L; TP 2.1 g caffeic acid/L)	Fenton's reagent pre-treatment combined with an aerobic biological process	Fenton reagent-biologic combined process allowed a global removal of 80.7% COD and 93.7% TP using H <sub>2</sub> O <sub>2</sub> /COD ratio of 0.20, a pH=3.5 and a H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> molar ratio of 15	[30]
OMW from the homogenization tank of an olive oil mill plant in Bursa, western Turkey (pH 4.91; COD 128 g/L; SS 36.3 g/L; phenols 3.44 g/L; TOC 26.4 g/L)	Physicochemical methods (acid cracking, oil separation and coagulation-flocculation) ultrafiltration and advanced oxidation processes (AOPs)	Physicochemical methods and ultrafiltration: removal of 85% of COD, >97% of oil & grease, >99% of TS and 92% of phenols;  AOP with O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /UV combination achieved 99% removal for COD, phenol and TOC	[31]
OMW anaerobically treated and diluted 1:10 (COD 1960 mg/L; TP 90 mg/L)	Suspended mixture of TiO <sub>2</sub> and powdered activated carbon (PAC)	Under optimal conditions (24 hours exposure to 7.6 W/m <sup>2</sup> irradiation; 3 g/L TiO <sub>2</sub> ; 0.45 g/L PAC; pH 4.3) were obtained 57.9% of COD removal and 87% of TP.	[32]
OMW from Andalusian provinces of Jaén (pH 7.24; COD 1673 mg/L; TP 44 mg/L) and Granada (pH 6.32; COD 4137 mg/L; TP 50.6 mg/L), Spain mixed in portion 1:1	Fenton-like reaction using FeCl <sub>3</sub> as catalyst	Under operational conditions (pH 3.0, 100 g/L H <sub>2</sub> O <sub>2</sub> , [FeCl <sub>3</sub> ]/[H <sub>2</sub> O <sub>2</sub> ] ratio = 0.04, and ambient temperature) 92.6% of COD and 99.8% of TP were removed	[33]
OMW from several olive-oil mills in the provinces of Granada, Spain (pH 6.1; COD 4017 mg/L; TP 66.2 mg/L)	Pilot scale Fenton-like process	Under operational conditions (3h at pH 3, [FeCl <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> ] ratio between 0.026-0.058, [Fe <sup>3+</sup> ] between 0.35-0.40 g/L) achieve 96% COD reduction and 99% to total phenols	[12]
OMW collected from an olive oil production plant located in Irbid, North West part of Jordan (pH 5.6; COD 117.1 g/L; BOD 38 g/L; TSS 29.3 g/L; TP 2.7 g/L)	Combined advanced oxidation (O <sub>3</sub> and UV/O <sub>3</sub> ) and biodegradation	Sequential UV/O <sub>3</sub> and biodegradation reach higher COD reduction (90.7%) with diluted samples (COD <sub>0</sub> = 45 g/L)	[34]
OMW from the homogenization tanks of an olive mill in Bursa City, Turkey (pH 5.2; COD 115 g/L; TSS 32 g/L; TP 5.58 g/L)	Physicochemical pre-treatment (acid cracking and coagulation) and Fenton and Fenton-like processes	Acid Cracking combined with Fenton-like process (pH 3; [H <sub>2</sub> O <sub>2</sub> ]= 3 g/L; [FeCl <sub>3</sub> ]=2.5 g/L) achieve a COD and phenols reduction of 93% and 95% respectively.	[35]

Although the sequential chemical oxidation followed by biological process may be the most suitable combination in OMW treatment, other options like biological/chemical or biological/chemical/biological have been investigated. The

existing biodegradable fractions in OMW make such alternatives a feasible option. Sugars and proteins could be easily removed when subjected to a biological process, thus would not compete with other contaminants in the oxidation step. Accordingly, Benitez *et al.*<sup>[22]</sup> compared ozonation followed by aerobic process, aerobic followed by ozonation, ozonation alone and aerobic process alone. Both combined processes resulted in higher COD removal than either single stage treatment under similar operating conditions. In particular, aerobic pre-treatment followed by ozonation resulted in an overall COD removal of 82%, and the ozone oxidation of the biologically pre-treated OMW decreased COD of 30%, which was significantly greater than that (20%) achieved in the ozonation process alone, thus suggesting that aerobic pre-treatment can enhance the subsequent ozone oxidation by removing most of the biodegradable organic matter. Lafi *et al.*<sup>[34]</sup> also studied the combination of processes using ozone oxidation (with or without UV radiation) and aerobic biodegradation. In this study it was verified a lower COD reduction to ozonation step (21.5% and 28.9% to O<sub>3</sub> and UV/O<sub>3</sub>, respectively). Combination process reveal a higher COD reduction, however, contrary to Benitez *et al.*<sup>[22]</sup>, the sequence UV/O<sub>3</sub> followed by biodegradation reached higher COD removal (91%), while biodegradation followed by UV/O<sub>3</sub> reached 82% of COD removal. This occurrence may be due to the fact that ozone oxidizes the phenolic compounds which are inhibitors of aerobic microorganisms.

In this way, other AOPs can be used as pre-treatment in order to remove aromatic compounds, toxic to many microorganisms and after subject to biological process. Lucas *et al.*<sup>[30]</sup> first evaluated COD degradation level to the biological process individuality. Since it was not possible to achieve the desired COD reduction, it was evaluated the Fenton reagent and its combination with biological treatment. Coupling treatments leads to a greater decrease in COD and phenolic compounds (80.7% and 93.7%, respectively). This treatment had a high retention time since it was required a reactor inoculation to biomass acclimatization and biological experiments were carried out during 7 days.

The efficiency of two treatments involving fungi and photo-Fenton oxidation, sequentially applied to OMW was investigated<sup>[25]</sup>. Biological treatment by fungi (*Pleurotus sajor caju*) of diluted OMW samples decreased acute toxicity to *Daphnia longispina* as well as COD (72%) and total phenols (91%); but no significant colour

reduction was observed. After biological treatment, photo-Fenton oxidation decreased colour but toxicity remained relatively high. On the opposite, when OMW was pre-treated by photo-Fenton, the biological treatment with fungi did not promote substantial benefits on reducing COD, total phenolic content and toxicity.

Nieto *et al.*<sup>[33]</sup> and Hodaifa *et al.*<sup>[12]</sup> used only Fenton reagent with  $\text{FeCl}_3$  as catalyst to the reaction. Both studies achieved COD reduction above 90% with similar ratio of  $[\text{FeCl}_3]/[\text{H}_2\text{O}_2]$ . Hodaifa *et al.*<sup>[12]</sup> range the optimum ratio between 0.026 - 0.058 w/w, while Nieto *et al.*<sup>[33]</sup> present the optimum ratio value in 0.04.

Studies with combination of two chemical processes were also tested in some works, particularly using coagulation-flocculation prior to different Fenton process. Michael *et al.*<sup>[29]</sup> achieved a high COD removal (87%), while the polyphenolic fraction was eliminated using a solar photo-Fenton; Papaphilippou *et al.*<sup>[28]</sup> used a UV lamp photo-Fenton and reduced COD and TP by 73% and 87%, respectively; Kiril Mert *et al.*<sup>[35]</sup> obtained COD reduction of 93% and 95% to TP with Fenton reagent. This combination of processes may constitute a potential solution for purification of OMW. Coagulation-flocculation successfully removed the suspended solids and the colour of OMW becoming essential to photo-Fenton processes.

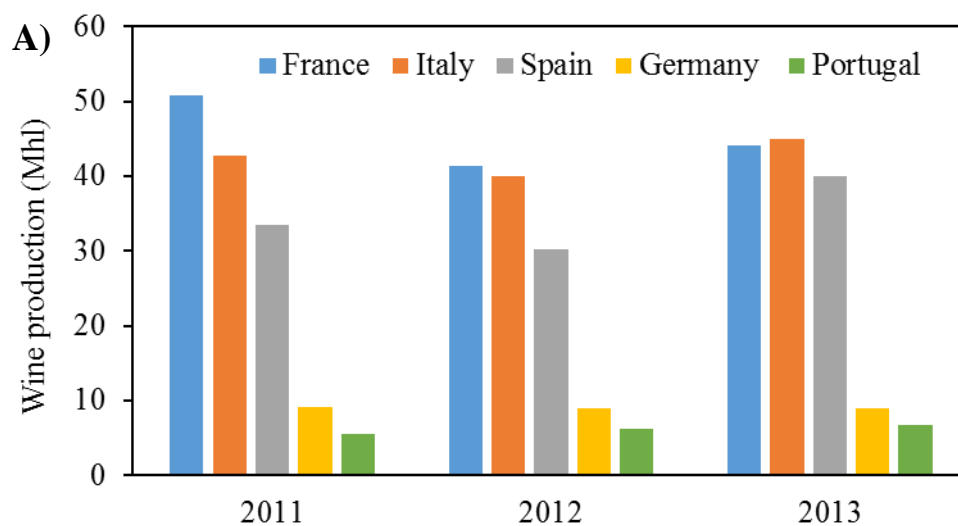
### **1.3. Winery industry**

The worldwide wine production in last years has exceeded 240 MhL with Europe being the main producer. France was the leading wine producer with an annual average of 45.4 MhL of wine produced between 2011 and 2013, followed by Italy and Spain.

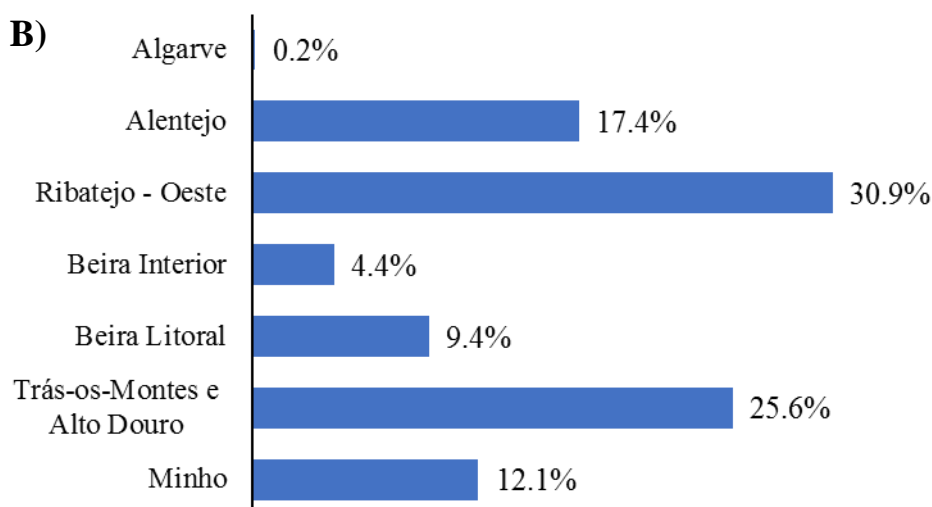


**Figure 1.5** - Douro vineyard.

Portugal is included in this list of producers (Figure 1.5) as can be observed in Figure 1.6A. Production is distributed along the Continent (Figure 1.6 B) with major emphasis in Ribatejo-Oeste and Trás-os-Montes e Alto Douro which represent 30.9% and 25.6% of total wine production in country, respectively.







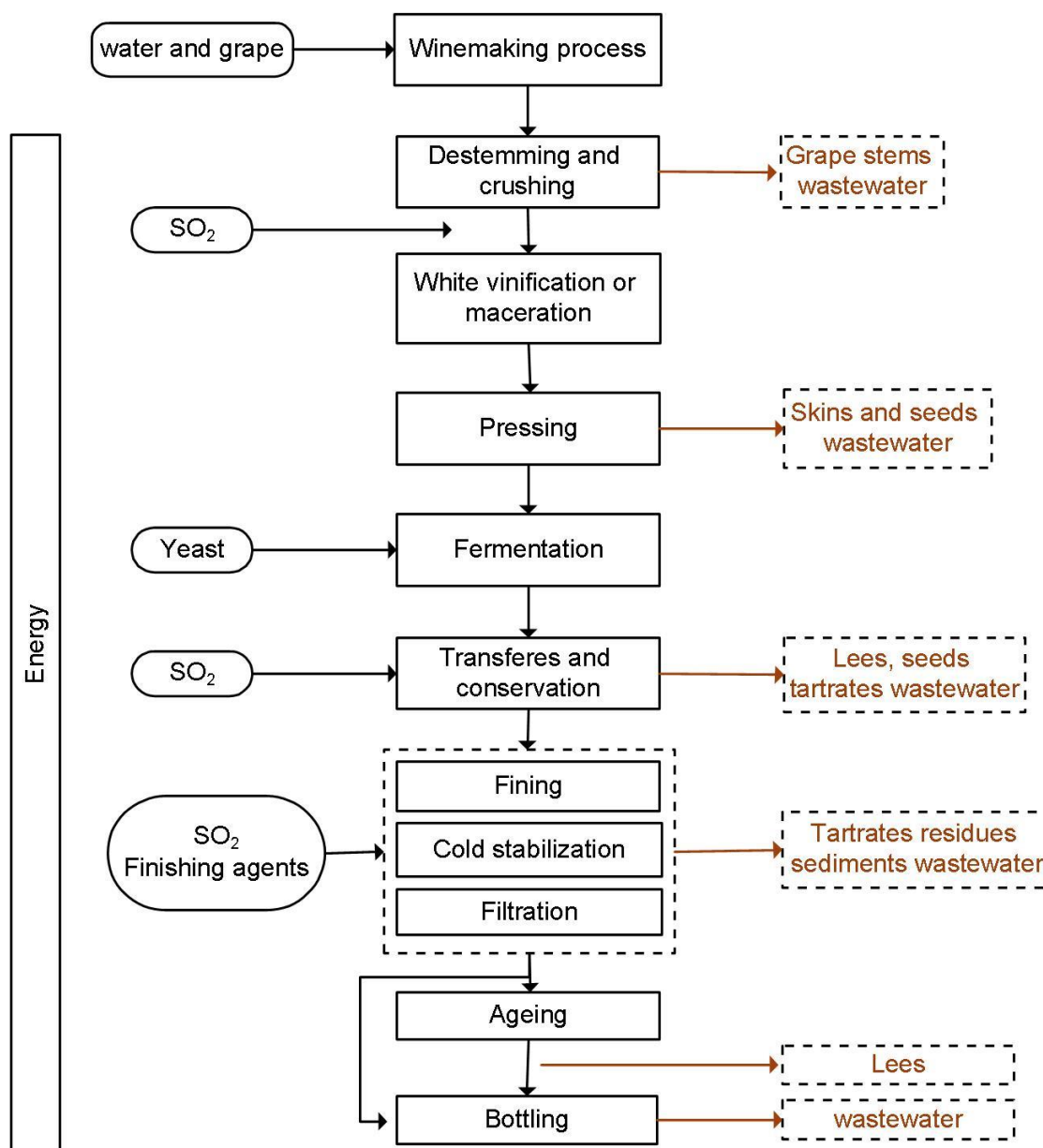
**Figure 1.6 - (A) Wine European top production in 2011-2013<sup>[36]</sup> (B) and distribution in Portugal regions 2011-2013<sup>[6]</sup>.**

The higher the wine production the greater the amount of wastewater generated, which have to be properly treated before disposal. In order to understand the characteristics of winery wastewater a short description of the winemaking process is given in the following subsection.

### ***1.3.1. Process of wine production***

Winemaking procedure (Figure 1.7) includes several and different steps as well as crushing (to break grape) and destemming (to take off stems from grapes). Two vinification processes are typically used: (i) white vinification, where solids are take-off, and (ii) red vinification, where solids are not removed. After vinification, other processes follow: pressing, fermentation, transfers, fining, cold stabilization, filtration, ageing and bottling, thus obtaining the desired final product.

During this process large amounts of water are used at different phases of production and washing. The unwanted water and residues also coming from those steps are obtained in parallel to wine and represent the by-products line. This industrial sector produces large volumes of wastewaters, between 1.3 and 2.5 L/L of wine depending on several features<sup>[37]</sup>.



**Figure 1.7** - Winemaking process and mass balance (from Lofrano *et al.*<sup>[38]</sup>).

### 1.3.2. Winery wastewater

Agro industrial winery activities have a seasonal work. For that reason, the wastewater production occurs mainly during harvesting and at the time of wine making. The wastewaters can be treated as they are produced, or they can be stored (generally after good sieving) and treated within several months<sup>[39]</sup>.

The amount and characteristics of WWs strongly depends on the winemaking stage (e.g., vintage, racking, bottling) and technology (e.g., production of red, white and

special wines). WWs originate from various unit operations such as washing of the presses used to crush the grapes, rinsing of fermentation tanks, barrels, bottles and other equipment's or surfaces. The majority of the pollutant load can be attributed from the washing phases and from losses of must, decanting and wine. These losses are due to transference of generated product from each phase to another. In addition, there are sporadic peaks in organic load related with maximum pressing activity and refiltration of the newly fermented wine.

The ranges of some parameters for physical, chemical and biological characterization of WWs are shown in Table 1.3.

**Table 1.3 - Winery wastewaters main characteristics.**

<b>Parameter</b>	<b>Range</b>	<b>References</b>
pH	3.5 – 4.95	[40-45]
BOD <sub>5</sub> (mg/L)	6400 – 18 000	[40,42,44]
COD (mg/L)	800 – 23 000	[40-46]
TSS (mg/L)	200 – 1700	[40-42]; [44, 46]
Total phenols (mg/L)	10 – 700	[40, 41, 43]

WWs are characterized by low pH (also if in some steps of winemaking process such as bottling step, pH increases) and high loadings of organic matter (BOD<sub>5</sub> and COD).

The typical components are suspended solids, polyphenols compared to urban wastewater (but low compared to OMWs), organic acids, alcohols, sugars (maltose, glucose, fructose), aldehydes, soaps and detergents, nitrogen compounds and inorganics, including some traces of heavy metals<sup>[47]</sup>.

The wastewater quality within a particular winery has even been shown to vary on an hourly basis. Given the dynamic nature of wine production, this is not entirely unexpected. The variability arises from the differences between winemaking processes and techniques, amounts of water used, and overall winery design. All these factors highlight the complex nature of WWs, and therefore the challenge it presents in terms of its characterization, management and treatment<sup>[48]</sup>. The purposes of wastewater

management are to be protective of the receiving environment and enhance water reuse opportunities.

### ***1.3.3. Winery wastewater treatment by AOPs***

An extensive variety of wastewater treatment expertise is available on the market, aiming the reduction of organic/inorganic load and suspended solids<sup>[49]</sup>. Among the several biological and chemical processes applied to winery wastewaters it is possible highlight the following: anaerobic digestion, aerated lagoons, activated-sludge units, adsorption on activated carbon, coagulation/flocculation and Advanced Oxidation Processes (AOPs)<sup>[39]</sup>.

In scientific literature several review papers are available, stating the concern of the production and management of winery wastewater. The review of Mosse *et al.*<sup>[48]</sup> presents a summary of different treatment options (biological and physico-chemical), and describes the advantages and disadvantages of their use within the Australian wine industry. They contended that a knowledge and understanding of the composition of the wastewater and the effect of the constituents on the natural environment will be essential, in terms of management, treatment and reuse options. Ioannou *et al.*<sup>[49]</sup> present the state-of-the-art of the processes currently applied for the treatment of winery wastewater and discussed the advantages and disadvantages, as well as the main factors affecting the efficiency of winery wastewater treatment. From the conclusions we can highlight that biological treatment is particularly appropriate, since the major part of its organic load is readily biodegradable and advanced chemical oxidation processes hold good promises, with homogeneous solar Fenton oxidation and ozonation, which appears to be a very effective and promising processes.

In this way, in Table 1.4 are presented several studies about application of AOPs to WWs treatment to be discussed. Several works are now available in the scientific literature. Most of these deal with ozone based AOPs<sup>[43,50,51]</sup> and photo-Fenton process<sup>[52-54]</sup>, but other oxidation processes have been investigated (Table 1.4).

COD removal by ozonation of WWs was found to be higher at alkaline pH than acidic pH; the opposite was found out for polyphenols removal which was higher at acidic pH<sup>[43, 55]</sup>. Taking into account that molecular ozone prevails at acidic pH and

radical's formation is higher at alkaline pH, the selectivity of molecular ozone towards polyphenols is higher than the selectivity of the radicals for polyphenols. Accordingly, ozonation should be operated at natural (acidic) pH rather than alkaline pH if the purpose of the treatment is the removal of the phenolic compounds from WWs, in order to reduce toxicity and improve biodegradability before biological treatment. Benitez *et al.*<sup>[50]</sup> found out the COD removal by activated sludge process (48 h) can be improved by ozonation pre-treatment (6 h) increasing from 27.7% to 39.3%. The efficiency of ozonation treatment strongly improved after simultaneous application of UV radiation and H<sub>2</sub>O<sub>2</sub>.

COD removal increased from 9.1% (O<sub>3</sub>) to 58.4% (O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>) after 6 h treatment time. Moreover, the ozonation process in combination with UV-C radiation decreased the initial COD by 21% (ozonation alone 12%) after 180 min of reaction, and a further increase in COD removal (35%) was achieved by adding H<sub>2</sub>O<sub>2</sub> (COD/H<sub>2</sub>O<sub>2</sub> (w/w) = 4)<sup>[51]</sup>.

Higher efficiencies in shorter contact times can be achieved in WWs oxidation by Fenton reaction based treatment compared to ozonation treatment. Beltran de Heredia *et al.*<sup>[56]</sup> observed high removal (>90%) of aromatic and total polyphenolic compounds from biologically treated wastewater in the early 5 min of Fenton oxidation. When photo-Fenton process was investigated on synthetic wine and synthetic grape juice wastewaters an high efficiency in TOC removal was observed (95%) in short reaction times (5-30 min); moreover, the influence of the initial organic matter concentration and the reaction time were almost negligible for the confidence level selected (90%) compared to Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> dosages<sup>[52]</sup>. The same group of investigators observed a decreased efficiency (50% TOC removal) when heterogeneous photo-Fenton process was applied<sup>[53]</sup>.

Application of photo-Fenton process using sunlight as source of irradiation were also investigated to WWs treatment<sup>[57,58]</sup>. Due to the differences between effluents, which represent optimal [Fe]/[H<sub>2</sub>O<sub>2</sub>] ratio to each one, studies cannot be compared. However, solar photo-Fenton process proved to be highly efficient in the mineralization and detoxification of real winery wastewater. Velegraki and Mantzavinos<sup>[57]</sup> achieved 80% of DOC and TOC removals and concluded that increasing iron dosage enhanced the reaction rate due to higher hydroxyl radical production. Souza *et al.*<sup>[58]</sup> reached a

COD value lower than 150 mg O<sub>2</sub>/L, therefore in agreement with Portuguese legislation for discharge into water bodies (Decree-Law n° 236/98).

Ioannou and Fatta-Kassinos<sup>[59]</sup> also investigated solar photo-Fenton efficiency WWs treatment. In this case effluents were previously treated by a membrane bioreactor (MBR). After MBR treatment, effluent presented a yellowish colour which meant the presence of biodegradable resistant compounds. However, solar photo-Fenton oxidation was able to effectively oxidize these compounds and combined treatment reached a COD removal of approximately 70%; while the major part of COD (58%) was removed in the first 30 min of solar treatment.

A quite poor efficiency in terms of TOC removal (roughly 35% after 60 min.) was reached also after prolonged (6 h) reaction time, when TiO<sub>2</sub> photocatalysis was investigated<sup>[60]</sup>. In particular photolysis process was found to be more efficient than photocatalysis process and TOC removal efficiency decreased as photocatalyst loading was increased. This result is not unusual in water and wastewater treatment by heterogeneous photocatalysis because, generally photocatalytic efficiency increases as photocatalyst loading increases up to reach an optimum value<sup>[61]</sup>; above this threshold, the solution opacity is so high that light penetration is significantly reduced. When TiO<sub>2</sub> adsorption, ozonation, photolytic ozonation (UV/O<sub>3</sub>), photocatalysis (UV/TiO<sub>2</sub>), and photocatalytic ozonation (UV/TiO<sub>2</sub>/O<sub>3</sub>) were comparatively investigated photocatalytic ozonation resulted in 80% of COD removal<sup>[62]</sup>.

**Table 1.4 - Application of AOPs to WWs treatment.**

Wastewater	Treatment	Remarks	Reference
Vinasses from industrial distillery located in Villafranca de los Barros, Extremadura (south-west of Spain) (pH 3.7–4.1; COD 24.5 g/L; TS 21.51 g/L; TSS 12.51 g/L; BOD <sub>5</sub> 11.15 g/L)	O <sub>3</sub> , O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> and biological treatment by activated sludge system. Vinasse samples were centrifuged and filtered before treatment	The organic matter removal by O <sub>3</sub> alone (9%, 6 h) was improved by the simultaneous presence of UV and H <sub>2</sub> O <sub>2</sub> (58%, 6 h). O <sub>3</sub> pre-treatment improved (from 28 to 39%) activated sludge process efficiency	[50]
Synthetic wine (WV) and synthetic grape juice (WG) wastewaters were prepared by diluting commercial red wine or commercial grape juice in Milli-Q water (COD	Photo-Fenton process with solar simulator	Up to 95% TOC removal was achieved. The influence of the initial organic matter concentration and the reaction time were almost negligible for the confidence level selected	[52]

5000 -10 000 mg/L; TOC 1500-3000 mg C/L)		(90%) compared to Fe <sup>3+</sup> and H <sub>2</sub> O <sub>2</sub> dosages	
Synthetic wine (WV) and synthetic grape juice (WG wastewaters were prepared by diluting commercial red wine or commercial grape juice in Milli-Q water (COD 5000-10 000 mg/L; TOC 1500-3000 mg C/L)	Heterogeneous photo-Fenton (natural clay as iron source) with solar simulator	Up to 50% TOC removal was achieved. The degree of organic matter removal from WG did not depend on the particle size of the clay. For WV the degree of organic matter removal depends neither on the concentration of the clay nor the initial concentration of organic matter	[53]
WWs from a wine industry located in Almedralejo, province of Badajoz, southwestern Spain (COD 9250 mg/L; BOD 7100 mg/L; pH 7.1; TP 268 mg gallic acid/L)	TiO <sub>2</sub> adsorption, O <sub>3</sub> , UV/O <sub>3</sub> , UV/TiO <sub>2</sub> , and UV/TiO <sub>2</sub> /O <sub>3</sub> . WWs samples were diluted with tap water before treatment (COD 800 ±100 mg/L)	Contrary to the use of ozone alone, UV/O <sub>3</sub> /TiO <sub>2</sub> process led to the total mineralization of the COD removed	[62]
WWs from a commercial wine company located in the Swan Valley, Western Australia	UV and UV/TiO <sub>2</sub> (0.5, 1.0 and 3.0 g TiO <sub>2</sub> /L)	The best COD and TOC removals were achieved with UV alone probably because of the TiO <sub>2</sub> shading effect on the light (UV/TiO <sub>2</sub> efficiency increased as catalyst loading decreased)	[60]
WWs from a wine production factory located in the Douro region, north of Portugal (pH 4; COD 4650 mg/L; UV <sub>254</sub> 1.562 L/cm; TC 1255 mg/L; TP 103 mg acid gallic/L)	A pilot-scale, bubble column ozonation reactor	The higher removal rates (COD and UV <sub>254</sub> ) were observed at alkaline pH as a result of higher formation of radicals	[43]
WWs from a wine production factory located in the district of Paphos, Cyprus (pH 10.6 <sup>*</sup> ; COD 1625 mg/l; TS 15 086 mg/L; TSS 1259 g/L; BOD <sub>5</sub> 3250 mg/L)	Photo-Fenton process as post- treatment of physical-biological treatment.	COD or BOD removal in photo Fenton process was as high as 80% after 4 h of reaction. The combined biological + photo- Fenton oxidation resulted in 95% COD removal	[54]
WWs as for Lucas <i>et al.</i> 2009	Ozone-based AOPs (O <sub>3</sub> , O <sub>3</sub> /UV and O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> )	At the natural pH (4) process efficiency was in the following order: O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> > O <sub>3</sub> /UV > O <sub>3</sub> > UV-C. COD and TOC removal increased as pH was increased to 7 and 10). The O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> may be the most economical process (1.31	[51]

\* high pH is due to washing of various items of equipment with KOH.

		Euro/m <sup>3</sup> /g of TOC mineralised under optimised conditions)	
Winery wastewater at vintage period in October 2012 (pH 6; COD 5353 mg/L; TS 5040; BOD <sub>5</sub> 424 mg/L; TP 20 mg/L)	Reverse osmosis (RO) and oxidation of the concentrate by solar photo-Fenton	The removal of COD by the RO process reached 97% total suspended solids 94%, and total solids 96%.  Treatment of the concentrate (COD 10290 mg/L) by solar photo-Fenton oxidation achieved a COD reduction of 75%	[63]
The wastewater was collected from the winery near Zagreb, Croatia, during the vintage period (pH 3.74; COD 10 240 mg/L; SS 2860 mg/L; turbidity 3190 NTU)	Electrochemical methods (EC) and ultrasound (US) combined with AOPs (O <sub>3</sub> + UV + H <sub>2</sub> O <sub>2</sub> )	The combined treatment achieved 77 % of COD reduction and over 99% on colour, turbidity, suspended solids and phosphates	[64]
Winery wastewater from a Spain wine producer located in Castilla-La Mancha (pH 12.4; TS 12.06 g/L; TOC 2674 mg/L)	Pre-treatment using coagulation-flocculation or precipitation + ferrioxalate induced solar photo-Fenton process	Under optimal conditions, 61% TOC removal (H <sub>2</sub> O <sub>2</sub> 260 mg/L; H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 80 mg/L; pH 3.5)	[65]
Winery wastewater that had already been treated in an MBR operating at a winery located in Limassol, Cyprus (pH 8.2; TS 2 g/L; COD 120 mg/L; DOC 30 mg/L)	Solar photo-Fenton oxidation process (hv/Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> )	COD, DOC and colour removal of 70 ± 3.3%, 53 ± 3.7% and 75 ± 2.2%, respectively (optimal conditions: 120 min. of reaction time; Fe <sup>2+</sup> 3 mg/L; H <sub>2</sub> O <sub>2</sub> 250 mg/L;	[59]
WW from red wine company located in the northeast of Portugal after the vintage season (pH 4.1; COD 2958 mg/L; DOC 882 mg/L; TP (as gallic acid) 12 mg/L)	Solar photo-Fenton	COD removal of 95% (optimal conditions: pH 2.8; 55 mg Fe <sup>2+</sup> /L; 338 mM H <sub>2</sub> O <sub>2</sub> consumption and UV dose of 100 kJ <sub>UV</sub> /L)	[58]
WW from local winery in Chania, W. Crete, Greece, after vinification process (pH 5.5-6.5; COD 1200 mg/L; DOC 435 mg/L)	Solar photo-Fenton	COD removal of 80% after 240 min irradiation ( 2000 mg/L H <sub>2</sub> O <sub>2</sub> consumption; 25 mg/L Fe <sup>2+</sup> ) and after 340 min irradiation (1270 mg/L H <sub>2</sub> O <sub>2</sub> consumption; 5 mg/L Fe <sup>2+</sup> )	[57]
Samples from a wine factory located in Badajoz, Spain (pH 3.8; COD 35 g/L; TOC 11.3 g/L)	Wet oxidation processes	Catalytic wet peroxide oxidation achieved 80% COD and TOC removals (optimal conditions: 4 h reaction time, graphite at 5 g/L; pH 3.8; 125°C)	[37]

Dominguez *et al.*<sup>[37]</sup> investigated the treatment of high-strength real winery wastewater by wet oxidation processes. From the different oxidation processes tested,



results that Catalytic Wet Air Peroxide Oxidation (CWAPO) was the unique capable to achieve an effective reduction of the organic load. Using graphite as catalyst and  $\text{H}_2\text{O}_2$  as oxidant, under operational conditions were achieved 80% COD and TOC removals.

Orescanin *et al.*<sup>[64]</sup> work proposed a new development system to winery wastewater treatment based on application of electrochemical methods simultaneously with ultrasound and a subsequent with  $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ . In the end of the first treatment step, highest removals were verified to colour, turbidity, suspended solids (98%), ammonia (72%), and phosphates and iron (93%). As sulphates and COD values were still significantly higher than allowed, the subsequent treatment improved COD and sulphates removals, achieving 76% and 62%, respectively. From most of others parameters, removals did not improve when compared to the previous step with the exception for ammonia, which achieved an additional 25.7% of reduction.

#### **1.4. Pulp and paper mill industry**

The European economies are largely dependent on the pulp and paper (P&P) industry. In Portugal these industries represent over 4% of the gross domestic product (GDP) and 5% of the active employees. The P&P sector is one of the energy intensive sectors within the Portuguese, Spanish, Canadian, Swedish, Brazilian and other economies and is therefore of particular interest in the context of both local and global environmental discussions<sup>[66]</sup>.

Pulp and paper industry is considered a large user and producer of biomass based energy and materials<sup>[67]</sup>, as well as the major source of industrial pollution worldwide. In this industries two types of facilities can be evidenced: (i) pulp and paper mills process raw wood fibre or recycled fibre to make pulp and/or paper; and (ii) facilities that use these primary materials to manufacture more specialised products such as paperboard boxes, writing paper and sanitary paper<sup>[68]</sup>.

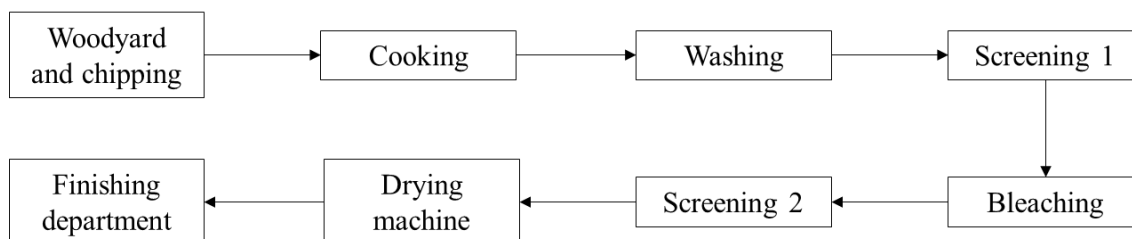
The water used in manufacturing processes has been decreasing and in modern paper mills its consumption varies between 4 and 100  $\text{m}^3/\text{t}$ <sup>[69]</sup> which has resulted in the progressive accumulation of pollutants in water that must be removed in order to accomplish standards required for water to be reused or discharged. This consumption

mainly depends on the water circuit optimization level that has been achieved within each paper mill.

#### **1.4.1. Pulp & paper mill process**

Virgin fibres (derived from wood pulp) and recycled fibres (derived from recovered paper) are the main raw materials used during the production of paper. These raw materials can be manufactured on-site, obtained from other mills by purchase or intra-company transfer<sup>[68]</sup>. Its composition (such as filler and coatings) used in the paper-making process also has a major effect on production costs, product quality and the overall environmental impact of the process.

Each paper mill uses a different manufacture process, however it is possible to present a simplified flow diagram of an integrated mill including the main steps, such as chemical pulping, bleaching, and paper production (Figure 1.8). Pulp stock preparation and the final product manufacture are the only common processes to all mills.



**Figure 1.8** - Flow diagram of an integrated mill. Adapted from Tunay *et al.*<sup>[68]</sup>.

#### **1.4.2. Pulp and paper mill wastewater characterization**

All pulp and papermaking processes require the use of water. However, water use, wastewater sources and wastewater characteristics for any mill are dependent upon the combination of raw materials, processes used and products manufactured. Wood preparation, pulping, pulp washing, screening, bleaching, papermaking and coating operations are the major sources of contamination in different stages<sup>[70]</sup>.

The pulp and paper industry is now facing challenges to comply with stringent environmental regulations, mainly in prevention of water bodies pollution, due to the

considerable amounts of wastewaters produced for each metric ton of paper produced<sup>[71]</sup>. Such effluents have the potential to adversely affect the receiving aquatic environment<sup>[72]</sup>.

The characteristics of wastewater to be treated depends on the type of process, the type of wood, the amount of water that the mill is able to circulate, the technology used and the selected management practices<sup>[68]</sup>.

Despite the differences of each generated wastewater, all generally contain large amount of organic materials with high values of chemical oxygen demand (COD), chlorinated compounds, fatty acids, total suspended solids (TSS), tannins and lignin which could potentially cause severe pollution problems<sup>[70,71]</sup>.

Table 1.5 presents the main characteristics of the generated pulp and paper mill wastewater reported in different studies. As it can be observed the values have a high range which means that each industry generates a different effluent due the reasons already stated.

**Table 1.5** - Pulp and paper mill wastewater main characteristics.

Parameter	Range	References
pH	3.9–8.2	[72 – 75]
BOD <sub>5</sub> (mg/L)	480–1353	[72 – 75]
COD (mg/L)	1314–4100	[72 – 75]
TSS (mg/L)	83–605	[72 – 75]
Sulphates (mg/L)	238–596	[72]
Total polyphenols (mg/L)	198–217	[74]

In addition, chemical pulping processes generate low biodegradable organics in the effluent organic matter, as well as low biodegradable sulfonic compounds as by-products due the sulfite used in some processes<sup>[76]</sup>. Pulp mills wastewater are also characterized by a strong smell due to the presence of reduced sulphur compounds such as hydrogen sulphide, dimethyl sulphides<sup>[77,78]</sup>.

Pollution from these industries can be minimised by internal prevent techniques to water reduction and pollutant releases. However, waste generation and wastewater

cannot be totally controlled. Thus, the technologies to treat wastewater are essential for accomplishing the defined legislation for its discharge.

#### 1.4.3. Pulp mill treatment by AOPs

An initial wastewater characterization is fundamental to choose which methodology will be adopted to achieve an efficient treatment. Thus, many treatments are nearly universal across the industries. The application of advanced oxidation processes represents one of this, and have been largely used in pulp mill wastewater treatment mainly to remove the toxic pollutants. If applied as pre-treatment, AOPs aim the removal of toxic and bio-recalcitrant organic compounds in order to reduce the toxic effects in subsequent biological treatments and improve biodegradability. In post-treatment, AOPs remove the residual organic compounds and highly resistant colour.

**Table 1.6** - Pulp and paper mill wastewater treatment by AOPs.

Wastewater	Treatment	Remarks	Reference
Wastewater from company of paper pulp preparation in Columbia (pH 7.7; TOC 2129 mg/L; chlorophenol 15,3 mg/L)	Biological and photocatalytic coupled system	After 10 days of biological treatment coupled with ZnO and TiO <sub>2</sub> systems were obtained degradation rates over 90%	[79]
Pulp mill wastewater (PMW) from cellulose company in Portugal (pH 7.9; DOC 348 mg/L; COD 899 mg/L; TP 217 mg/L)	Solar photo-Fenton	With 5 mg Fe/L reaches 90% of DOC mineralisation with 31 kJ/L of UV energy and 50 mM of H <sub>2</sub> O <sub>2</sub> ; with 20 and 50 mg Fe/L can reach the same DOC degradation (90%), however, consuming less H <sub>2</sub> O <sub>2</sub> and time.	[80]
Pulp mill wastewater from pulp and paper industry located in Aliaga/Izmir, Turkey (pH 7.12 – 8.50; COD 608 – 1500 mg/L; TOC 206.2 – 303.2 mg/L)	AOP (TiO <sub>2</sub> /Fe(III)/solar UV)	With 188 mg/L TiO <sub>2</sub> and 0.5 mM Fe (III) achieved 78% and 64% removal of colour and TOC, respectively.	[73]
Wastewater used was obtained from Egyptian board paper mill industrial plant (pH 6.5; COD 2075 mg/L; TSS 1165 mg/L)	AOP (TiO <sub>2</sub> /solar UV)	At optimum dose of 0.75 g/L TiO <sub>2</sub> and pH value of 6.5, 70.5% COD removal and 80% of TSS was achieved within 180 min. solar irradiation time.	[81]
Wastewater provided by a paper pulp mill located in the centre of Portugal (pH	Sequential biological (using yeasts) process and	Using <i>Cryptococcus podzolicus</i> (AGG 691) with 32 h of incubation achieved	[74]

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7.7; COD 1802 mg/L; TSS 443 mg/L; DOC 820 mg/L)	solar photo-Fenton	68% of COD removal; solar photo-Fenton under best conditions (with 19 hJ/L of energy, 41 mM of H <sub>2</sub> O <sub>2</sub> consumed and [Fe <sup>2+</sup> ]=10 mg/L) achieved 90% DOC mineralization
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Botía *et al.*<sup>[79]</sup> evaluated the influence of a biological – photocatalytic coupled system in the removal of TOC, chlorophenols and toxicity from a pulp mill effluent. Biological process was carried out with 180 foam cubes colonized with *T. pubescens* (pre immobilized during 8 days at 30 °C) and 1.7 L of effluent along 10 days. In photocatalytic treatment, TiO<sub>2</sub> and ZnO were compared on two substrates: aluminium foil and *L. cylindrical*, using electrodeposition and impregnation methods, respectively. Electrodeposition consisted in submerging the foil and the electrode in the electrolyte solution contained in a glass flask, and applying a voltage whereas impregnation consisted in placing the support and the solution containing the catalytic species in contact for a period of time (immobilization in loofah).

Biological treatment and photocatalytic were performed, in a first phase, individually, and achieved 87% and 28% of TOC removal, respectively. In photocatalytic treatment this removal rate is observed for the ZnO foil system. Coupled system was tested in order to improve previous removal efficiencies. Thus, using coupled treatment obtained degradation rates were over 90% for two different catalysts. However, those catalysts supported on aluminium foils complete the process after 30 min of treatment, while catalysts supported on loofah needed 120 min.

Lucas *et al.*<sup>[80]</sup> presented a tertiary treatment solution to a biological treated pulp mill wastewater in order to fulfil with the legal restrictions on wastewater discharge into natural waters. To obtain an effectiveness solution for this problem, some Advanced Oxidation Processes were performed by means of Fenton, photo-Fenton and photolysis trials. After optimization essays experiments with 20 and 50 mg/L of iron revealed that solar photo-Fenton can reach the same DOC degradation (90%) consuming less H<sub>2</sub>O<sub>2</sub> and time.

Baycan Parilti and Akten<sup>[73]</sup> and Ghaly *et al.*<sup>[81]</sup> studied the solar degradation of effluents of pulp mill industry using synthesized nano TiO<sub>2</sub> as catalyst.

The results of both reports showed that prepared  $\text{TiO}_2$  in the presence of solar light can be employed as an effective photocatalyst for the removal of chemical oxygen demand. At pH 6.5, using 0.75 g/L of  $\text{TiO}_2$  within 180 min irradiation time achieved 70.5% COD removal and 80% suspended solids reduction. It was found that addition of  $\text{H}_2\text{O}_2$  increased the solar photocatalytic oxidation efficiency<sup>[81]</sup>. Experimental assays combining  $\text{TiO}_2$  and Fe (III) indicated that are also important parameters for colour and TOC removal. Thus, using 188 mg/L  $\text{TiO}_2$  concentration and 0.5 mM Fe (III) addition over 78% colour and 65% TOC removal from the pulp mill effluent was achieved.

Fernandes *et al.*<sup>[74]</sup> used a combination of processes to treat landfill leachate wastewater. In this report some yeasts were inoculated and used in a biological pre-treatment followed by solar photo-Fenton. *Cryptococcus podzolicus* proved to be very efficient achieving the best COD removals from 8 incubated yeasts (68%). A subsequent photo-Fenton with 19 hJ/L of energy, 41 mM of  $\text{H}_2\text{O}_2$  consumed and  $[\text{Fe}^{2+}] = 10$  mg/L) achieved 90% DOC mineralization and met the Portuguese legal requirements for discharge into natural waters.

## 1.5. Other industries and municipal landfill leachates

### 1.5.1. Varied/additional agro-industrial industries

The industrial wastewater characteristics are much more diverse than domestic wastewater, which is usually qualitatively and quantitatively similar in its composition. Moreover, industry produces large quantities of highly polluted wastewater containing toxic substances, organic and inorganic compounds such as: heavy metals, pesticides, phenols and derivatives<sup>[82]</sup>. In the industrial sector are parts of the agro food industries which lack a different approach. This specific sector, such as meat, poultry, dairy or beverages industries requires great amounts of water, since it is used throughout most of plant operations. During these operations (Figure 1.9) a consequent wastewater is generated with large total load of organic pollutants, suspended solids and chemicals used for cleaning and sanitizing processing equipment<sup>[83, 84]</sup>.



**Figure 1.9** - Fruit selection washing and selection stage in agroindustry.

Unregulated disposal of these effluents into the environment can lead to the contamination of surface and groundwater, arising with this ecosystem imbalances and human health risks<sup>[85]</sup>. The wastewater treatment in an on-site installation could present difficult challenges since increasing food production will increase the volume of sewage and the cost of disposal. In order to overcome these issues an efficient alternative should be adopted such as coagulation/flocculation and Advanced oxidation processes (AOPs).

These chemical treatments have been used to reduce the organic load or toxicity of wastewaters (and suspended solids) from different industries. AOPs are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential for complete mineralization of pollutants<sup>[86]</sup>. Table 1.7 presents some existing studies from different agro industrial wastewater treatments using chemical treatments or in combination with other.

Amuda and Amoo<sup>[87]</sup> focus his study on the efficiency of coagulation/flocculation process for beverage industrial wastewater with respect to removal of COD, TP and TSS using ferric chloride and non-ionic polyacrylamide. After exhaustive analysis, coagulant dose, polyelectrolyte dose, pH of solution and addition of polyelectrolyte as coagulant aid found to be important parameters for effective treatment of beverage industrial wastewater. The addition of 25 mg/L polyelectrolyte

reduced the dose of ferric chloride from 300 to 100 mg/L during which 99, 97 and 91% of TP, TSS and COD removal were, respectively, achieved.

**Table 1.7 - Agro-industrial wastewater treatment.**

Wastewater	Treatment	Remarks	Reference
Beverage industrial wastewater – juice drink from orange, grape and guava (pH 7.2; COD 1750 mg/L; BOD <sub>5</sub> 894 mg/L; TSS 1620 mg/L)	Coagulation/ Flocculation	Under optimal conditions (pH 9; 25 mg/L polyelectrolyte and 100 mg/L ferric chloride) 91% and 97% removal of COD, and TSS, respectively, were achieved.	[87]
Coffee industry wastewater (pH 4.6 and COD 4300 mg/L)	AOPs (UV/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> UV/H <sub>2</sub> O <sub>2</sub> and UV/O <sub>3</sub> )	The UV/H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> process is capable of reducing the COD content of the wastewater by 87% in 35 min at pH 2.0 while the UV/H <sub>2</sub> O <sub>2</sub> and UV/O <sub>3</sub> reduced 84% of COD content.	[88]
Cheese whey wastewater (pH 4.0; COD 13 494 mg/L; BOD <sub>5</sub> 11 686 mg/L; TSS 3317 mg/L)	Coagulation/ Flocculation + Aerobic biodegradation	At pH 8.5 using 250 ppm of ferric chloride and ferrous sulphate and subsequent aerobic biodegradation of supernatant achieve the reduction of COD and BOD to values close to 100%.	[89]
Palm oil mill effluent (pH 4.7; COD 67 700 mg/L; TSS 30 000 mg/L)	Coagulation/ Flocculation	Using <i>C. obtusifolia</i> seed gum as coagulant in optimal operational conditions (1.0 g/L of seed gum concentration, pH 3 and 45 min settling time) achieved 93% of TSS removal and 65% of COD.	[85]
Industrial wastewater from beverage industries (pH 5.35, COD 6500 mg/L, BOD <sub>5</sub> 4400 mg/L, TOC 1987 mg/L, )	Solar photo-Fenton mediated by ferrioxalate complexes	Under selected conditions (H <sub>2</sub> O <sub>2</sub> = 460 mL/h, H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> = 2100 mL/h, [Fe]= 150 mg/L, pH = 2.79, solar power= 35.8 Wh) 96.6% of TOC was removed 125 min, respectively.	[86]

Rivas *et al.*<sup>[89]</sup> report the study of cheese whey wastewater also by coagulation/flocculation, testing three different coagulants – FeSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and FeCl<sub>3</sub>. Iron salts (FeSO<sub>4</sub> and FeCl<sub>3</sub>) were more efficient under optimal conditions: using 250 ppm of coagulant at pH 8.5, where 50 and 60% of COD and BOD removal were obtained, respectively. The sludge formed in the coagulation-flocculation process did show acceptable settling properties, which is crucial in settling tank design.

Both studies proved to be efficient in respective agro-industrial wastewaters since BOD/COD ratio was enhanced and could be advanced to biological processes.



Rivas *et al.*<sup>[89]</sup> presented the results obtained in this complementary stage achieving the reduction of COD and BOD to values close to 100%.

Shak and Wu<sup>[85]</sup> used a natural seed as a feasible alternative to conventional coagulants based on metals (aluminium sulphate) and evaluated its efficiency to treat a high strength wastewater – palm oil mill effluent. Using *C. obtusifolia* as natural coagulant achieved better reduction than aluminium sulphate. In this case 1.0 g/L of seed gum concentration, pH 3 and 45 min settling time achieved 93% of TSS removal and 65% of COD. However flocs formed after coagulation/flocculation with aluminium sulfate showed higher thermal stability compared to *C. obtusifolia* seed.

Advanced Oxidation Processes were found to be an efficient process for the removal of colour and natural organic matter in agro industrial wastewater. Zayas Pérez *et al.*<sup>[88]</sup> studied a coffee processing wastewater treatment by the combination of coagulation/flocculation process as pre-treatment and a subsequent photo oxidative process. After numerous chemical coagulation/flocculation processes the application of lime (1.0 g) and a commercial coagulant named “*T-I*” (8 mL) at pH = 4.6 gave a greater reduction in COD (about 67%). To the photo-oxidative treatments a series of experiments was carried out to test the effectiveness of the UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, or UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. In this way, UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process was the most effective in reducing the COD, colour and turbidity of coffee wastewater. This process is capable of reducing the COD content of the wastewater by 87% in 35 min at pH 2.0 using a fixed flow of ozone of 40 mg/h and 0.030% (v/v) of H<sub>2</sub>O<sub>2</sub>; whereas UV/H<sub>2</sub>O<sub>2</sub> reached a similar COD reduction (86%) but required a long irradiation time of 120 min.

On the other hand, Durán *et al.*<sup>[86]</sup> assessed the mineralization of wastewater from beverage industries during a solar photo-Fenton enhanced process mediated by ferrioxalate. After some experiments, the optimal conditions achieved – H<sub>2</sub>O<sub>2</sub> flowrate = 460 mL/h, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> flowrate = 2100 mL/h, [Fe] = 150 mg/L, pH= 2.79, medium solar power = 35.8 Wh – allowed a TOC and COD reduction of 96.6% and 99.8%, respectively, after 125 min. This study also reports the synergism between the photo-Fenton process and the ferrioxalate photochemistry.

### **1.5.2. Landfill leachate**

Landfills are designed to receive different type of waste at economical costs with less environmental effects. An improper landfill management can represent serious environmental threats through discharge of high strength polluted wastewater also known as leachate<sup>[90, 91]</sup>. Landfill leachates, resulting from the percolation of water through solid wastes, are considered a great environmental impact<sup>[92]</sup>. Its composition depends on characteristics of wastes disposed, physico-chemical conditions, volume of water percolated and landfill age<sup>[93]</sup>. As an landfill become older lower is the leachate BOD<sub>5</sub>/COD ratio, indicating low biodegradability due to the release of high molecular weight recalcitrant organic molecules<sup>[94, 95]</sup>. Thus, to choose an efficient treatment to each leachate is essential taking into account this parameter. For example, leachates from older landfill are more difficult to being treated by conventional biological processes than a beginner landfill.

Landfill leachates are being continuously studied, due the resulting threatening of surrounding soil, groundwater, and surface water; and also due to its changes over time. Leachate treatment technologies fall into two basic types – biological and physical/chemical methods. Biological processes are successfully applied to young landfill leachates, rich in organic matter and nutrients, feasible for this type of treatments<sup>[96,97]</sup>. Advanced Oxidation Processes (AOPs) have been considered an attractive means to eliminate colour, reduce the organic load and improve the biodegradability of recalcitrant contaminants of mature leachates<sup>[94,98]</sup>. Integrated systems which combine both techniques are also used, depending on treatment goals.

Due to the advantages already stated, the interest on advanced oxidation processes (AOPs) has been growing<sup>[99]</sup>. Most of them use a combination of strong oxidants (O<sub>3</sub> and/or H<sub>2</sub>O<sub>2</sub>), irradiation (ultraviolet, ultrasound) and catalysts (transition metal ions or photocatalyst).

The effectiveness of each process can be assessed by evolution of key parameters (COD, BOD<sub>5</sub>, BOD/COD, oxidant dose) summarized in Table 1.8.

**Table 1.8** - Landfill leachate chemical treatments.

Wastewater	Treatment	Remarks	Reference
Leachate from landfill site of northern Greece (pH 7.9; COD 5350 mg/L; BOD <sub>5</sub> 1050 mg/L TSS 480 mg/L)	Coagulation/ Flocculation	About 80% of COD removal using ferric chloride as coagulant (2 g/L of iron)	[100]
Leachate from landfill site in southern Taiwan (pH 8.1; COD 6500 mg/L; TOC 4000 mg/L; BOD <sub>5</sub> 500 mg/L)	Coagulation/ Flocculation + Ozone-based advanced oxidation processes	Coagulated leachate by ferric chloride (900 mg/L) followed by ozone oxidation (1.2 g/L O <sub>3</sub> ) reach 15% of TOC removal and about 90% for colour.	[101]
Leachate from landfill site (over 14 years old) located in Curitiba (Brazil) (pH 8.4; COD 5200 mg/L; TOC 1058 mg/L; BOD 720 mg/L)	AOPs (Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV and H <sub>2</sub> O <sub>2</sub> /UV)	After obtaining optimized experimental conditions in Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV process BOD <sub>5</sub> /COD improved from 0.13 to 0.37 and for the H <sub>2</sub> O <sub>2</sub> /UV system from 0.13 to 0.42. During 60 min. of treatments the TOC removal were 89.9% and 97.2, respectively.	[102]
Leachate from Asturias landfill site on the north coast of Spain (pH 8.3; COD 18350 mg/L; BOD <sub>5</sub> 10600 mg/L)	Coagulation/ Flocculation	At optimum working pH situated around 5.2 for ferric chloride (1.7 g/L) and around 7.0 for aluminium polychloride (4 g/L) were obtained 73% and 62% of COD removal; and colour and turbidity removals higher than 96%.	[103]
Leachate from municipal landfill in the north of Portugal (pH 3.5; COD 743 mg/L; TOC 284 mg/L; BOD <sub>5</sub> 10 mg/L)	Fenton process	At pH 3, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> molar ratio of 3, Fe <sup>2+</sup> dosage of 4 mmol/L, and reaction time of 40 min about 46% COD was removed and BOD <sub>5</sub> /COD ratio increased from 0.01 to 0.15.  After the application for 60 min of ozone at 5.6 g O <sub>3</sub> /h, pH 7, and 400 mg/L of hydrogen peroxide, COD removal efficiency was 72% and BOD <sub>5</sub> /COD increased from 0.01 to 0.24.	[104]
Leachate from landfill located near Tetluma (Mexican state) (pH 8.04; COD 14680 mg/l; TC 8089 mg/L; BOD <sub>5</sub> 1500 mg/L);	Coagulation/ Flocculation followed by a photo-Fenton treatment	After coagulation process with 300 mg/L of ferric chloride and using the supernatant in photo-Fenton process with a ratio [H <sub>2</sub> O <sub>2</sub> ]/[Fe <sup>2+</sup> ] of 114 56% reach 56% of COD removal and 95% for TC.	[91]

Tatsi *et al.*<sup>[100]</sup> and Castrillon *et al.*<sup>[103]</sup> studies examined the application of coagulation/flocculation process for the treatment of leachates. In the first work numerous jar-test trials were done in order to determine the best coagulant/flocculant combination, effective dosage and pH for the removal of organic matter and colour. Thus, for an iron dosage of 2 g/l (using ferric chloride), when the pH value was adjusted at 10 reached 80% of COD removal. They also established that addition of organic polyelectrolytes and mixtures of coagulants presented an antagonistic effect of pollutant removal. The second research group reported the feasibility of biological and chemical treatments in leachate treatment. In respect to chemical treatments, they showed that coagulation/flocculation reveal to be more efficient to stabilized leachates. To old landfill leachate it was possible to reduce the non-biodegradable organic matter by 73 - 62%, turbidity and colour by more than 97%. Higher COD reduction was achieved with 1.7 g/L of ferric chloride at pH 5 and lower reduction with 4.0 g/L of aluminium polychloride at pH 7. The application of same dosages to young landfill leachates only 28–35% of COD removal was observed, respectively.

Wu *et al.*<sup>[101]</sup> and Vedrenne *et al.*<sup>[91]</sup> presented a combination of chemical processes, i.e., coagulation/flocculation and advanced oxidation processes. The research group of Wu *et al.*<sup>[101]</sup> used several ozone-based advanced oxidation processes and Vedrenne *et al.*<sup>[91]</sup> tested a photo-Fenton oxidation in pre-coagulated leachate treated. The results obtained in coagulation/flocculation process and subsequently ozone based-AOPs indicate that using 900 mg/L of ferric chloride as coagulant to all tested AOPs result in a significant increase on the ratio of BOD<sub>5</sub>/COD from 0.06 to 0.5 and demonstrated to decolourize the leachate for 90% removal at the applied ozone dosage of 1.2 g/L. However, the TOC removal was limited achieving only 35% removal<sup>[101]</sup>. This suggests applying a complementary biological treatment to further pollutants reductions. In case of coagulation/flocculation process combined with photo-Fenton process, presented such high removal rates that do not require any additional treatment. For the leachate's treatment, 300 mg/L of FeCl<sub>3</sub> at pH 3 was selected as the optimal condition to photo-Fenton treatment mediated by a [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] ratio= 114, and after a total irradiation of 90 kJ/L. Under this condition was achieved 96.5% removal efficiency for TC and 63.0% for COD<sup>[91]</sup>.

The application of AOPs as a single process were also studied in the landfill leachate treatment<sup>[102, 104]</sup>. However, these adopted methodologies do not mean that high efficiency of treatment was achieved. The report of de Morais and Zamora<sup>[102]</sup> studied the AOPs in leachate treatment with the objective of improving its overall biodegradability up to a value compatible with biological treatment. In  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  process were obtained 2000 mg/L of  $\text{H}_2\text{O}_2$  and 10 mg/L of  $\text{Fe}^{2+}$  as optimal operational conditions, and in  $\text{H}_2\text{O}_2/\text{UV}$  process were obtained 3000 mg/L of  $\text{H}_2\text{O}_2$ . In both methods biodegradability was significantly improved from 0.13 to 0.37 or 0.42 (as  $\text{BOD}_5/\text{COD}$  ratio) allowing total removal of COD and colour by a conventional biological process. Based on results of Cortez *et al.*<sup>[104]</sup> a  $\text{BOD}_5/\text{COD}$  ratio of 0.4 was not achieved, which indicates the refractory nature of the landfill leachate. They suggest additional work focus on optimising the mature landfill in order to obtain a more biodegradable leachate, such as ozonation at alkaline pH or combined with hydrogen peroxide.

## 1.6. Conclusive remarks

The efficiency of AOPs in the oxidation of OMWs and WWs strongly depends on the type of treatment and wastewater characteristics. Different AOPs (including  $\text{TiO}_2$  photocatalysis) have the potential to improve OMWs biodegradability, although in most cases wastewater must be diluted before treatment. Studies involving  $\text{Fe}^{3+}$  ions in Fenton and photo-Fenton processes are being studied and reveal higher efficiencies on COD and phenols reductions.

The high OMWs polluting loading results in a really high oxidant/catalyst/energy demand thus strongly increasing operative costs; but process optimization, suitable combination with biological process and more stringent regulations on OMWs disposal may do AOPs more competitive.

The combination of AOPs and biological treatment (as pre- or post-treatment) can lead to a higher level of COD reduction than any single-stage treatment under the same operating conditions. More specifically, in the case of pulp mill wastewater, the use of AOPs as post-treatment of biological processes was found to be the most effective combination since it permits almost complete decontamination.

The physico-chemical processes (i.e., coagulation/flocculation) have been found to be effective for the pre-treatment of agro industrial wastewater and landfill leachate, and more specifically, for lowering the TSS, the turbidity, as well as a part of the organic content to levels which can facilitate further treatment by AOPs and/or other conventional biological processes.

## **1.7. Thesis organization**

This PhD thesis structure is a straight consequence from the performed work and the achieved results that permitted to write different papers published in international journals, throughout the work carried out at the Chemistry Centre of Vila Real (CQVR), School of Life and Environment Sciences (ECVA), University of Trás-os-Montes and Alto Douro (UTAD).

The main goal of this thesis was the application of several treatment schemes mainly based on Advanced Oxidation Processes (AOPs) to answer real existent needs to treat several industrial wastewaters and determine the main operational conditions that favour these effluents remediation. To attain this target, scientific knowledge is a remarkable contribution in increasing the treatments efficiency when applied to different industrial wastewaters, as well as a more detailed understanding of the limitations and benefits of new/classical technologies will greatly support the selection of the effective treatments to be applied to each specific effluent.

The thesis is structured as a compilation of the research conducted in different projects. The Chapter 1 (Introduction) considers a general introduction focused in the water problematic and presents a state-of-art of the industrial wastewaters treatment studied. The main manuscript includes six papers that are published in different international journals (Chapters 2 to 7).

In the main part of this thesis the experimental work performed for the treatment of wastewater using different strategies is presented and synthesized in Table 1.9. All studies showed high removal rate of the organic fraction, obtaining in some cases a treated effluent that can be discharged into a watercourse or be sent to an urban municipal treatment plant.

**Table 1.9** - Industrial wastewaters and treatment methods studied in this work.

Effluent	Treatment method/Remarks	Chapter
Pulp mill wastewater	Fenton reagent, solar photolysis, solar photo-Fenton using CPC (compound parabolic collector) photoreactor, respirometric tests.	2
Mature landfill leachate	Coagulation/flocculation, Fenton's treatment, solar photo-Fenton using CPC photoreactor, toxicity analyses and biodegradability evolution.	3
Olive mill wastewater	Fenton's reagent, anaerobic biological process, combination of anaerobic biological process and Fenton's reagent, discontinuous anaerobic digestion reactor.	4
Crystallized fruit effluent	UV-A LED photo-Fenton, coagulation-flocculation-decantation.	5
Winery wastewater	$\text{HSO}_5^-/\text{Fe(II)}$ /UV-A LED process, $\text{HSO}_5^-/\text{M}^{n+}$ /UV-A LED process, photo-Fenton process.	6
Concentrated fruit juice wastewater	Aerobic biological process, chemical coagulation/flocculation, combination of processes.	7

Finally, the main conclusions drawn from the present work are summarized in Chapter 8 and future research suggestions are proposed as well.

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## **2. TERTIARY TREATMENT OF PULP MILL WASTEWATER BY SOLAR PHOTO-FENTON**

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## **2. TERTIARY TREATMENT OF PULP MILL WASTEWATER BY SOLAR PHOTO-FENTON<sup>†</sup>**

### **Abstract**

This work reports on pulp mill wastewater (PMW) tertiary treatment by Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and solar photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ ) processes in a pilot plant based on compound parabolic collectors (CPCs). Solar photo-Fenton reaction is much more efficient than the respective dark reaction under identical experimental conditions. It leads to DOC mineralization, COD and total polyphenols (TP) removal higher than 90%. The solar photo-Fenton experiment with 5 mg Fe L<sup>-1</sup> reaches 90% of DOC mineralization with 31 kJ L<sup>-1</sup> of UV energy and 50 mM of H<sub>2</sub>O<sub>2</sub>. The initial non-biodegradability of PMW, as shown by respirometry assays and BOD<sub>5</sub>/COD ratio, can be changed after a solar photo-Fenton treatment. Experiments with 20 and 50 mg Fe L<sup>-1</sup> revealed that solar photo-Fenton can reach the same DOC degradation (90%), however, consuming less H<sub>2</sub>O<sub>2</sub> and time. Diluting the initial organic load to 50% also diminishes the dosage of H<sub>2</sub>O<sub>2</sub> and the necessary reaction time to achieve high DOC removals. Accordingly, solar photo-Fenton can be considered an alternative or complementary process to improve the performance of a biologic treatment and, subsequently, achieve legal limits on discharge into natural waters.

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<sup>†</sup>Adapted from: Lucas, M.S., Peres, J.A., Amor, C., Prieto-Rodriguez, L., Maldonado, M.I., Malato, S. *Tertiary treatment of pulp mill wastewater by solar photo-Fenton*. Journal of Hazardous Materials. **2012**, 225-226: 173-181.



## **2.1. Introduction**

Pulp and paper industries are intensive water consumers. This high water usage generates an effluent that needs to be properly managed, making water treatment a key environmental concern for these industries. The release of pulp and paper effluents into natural waters can cause significant environmental problems, such as: slime growth; thermal impacts; death of zooplankton and fish; scum formation; colour and aesthetic problems<sup>[1]</sup>.

Lignin and its derivatives are responsible for the strong colouring in the pulp and paper effluents and they may produce highly toxic and refractory compounds which are very difficult to degrade<sup>[2]</sup>. Today, most pulp and paper mills use conventional processes to treat their effluents. These involve physical and biological techniques with no complete degradation of recalcitrant organic matter<sup>[3,4]</sup>.

On the other hand, many pulp and paper mills face a shortage of available water supply due to water scarcity. Thus, water consumption and consequent wastewater production must be reduced. This fact highlights the necessity of recycling treated wastewater in order to reduce freshwater consumption. Hence, a study of an advanced treatment to improve wastewater discharge quality and to allow the inclusion of wastewater as process water is needed.

Advanced Oxidation Processes (AOPs) are known for their capability to mineralise a wide range of organic compounds. AOPs involve the generation of highly reactive radical species, mainly the hydroxyl radical (HO<sup>•</sup>)<sup>[5,6]</sup>.

Among AOPs, Fenton and solar photo-Fenton are known within the scientific community for their effectiveness to treat wastewater with high polyphenols content, such as that from the cork manufacturing industry<sup>[7,8]</sup>, olive oil industry<sup>[9,10]</sup>, winery industry<sup>[11-13]</sup> and pulp and paper industry<sup>[14,15]</sup>. Solar photo-Fenton is considered as one of the most promising AOPs for the treatment of recalcitrant organic compounds in aqueous solutions<sup>[16,17]</sup>. Furthermore, the use of sunlight as source of irradiation to perform AOPs reduces processing costs and makes it more affordable for commercial use as a water treatment technology<sup>[18]</sup>.

In this study, a biological effluent from a pulp mill company has been examined. The effluent from the biological treatment still contains a significant organic load,

which makes direct release into a water course inappropriate. Consequently, the goal of this work is to find a tertiary treatment solution, which complies with the legal constraints on wastewater discharge into natural waters, for this biological effluent. Furthermore, the reuse of treated wastewater in the productive process could also be considered, depending on the results. Several Fenton and solar photo-Fenton processes were performed in order to evaluate the potential and the economic viability of some of the operational parameters that affect solar photo-Fenton kinetics, such as the accumulated energy needed, or the amount of hydrogen peroxide consumed.

## 2.2. Experimental

### 2.2.1. Pulp mill wastewater

Pulp mill wastewater (PMW) used during this study is the final effluent of the wastewater treatment plant (WTP) of a cellulose company located in the centre of Portugal. The main characteristics of the WTP final effluent are presented in Table 2.1.

**Table 2.1** - Physical-chemical characteristics of the WTP final effluent.

<i>Parameter</i>	<i>Final effluent</i>	<i>Parameter</i>	<i>Final effluent</i>
<b>TC</b> (mg C L <sup>-1</sup> )	393.5	<b>Potassium</b> (mg L <sup>-1</sup> )	36.3
<b>DOC</b> (mg C L <sup>-1</sup> )	348.0	<b>Sulphates</b> (mg L <sup>-1</sup> )	957.4
<b>N<sub>t</sub></b> (mg N L <sup>-1</sup> )	3.70	<b>Nitrites</b> (mg L <sup>-1</sup> )	6.4
<b>P<sub>t</sub></b> (mg P L <sup>-1</sup> )	0.001	<b>Nitrates</b> (mg L <sup>-1</sup> )	0.06
<b>pH</b>	7.9	<b>Phosphates</b> (mg L <sup>-1</sup> )	6.0
<b>Conductivity</b> (mS cm <sup>-1</sup> )	2.96	<b>Calcium</b> (mg L <sup>-1</sup> )	228.8
<b>Total polyphenols</b> (mg L <sup>-1</sup> )	217.7	<b>Magnesium</b> (mg L <sup>-1</sup> )	210.0
<b>COD</b> (mg O <sub>2</sub> L <sup>-1</sup> )	898.9	<b>Sodium</b> (mg L <sup>-1</sup> )	454.4
<b>BOD<sub>5</sub></b> (mg O <sub>2</sub> L <sup>-1</sup> )	117.7	<b>Chlorides</b> (mg L <sup>-1</sup> )	91.9
<b>BOD<sub>5</sub>/COD</b>	0.13	<b>Fluoride</b> (mg L <sup>-1</sup> )	3.31
<b>TSS</b> (mg L <sup>-1</sup> )	16.0	<b>Biodegradability</b>	0.01 (<0.3)
<b>Total iron</b> (mg L <sup>-1</sup> )	1.31	(rbCOD/COD mg L <sup>-1</sup> )	Non-biodegradable
		<b>Toxicity Inhibition</b> (%)	0



### 2.2.2. Chemicals

Fenton and photo-Fenton experiments were performed using ferrous iron sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), hydrogen peroxide (30% w/w) and sulphuric acid for pH adjustment, all supplied by Panreac. Treated samples were neutralized by means of NaOH (reagent grade, Panreac) for biodegradability and toxicity tests. Ultrapure distilled-deionised water was collected from a Milli-Q (Millipore Co.) system, and distillate water used at the pilot plant was from the Plataforma Solar de Almeria (PSA) distillation plant (conductivity  $< 10 \mu\text{S cm}^{-1}$ ,  $\text{Cl}^- = 0.7\text{-}0.8 \text{ mg L}^{-1}$ ,  $\text{NO}_3^- = 0.5 \text{ mg L}^{-1}$ , organic carbon  $< 0.5 \text{ mg L}^{-1}$ ), in order to avoid possible analytical interference. Other chemicals used in these experiments were reagent grade and used as received.

### 2.2.3. Experimental Setup

Photo-Fenton experiments were carried out in a pilot plant located at the Plataforma Solar de Almeria, Spain (latitude  $37^\circ\text{N}$ , longitude  $2.4^\circ\text{W}$ ). The pilot plant consists of a photocatalytic system constituted by: compound parabolic collectors (CPCs), a spherical recirculation tank made of borosilicate glass, one centrifugal pump (PAN WORLD, Model: NH-100 PX, 100 W), which returns the wastewater to the CPCs with a flow-rate of  $22 \text{ L min}^{-1}$ , and connective tubing. The plant is operated in batch mode. Solar collectors are made-up of two CPC units ( $3.02 \text{ m}^2$ ), with 24 borosilicate tubes (internal diameter 28 mm, external diameter 32 mm, length 1502 mm, transmissivity between 0.900 and 0.915 for  $\lambda \geq 350 \text{ nm}$ ) connected by plastic junctions made of high density polyethylene (HDPE). The CPC photoreactor is able to treat up to 40 L of wastewater having an irradiated volume of 22 L. A diagram of this system has been published elsewhere<sup>[13]</sup>. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, Model CUV 3) mounted on a platform tilted  $37^\circ$  (the same as the CPC reactor).

Eq. (3.1) allows the obtention of the amount of accumulated UV energy ( $Q_{UV}$  kJ/L) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval  $\Delta t$ <sup>[19]</sup>:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (\text{E3.1})$$

where  $t_n$  is the time corresponding to  $n$ -water sample,  $V_i$  the total reactor volume,  $A_r$  the illuminated collector surface area and  $\overline{UV}_{G,n}$  the average solar ultraviolet radiation measured during the period  $\Delta t_n$ . All experiments were carried out from June to July 2011 during cloudy and sunny days. As the system is outdoors and is not thermally controlled, the temperature inside the reactor is continuously recorded by a PT-100 inserted in the pipe.

#### **2.2.4. Experimental procedure**

Different sets of experiments were performed. Firstly, a set of Fenton processes was performed at laboratory scale to ascertain the influence of the iron dosage on DOC removal. Tests were performed with 1.3, 20 and 50 mg L<sup>-1</sup> of iron at pH 2.8 in 3 L glass beakers containing 2 L of wastewater and excess hydrogen peroxide concentration was maintained (around 200 – 300 mg L<sup>-1</sup>). During these experiments, beakers were always covered in order to maintain conditions of darkness.

Secondly, a set of photo-Fenton experiments at pilot plant scale was performed. At the beginning of the process, the collectors were covered, pH was adjusted to 2.8 – 3.0 and ferrous iron salt was added. Tests were performed with 1.3, 5 and 10 mg L<sup>-1</sup> of iron. After each addition of reagents, the wastewater was well homogenised by recirculation for at least 15 minutes. Then, a sample was taken (time zero), after that, the initial dosage of hydrogen peroxide was added and the CPC uncovered (RAD-ON). At that point, photo-Fenton reaction began. Hydrogen peroxide concentration was kept between 200 and 300 mg L<sup>-1</sup>. It was monitored during the whole experiment and continuously replaced to maintain the original concentration throughout the reaction.

Finally, another set of two photo-Fenton experiments were performed with superior dosages of iron, 20 and 50 mg Fe L<sup>-1</sup>. A final experiment was performed with a 50% dilution of the pollutant load, to evaluate the DOC removal kinetics and H<sub>2</sub>O<sub>2</sub> consumption.

### **2.2.5. Analytical Determinations**

Organic matter concentration and mineralisation were monitored by measuring the DOC by direct injection of filtered samples into a Shimadzu TOC-V CSN analyser, equipped with an ASI-V autosampler, provided with an NDIR detector and calibrated with standard solutions of potassium phthalate. COD analysis was performed by Merck Spectroquant® cuvette tests. Samples were pre-filtered through 0.20 µm syringe nylon filters (25 mm, Millex® GN, Millipore). Biochemical oxygen demand (BOD<sub>5</sub>) was determined according to Standard Methods using an OXITOP® system. Total iron and hydrogen peroxide were both determined spectrophotometrically using a UNICAM 2 spectrophotometer. Colorimetric determination of total iron concentration with 1,10-phenantroline (510 nm) was used according to ISO 6332. Hydrogen peroxide concentration was determined using titanium (IV) oxysulfate (DIN 38 402 H15 method) at 410 nm. The total polyphenol content was measured in filtered samples by spectrophotometry at 765 nm using the reagent Folin-Ciocalteau (Merck)<sup>[20]</sup>. The polyphenol content is expressed as mg L<sup>-1</sup> of gallic acid.

Anions concentrations were determined with a Dionex DX-600 Ion chromatograph system equipped with a chromatographic column (Dionex Ionpac AG11-HC 4mm x 250mm), a suppressor (Dionex ASRS-Ultra II 4mm) and an electric conductivity detector (Dionex ED50). The gradient program for anions determination comprises a 15 min run with 100 mM H<sub>2</sub>O/NaOH at a flow rate of 1.5 mL min<sup>-1</sup> in gradient mode. The cations IC system used was the Dionex-120 IC system. The mobile phase (H<sub>2</sub>SO<sub>4</sub> 20 mM) passes, at 1.2 mL min<sup>-1</sup> in isocratic mode during 15 minutes through the chromatographic column (Dionex Ionpac CS12A 4mm x 250mm), the suppression module (Dionex CSRS-Ultra 4mm) and the same electric conductivity detector (Dionex ED50). Total and volatile suspended solids were determined according to Standard Methods<sup>[21]</sup>.

### **2.2.6. Biocompatibility assays**

In order to assess the biocompatibility of PMW, toxicity and biodegradability, tests were carried out at different stages of solar photo-Fenton reaction. The photo-treated samples at different photo-treatment times were obtained by performing a new

photo-Fenton experiment, where small amounts of H<sub>2</sub>O<sub>2</sub> were added to the photoreactor. After H<sub>2</sub>O<sub>2</sub> total consumption, a sample was taken for bioassays and another amount of H<sub>2</sub>O<sub>2</sub> was added. This procedure is important since it prevents Fenton reaction during storage after sample collection and possible interferences in the bioassays.

i. Toxicity

Toxicity evolution during photocatalytic experiments was analyzed by respirometry using a BMT Respirometer (SURCIS, S.L), provided with an oxygen probe (Hamilton). The respirometer was loaded with the required amount of activated sludge (1000 mL, according to the manufacturer specifications) taken from a conventional municipal wastewater treatment plant. Afterwards, in order to inhibit the nitrification process and measure the sample effect only on the heterotrophic bacteria, 3 mg of N-allylthiourea per gram of volatile suspended solids (VSS) was added to the activated sludge half an hour before the experiments. Continuous aeration and agitation were applied on the respirometer to attain air saturation conditions. Temperature was maintained at 20° C during the experiment. Samples were previously adjusted to pH 6.5–7.5 and filtered. The toxicity of the wastewater was evaluated by comparing the bacterial activity in two assays: one containing the sludge and 50 mL of distilled water with a biodegradable substrate (reference) and the other containing the sludge and 50 mL of the target sample with the same biodegradable substrate. The substrate used in both cases was sodium acetate (0.5 g/g VSS). In both cases, the tests were extended until the biomass reached the maximum respiration rate ( $R_{s_{max}}$ ) and the inhibition percentage of each sample (I) is expressed quantitatively according to the following equation:

$$\% I = 100 \times \left(1 - \frac{R_{s_{max} \text{ SAMPLE}}}{R_{s_{max} \text{ REFERENCE}}}\right) \quad (\text{E2.2})$$

where  $R_{s_{max} \text{ SAMPLE}}$  and  $R_{s_{max} \text{ REFERENCE}}$  are expressed in terms of mg O<sub>2</sub> L<sup>-1</sup> h<sup>-1</sup>.

ii. Biodegradability

For those samples which presented non toxicity values, biodegradability assays based on respirometry were also carried out with the same BM-T respirometer. For these tests, the respirometer was also loaded with 1000 mL of activated sludge taken from a conventional municipal wastewater treatment plant. As above, the nitrification process was inhibited and continuous aeration and agitation were applied in the reactor flask. When the temperature and dissolved oxygen concentration were stable, 50 mL of the partially treated wastewater (after adjusting the pH to 6.5–7.5, and once filtered and aerated) was added to the respirometer reactor. Oxygen consumption rate was monitored automatically during the assay, and at the end of the test, the respirometer software gave the readily biodegradable fraction of the filtered COD (rbCOD) according to the total oxygen consumption registered by the equipment. The rbCOD/COD<sub>f</sub> ratio shows the sample biodegradability (where COD<sub>f</sub> is the filtered COD of the sample), taking into account that values of <0.3 mean that sample can be classified as non-biodegradable, samples with values > 0.3 and <0.7 as low-biodegradable, >0.7 and <0.8 biodegradable and >0.8 as high-biodegradable.

## **2.3. Results and discussion**

### ***2.3.1. Pulp mill wastewater***

The cellulose company's main product is totally chlorine free eucalyptus sulphite pulp and it operates using an acid bisulphite pulp cooking process. The mill's effluent treatment installations consist of two biological steps: anaerobic and activated sludge. Raw wastewater, which flows to the anaerobic reactor, presents COD values in the range of 11 230 – 15 380 mg O<sub>2</sub> L<sup>-1</sup> with a flow rate of 1280 m<sup>3</sup> day<sup>-1</sup>. The activated sludge reactors normally receive wastewater with COD values from 2800 to 3500 mg O<sub>2</sub> L<sup>-1</sup>.

After the aerobic treatment, the final effluent maintains a dark-brown colour allied to a significant organic load (DOC = 348 mg C L<sup>-1</sup>; COD = 899 mg O<sub>2</sub> L<sup>-1</sup>) and high polyphenols content (218 mg gallic acid L<sup>-1</sup>) making its treatment difficult (Table 2.1). The biodegradable fraction of the organic carbon is almost completely removed, since the pre-treated wastewater presents a low BOD<sub>5</sub>/COD ratio (0.13), which indicates

that the remaining organic carbon is recalcitrant and possibly inhibitory to microbial metabolism.

The final effluent obtained does not comply with the discharge limits imposed by Portuguese legislation. At present, the final effluent is transported to a Municipal Wastewater Treatment Plant (MWTP), and is diluted by the high flow rates of the MWTP.

In a first approach a strategy to deal with this effluent was outlined following that presented by Oller *et al.*<sup>[22]</sup>. In this study, the authors present a model to facilitate the selection of the best treatment process for a specific toxic and/or non-biodegradable industrial wastewater. Using the DOC, COD, BOD<sub>5</sub> and the toxicity and biodegradability analysis performed with the BM-T respirometer (Table 2.1), it is possible to say that: i) our wastewater is non-toxic; ii) presents a DOC < 500 mg/L and iii) it is non-biodegradable. Therefore, an Advanced Oxidation Process must be used to treat this wastewater, as suggested by Oller *et al.*<sup>[22]</sup>.

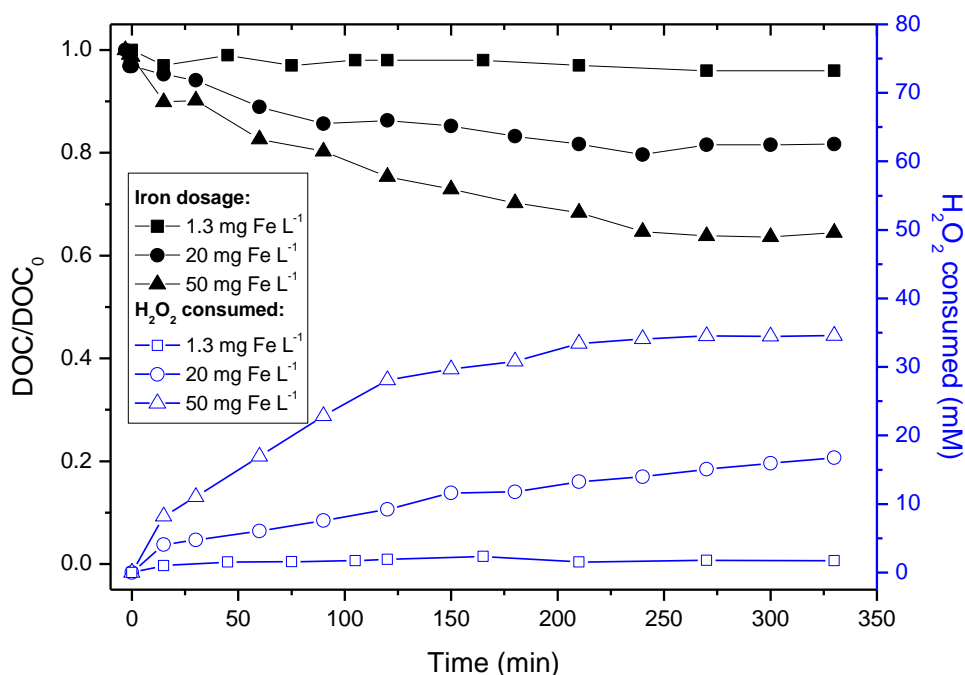
### 2.3.2. Fenton reagent

Having decided on AOPs as the best potential treatment, it was necessary to choose which one would be more suitable for our wastewater. Therefore, taking into account that: 1) the production process of the factory uses hydrogen peroxide (50% w/w) to bleach the pulp and 2) the wastewater already presents iron in its constitution, Fenton reagent process (Reactions 2.1-2.3) was selected as first approach to treat the final effluent of the pulp mill WTP.



PMW was treated by Fenton process evaluating the influence of the iron dosage on DOC removal. As a first step, one experiment was performed as a blank with 1.3 mg L<sup>-1</sup> of iron, since the wastewater already contains this amount of iron (Table 2.1), and no additional supply was needed. This experiment gives an idea of the remnant iron

salt capacity to catalyse the Fenton reaction. This experiment could be of significant importance since the iron concentration used ( $1.3 \text{ mg L}^{-1}$ ) precludes the necessity of any further iron precipitation steps and sludge elimination to comply with the European Community Directive. This directive allows the discharge of treated waters with a maximum of  $2 \text{ mg Fe L}^{-1}$  directly into the environment. Figure 2.1 presents the results obtained with Fenton reagent. The DOC removal achieved was 4%, 18% and 36% working with 1.3, 20 and  $50 \text{ mg L}^{-1}$  of iron respectively.



**Figure 2.1** - Fenton reagent experiments performed with 1.3, 20 and  $50 \text{ mg Fe L}^{-1}$ .

The removal achieved in the experiment without iron addition reveals that natural iron present in PMW it is unable to catalyse the Fenton reaction to a great extent. The low degradation capacity can be explained by the low iron concentration present in the wastewater, which makes the generation of  $\text{HO}^\bullet$  radicals difficult. Increasing iron concentration to 20 and  $50 \text{ mg L}^{-1}$  considerably improves the wastewater mineralization by the Fenton reaction. An increase in iron concentration of more than the double (from 20 to  $50 \text{ mg L}^{-1}$ ) results exactly in a double DOC removal (from 18% to 36%). This shows decreased efficiency of the process with higher iron dosages. This relatively lower mineralization with higher dosages of iron could be explained through

iron complexation with organic compounds present in wastewater as well as the reverse reaction (R2.3) in which  $\text{Fe}^{2+}$  scavenges  $\text{HO}^\bullet$  radicals and consumes  $\text{H}_2\text{O}_2$ .

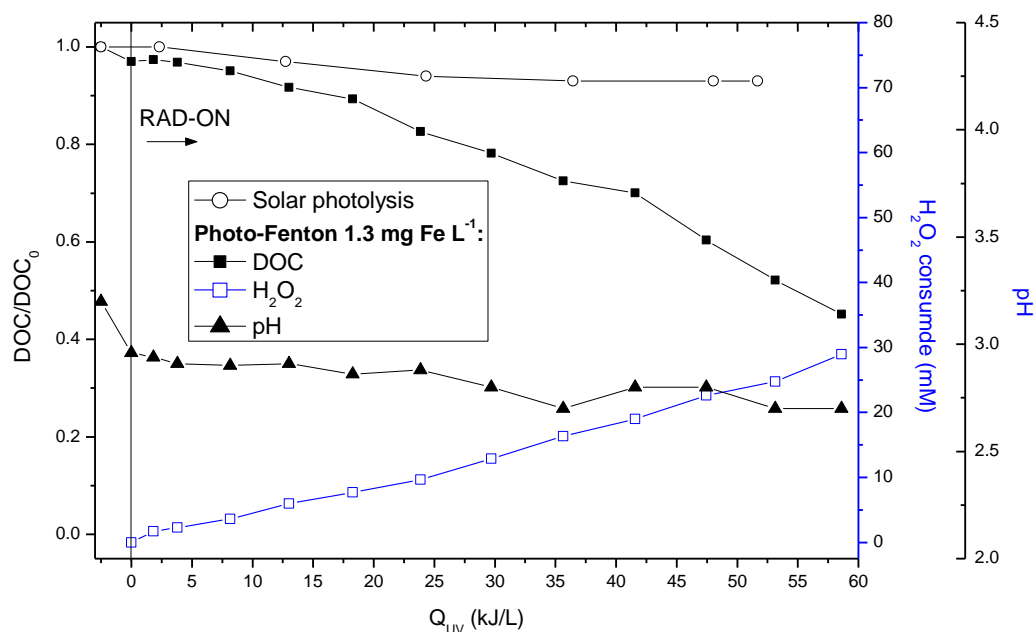
Results for the hydrogen peroxide consumed during the experiments with 20 and 50  $\text{mg Fe L}^{-1}$  are similar to those for DOC mineralization. For 20  $\text{mg Fe L}^{-1}$  an  $\text{H}_2\text{O}_2$  consumption of 17 mM was observed, and for 50  $\text{mg Fe L}^{-1}$  35 mM was consumed after 330 min of reaction time.

Figure 2.1 shows that Fenton reaction follows zero-order kinetics, which means that DOC degradation rate was not dependent on its concentration but on the amount of  $\text{HO}^\bullet$ . Since iron concentration was kept constant and there was excess of  $\text{H}_2\text{O}_2$ , the low reaction rate observed in the Fenton process can be explained by the low regeneration rate of the ferrous ions (reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ) (Reactions 2.2 and 2.3) in the absence of UV/visible light. It is clear that greater efficiency could be achieved if a higher concentration of iron is used. Taking these results into account, Fenton reaction cannot be considered an attractive option, because of the relatively long treatment time and high amount of iron needed to achieve complete mineralization. The capacity of Fenton process could be considerably improved by solar light, since under UV/visible light the regeneration of iron ( $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ) increases. This possibility is explored below.

### ***2.3.3. Solar photolysis and photo-Fenton***

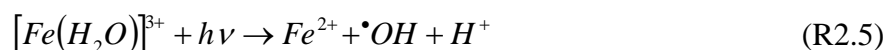
Figure 2.2 presents the mineralization results of the PMW by solar photolysis and photo-Fenton, making use of the natural iron salt present in the wastewater (1.3  $\text{mg Fe L}^{-1}$ ). From these data it is possible to observe that solar photolysis has little influence in DOC removal, just 6% of mineralization. On the other hand, solar photo-Fenton seems to be much more efficient than solar photolysis and also Fenton reaction. The combination of Fenton reagent with solar radiation leads to a carbon mineralization of 55% after 59  $\text{kJ L}^{-1}$ , working with only 1.3  $\text{mg Fe L}^{-1}$  and 29 mM of  $\text{H}_2\text{O}_2$  consumed.





**Figure 2.2** - PMW final effluent treated by solar photolysis and photo-Fenton with 1.3 mg Fe L<sup>-1</sup>.

The combination of UV/Vis radiation with Fenton's reagent (photo-Fenton process) promotes the photo-decarboxylation of ferric carboxylates and reduces ferric to ferrous iron reaction, yielding additional radicals by photolysis (reactions 2.4 – 2.6) (ligands (L) can be H<sub>2</sub>O, OH<sup>-</sup>, carboxylates, etc.)<sup>[23]</sup>.



The broad absorption bands of these complexes, ( $\lambda < 580$  nm) - or 35% of the solar radiation spectrum compared to approximately only 5% for UV light, are the reason why this reaction can be driven by visible light<sup>[23]</sup>.

This assay can be considered as a blank experiment, once it has revealed the capacity of remnant iron, initially present in wastewater, to catalyse the photo-Fenton process. However, the 55% of mineralization reached can be attributed not only to the photo-Fenton process, but also to the H<sub>2</sub>O<sub>2</sub>/UV system. The low amount of iron leaves a

considerable excess of  $H_2O_2$  to react under UV radiation throughout the experiment (reaction 2.7).

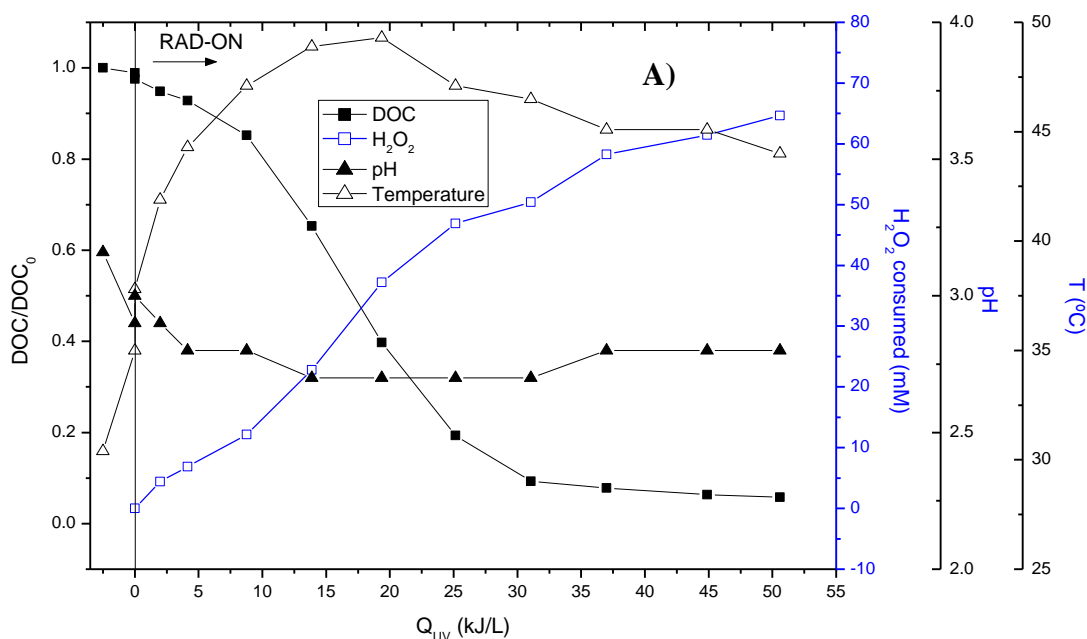


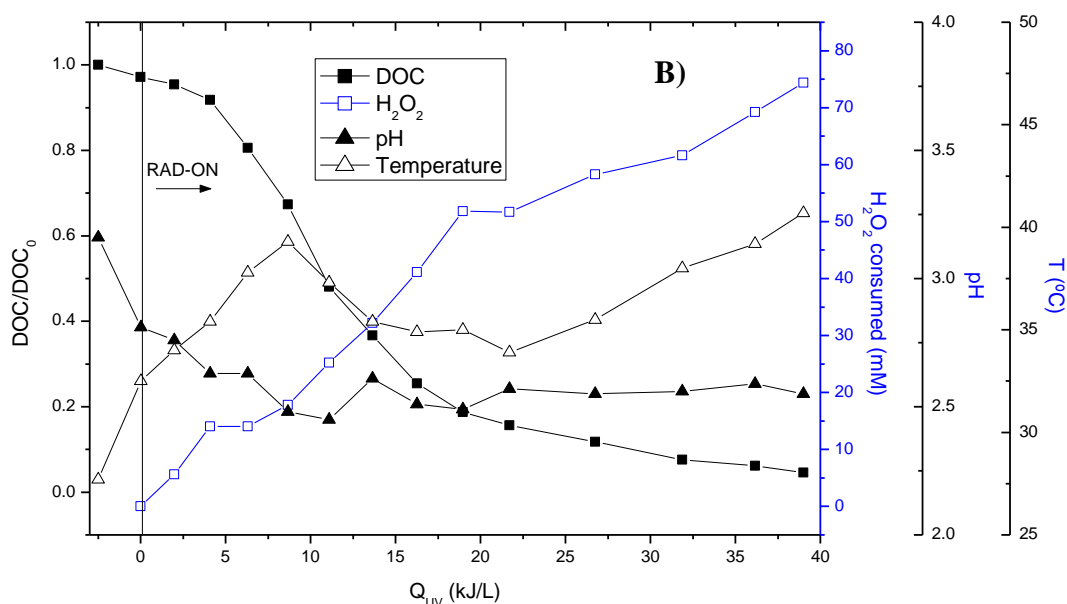
This experiment demonstrates that it is possible to degrade the PMW by solar photo-Fenton and that some operational parameters should be optimized to take into account the level of mineralization intended. For this reason, the influence of the iron dosage in solar photo-Fenton process is assessed below.

### i. Iron concentration effect on solar photo-Fenton

Figure 2.3 (A) and (B) present the mineralization results of the PMW by the solar photo-Fenton reaction using iron concentrations of 5 and 10 mg Fe L<sup>-1</sup>. These figures show an “initiation period” on DOC removal at the beginning of the experiment. This period can be identified by a soft plateau in DOC degradation as the firsts photons are received ( $Q_{UV}$  kJ L<sup>-1</sup>).

In the experiment with 5 mg Fe L<sup>-1</sup> that period is of approximately 8 kJ L<sup>-1</sup> and can be explained by the partial oxidation of the organics through the Fenton reaction (R2.1).





**Figure 2.3** - Solar photo-Fenton experiments performed with a) 5 mg L<sup>-1</sup> and b) 10 mg Fe L<sup>-1</sup>.

During this first period, the dark-brown colour of the wastewater substantially reduces light penetration in the CPC tube, so the oxidation that takes place is mainly due to the Fenton process. Thus, initially, the influence of the solar energy received by the CPCs can be negligible in comparison to the oxidation potential of the Fenton reagent during the first few minutes.

This fact can be confirmed by the smaller “initiation period” of Fenton reaction with 10 mg Fe L<sup>-1</sup>, which is only 4.1 kJ L<sup>-1</sup>. An increase in the iron dosage improves the DOC degradation during the first minutes due to the Fenton capacity to generate HO<sup>•</sup>. Afterwards, the colour of the solution starts to fade, which makes the absorption of solar UV photons by Fe<sup>3+</sup> ions possible, and improves the effectiveness of the photo-Fenton process.

Throughout this second part of the solar photo-Fenton, DOC degradation decreases faster in a relatively small period of time and presents a first order kinetic behaviour. For the experiment with 5 mg Fe L<sup>-1</sup> a constant rate,  $k$ , of 0.086 L kJ<sub>UV</sub><sup>-1</sup> was obtained up to 32 kJ<sub>UV</sub> L<sup>-1</sup>.

For the experiment with 10 mg Fe L<sup>-1</sup> there was an increased  $k$  value of 0.101 L kJ<sub>UV</sub><sup>-1</sup> up to 22 kJ<sub>UV</sub> L<sup>-1</sup>. This photo-Fenton performance can be explained by the iron regeneration promoted by UV radiation, (Fe<sup>3+</sup> into Fe<sup>2+</sup>, Reactions 2.4 and 2.5), once

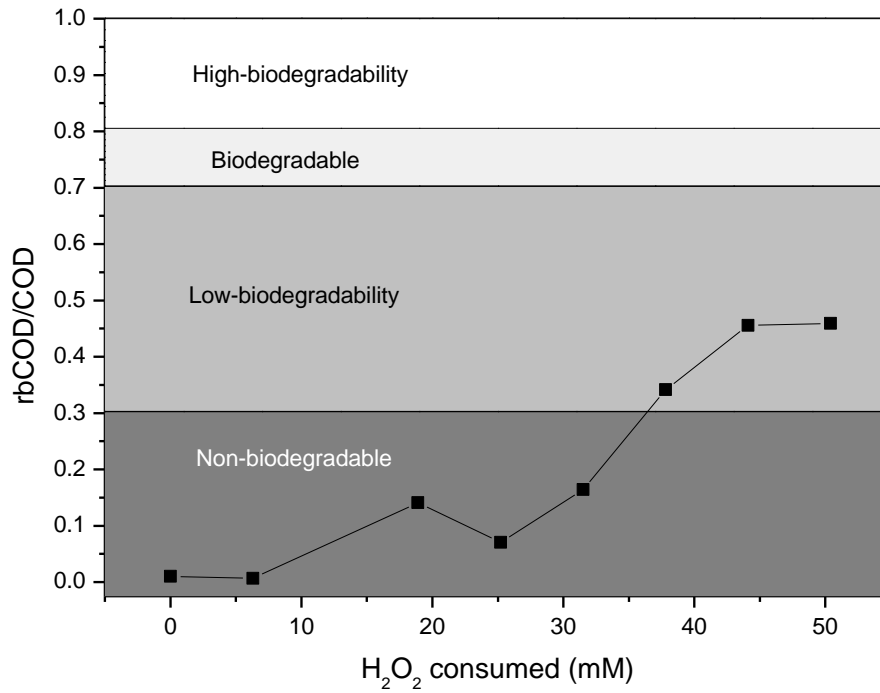
the wastewater colour fades, allowing photons deeper penetration into the CPC tubes. Although both experiments enabled the achievement of mineralization values higher than 90%, some operational parameters, such as temperature,  $\text{H}_2\text{O}_2$  consumed and the solar energy received ( $Q_{UV}$   $\text{kJ L}^{-1}$ ), were different in each experiment.

Using the mineralization value of 90% as a benchmark reference, it is possible to observe that with 5  $\text{mg Fe L}^{-1}$ , 31  $\text{kJ L}^{-1}$  of energy and 50 mM of  $\text{H}_2\text{O}_2$  were necessary to reach that DOC removal. In the experiment with 10  $\text{mg Fe L}^{-1}$  the energy necessary slightly decreases to 26  $\text{kJ L}^{-1}$  but the  $\text{H}_2\text{O}_2$  consumed was 59 mM.

#### ii. Biodegradability evolution during photo-Fenton process

At this point of the work it is possible to say that photo-Fenton allows the mineralization of the PMW. However, photo-Fenton requires a considerable investment in terms of chemical reagents (mainly  $\text{H}_2\text{O}_2$ ) and the CPC field's area, compared to a biological process. It follows that it would be worthwhile finding the point during the photo-Fenton process at which the wastewater begins to be biodegradable and which permits the optimal combination with a biological treatment process.

An activated sludge respirometric test was performed at different stages of the solar photo-Fenton reaction in order to determine the optimal photo-treatment time to reach a biodegradable effluent. Figure 2.4 shows the biodegradability evolution during a photo-Fenton experiment up to higher than 90% mineralization against  $\text{H}_2\text{O}_2$  consumption. This figure shows the different ranges of biodegradability (from non-biodegradable to high-biodegradable) obtained by the respirometric test using the ratio  $\text{rbCOD}/\text{COD}$ . The initial wastewater displays non-biodegradability, which agrees with the low  $\text{BOD}_5/\text{COD}$  ratio (Table 2.1).



**Figure 2.4** - Biodegradability evolution along a solar photo-Fenton experiment.

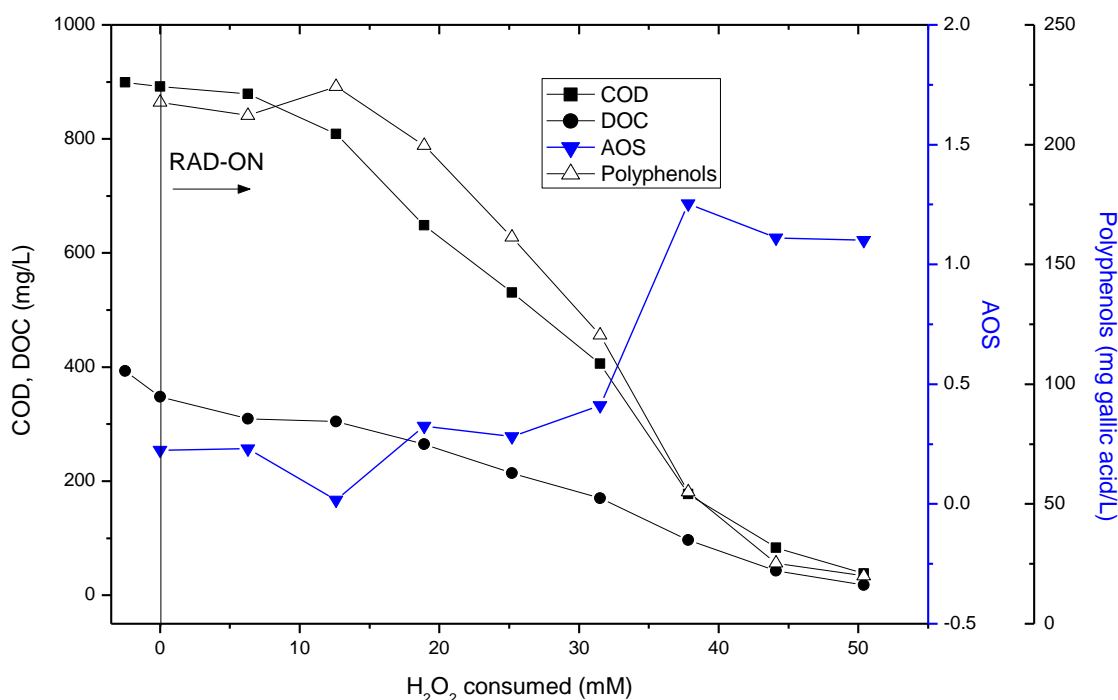
Throughout the photo-Fenton experiment the wastewater biodegradability increased until it reached the low-biodegradability stage. Therefore, although the photo-Fenton process improves wastewater biodegradability, it is not advisable to reintroduce the PMW into a biologic process once the DOC concentration remaining is very low. Ideally, the photo-Fenton process could be used until legal discharge limits are achieved. All the photo-Fenton samples revealed non-toxicity (data not shown).

The DOC and COD of solar photo-Fenton samples were used in order to determine the average oxidation state (AOS) (Eq.2.3) of the solution. The AOS is a rough parameter useful for estimating the oxidation degree of the process and which gives indirect information on wastewater biodegradability<sup>[24]</sup>.

$$AOS = \frac{4(DOC - COD)}{DOC} \quad (E2.3)$$

DOC is the dissolved organic carbon at time  $t$  (mmol of C L<sup>-1</sup>) and COD is the chemical oxygen demand at time  $t$  (mmol of O<sub>2</sub> L<sup>-1</sup>). AOS takes values between +4 for CO<sub>2</sub>, the most oxidized state of C, and -4 for CH<sub>4</sub>, the most reduced state of C.

Figure 2.5 shows that AOS starts at 0.22 and increases up to 1.25 (the highest value reached, after a consumption of 38 mM  $\text{H}_2\text{O}_2$ ) then slightly decreases to 1.10 at the end of the photo-treatment. The global increase of AOS suggests that more oxidized organic intermediates are formed during the treatment and, after AOS reaches a peak, the oxidation state of the intermediates has little change.



**Figure 2.5** - Evolution of COD, DOC, AOS and TP content during a solar photo-Fenton experiment.

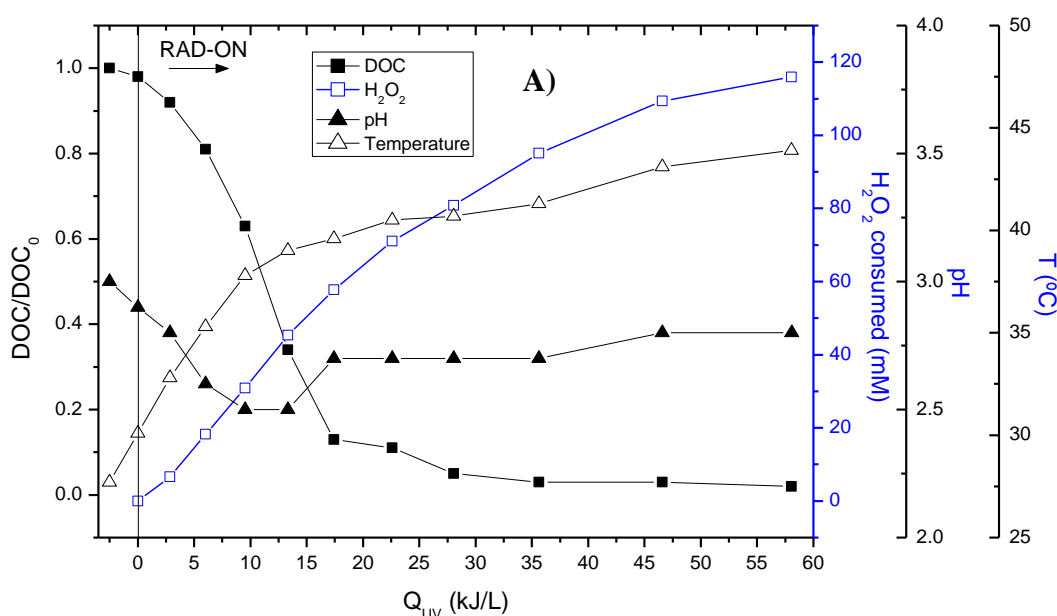
The formation of more oxidized intermediates indirectly demonstrates that the treatment can improve biodegradability, as observed during the activated sludge respirometric test. This AOS global increase is in agreement with the TP content reduction (Figure 2.5). The removal of TP is quite important to improving wastewater biodegradability since these compounds are sometimes toxic and/or non-biodegradable<sup>[13,25]</sup>. The PMW used in this study contains about 218 mg of gallic acid  $\text{L}^{-1}$  which is almost, (91%), completely removed during the solar photo-Fenton process, with a  $\text{H}_2\text{O}_2$  consumption of 50 mM.

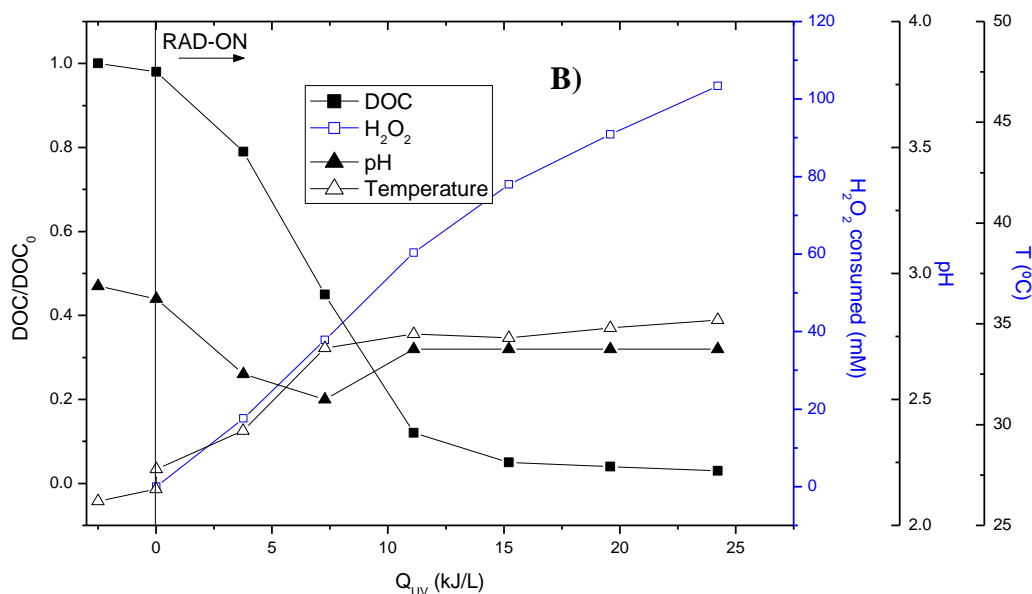
### iii. Economic factors and environmental impact reduction

At this point of the work it was quite clear that although solar photo-Fenton degrades the organic load present in the final effluent of PMW, reintroduction into a biologic process still did not appear to be feasible, using Fenton or solar photo-Fenton. Therefore, the next step was to collect additional information to optimize operational conditions of the solar photo-Fenton process.

The main solar photo-Fenton parameters, that must be optimized to reduce costs and environmental impact, are  $\text{H}_2\text{O}_2$  consumption and the solar collector field necessary to drive the process. Subsequently, several solar photo-Fenton experiments with superior dosages of iron were performed. These experiments attempted to verify the influence of the area of solar collectors' field on DOC removal kinetics.

Figure 2.6 (A) and (B) shows solar photo-Fenton experiments performed with 20 and 50  $\text{mg Fe L}^{-1}$ . In these assays, the “initiation period” observed in the experiments performed with 5 and 10  $\text{mg Fe L}^{-1}$ , disappears. The increase in iron concentration improves the generation of  $\text{HO}^\bullet$  radicals by Fenton reagent (R2.1), making the DOC removal much more effective. The obstacles arising from the dark-brown colour, witnessed in the first few minutes of earlier photo-Fenton experiments, can be overcome by iron increase. The reduced light penetration into the CPC tube during the photo-Fenton “initiation period” can thus be circumvented.





**Figure 2.6** - Solar photo-Fenton experiments performed with a) 20 mg L<sup>-1</sup> and b) 50 mg Fe L<sup>-1</sup>.

In both experiments, DOC degradation reaches a fast decay in a relatively small period of time and presents a first-order kinetic behaviour. In the experiment with 20 mg Fe L<sup>-1</sup> the constant rate  $k$  was 0.160 L kJ<sub>UV</sub><sup>-1</sup> up to 17.4 kJ<sub>UV</sub> L<sup>-1</sup> and with 50 mg Fe L<sup>-1</sup> the  $k$  value rises to 0.245 L kJ<sub>UV</sub><sup>-1</sup> up to 15.2 kJ<sub>UV</sub> L<sup>-1</sup>. This superior solar photo-Fenton performance can be explained by the iron increase, in comparison with experiments with only 5 and 10 mg Fe L<sup>-1</sup>, and also through the iron regeneration promoted by the UV radiation (R2.7).

These experiments make it possible reach mineralization superior to 90% with a small amount of accumulated solar energy. It is also possible to reduce the area of the solar collectors through iron increase, although a superior H<sub>2</sub>O<sub>2</sub> consumption occurs.

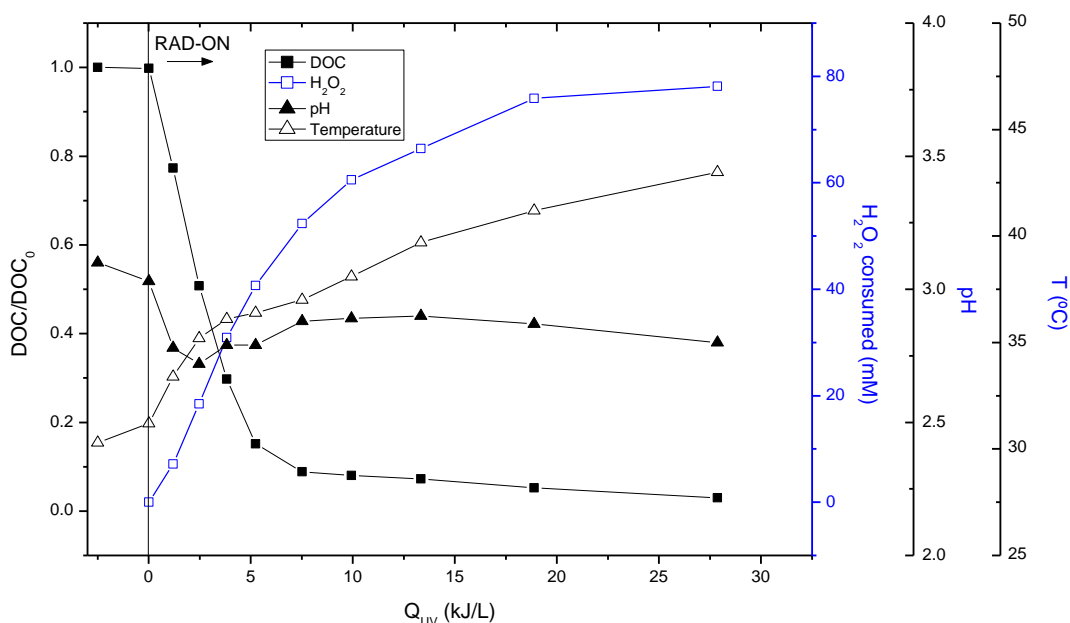
The high amount of iron used (20 or 50 mg L<sup>-1</sup>) can be considered an operational drawback to the solar photo-Fenton process, since it will increase the quantity of sludge produced. Additionally, it hinders compliance with the European Directive that restricts to 2 mg L<sup>-1</sup> the concentration of iron that can be released into a natural water course. However, some cheap and easy procedures can overcome this problem.

Increasing the pH of the final effluent to 6 or 7 before discharge into water courses, will promote the precipitation of the soluble iron, making it possible to reach



iron concentrations lower than  $2 \text{ mg L}^{-1}$ . The sludge generated can be used as iron source in photo-Fenton process. To do so, it would be necessary to acidify the sludges (to pH 1), to make the iron previously precipitated soluble. This iron solution can be reused as source of iron and acid in the solar photo-Fenton process – an option which diminishes the operational drawback under discussion.

Figure 2.7 shows the solar photo-Fenton results achieved with the PMW dilution at 50% of the initial pollutant load. The dilution was performed using tap water. From data it is possible observe that DOC removal is rapid and the “initiation period”, observed in the solar photo-Fenton experiments performed with 5 and  $10 \text{ mgFe L}^{-1}$ , does not exist. This is because the initial dark-brown colour of PMW was significantly reduced through wastewater dilution, facilitating the absorption of solar UV photons by the  $\text{Fe}^{3+}$  and effective photo-Fenton development. A kinetic analysis confirms the rapid DOC removal. The first-order kinetic rate obtained ( $k = 0.334 \text{ L kJ}_{\text{UV}}^{-1}$  up to  $7.5 \text{ kJ}_{\text{UV}} \text{ L}^{-1}$ ) was much higher than that observed in the photo-Fenton experiment with  $20 \text{ mgFe L}^{-1}$  ( $k = 0.160 \text{ L kJ}_{\text{UV}}^{-1}$  up to  $17.4 \text{ kJ}_{\text{UV}} \text{ L}^{-1}$ ) without PMW dilution.



**Figure 2.7** - Solar photo-Fenton experiment performed with  $20 \text{ mgFe L}^{-1}$  using PMW diluted 50%.

The increase in the kinetic rate is not surprising since the initial DOC load was reduced to half and the kinetic rate increased in the same order as the dilution. Thus, the

dilution of the wastewater can reduce the treatment time and the area of solar collectors necessary to reach legal discharge values.

## **2.4. Conclusions**

The final effluent of a cellulose company presents a high organic load even after two biologic treatment steps (one anaerobic and the other aerobic). After a detailed physical-chemical analysis, this final effluent was found to be non-biodegradable ( $\text{BOD}_5/\text{COD} = 0.13$ ). Therefore, AOPs were selected as the best treatment option. Fenton reagent was initially applied with different dosages of iron: 1.3, 20 and 50 mg  $\text{L}^{-1}$ , and the DOC removal achieved was 4, 18 and 36%, respectively. The low degradation rate observed in Fenton experiments can be explained by the low regeneration of the ferrous ions (reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ) in the absence of UV/visible light.

In an attempt to overcome this weakness, a solar photo-Fenton using CPCs was applied. As a first step, solar photo-Fenton experiments were performed with 5 and 10 mg  $\text{Fe L}^{-1}$  and DOC removal rates higher than 90% were obtained. Biodegradability assays were performed to determine the point at which solar photo-Fenton permits the introduction of the wastewater into a biological process, to try to reduce the solar photo-Fenton treatment costs. Activated sludge respirometric tests revealed that solar photo-Fenton increases the wastewater biodegradability up to the low-biodegradability level in the final period of the treatment. A combination of a solar photo-Fenton and a biological process can be applied, but only in the final phase of the chemical step, when the remaining DOC is very small. This led to the consideration of a single treatment process, the solar photo-Fenton.

COD and TP were clearly removed during a solar photo-Fenton experiment attaining a removal rate of around 90%, for a  $\text{H}_2\text{O}_2$  consumption of 50 mM. AOS was also monitored and a global increase from 0.22 to 1.10 was verified, suggesting that more oxidized organic intermediates are formed during treatment.

Finally, seeking economic and environmental impact reduction, experiments with 20 and 50 mg  $\text{Fe L}^{-1}$  and a 50% initial load dilution were performed. By increasing the iron concentration and diluting the wastewater with an equal part of tap water, it was

possible to raise the kinetic constants of the solar photo-Fenton experiments. In the experiment with 20 mg Fe L<sup>-1</sup> the constant rate  $k$  was 0.160 L kJ<sub>UV</sub><sup>-1</sup> and with 50 mg Fe L<sup>-1</sup> the  $k$  value rises to 0.245 L kJ<sub>UV</sub><sup>-1</sup>. The equal parts dilution allows a first-order kinetic rate  $k$  of 0.334 L kJ<sub>UV</sub><sup>-1</sup> to be achieved. Therefore, solar photo-Fenton can be considered a complementary process to improve the quality of the final effluent from cellulose production.

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**3. MATURE LANDFILL LEACHATE TREATMENT  
BY COAGULATION/FLOCCULATION COMBINED  
WITH FENTON AND SOLAR PHOTO-FENTON  
PROCESSES**

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### **3. MATURE LANDFILL LEACHATE TREATMENT BY COAGULATION/FLOCCULATION COMBINED WITH FENTON AND SOLAR PHOTO-FENTON PROCESSES\***

#### **Abstract**

This work reports the treatment of a mature landfill leachate through the application of chemical-based treatment processes in order to achieve the discharge legal limits into natural water courses. Firstly, the effect of coagulation/flocculation with different chemicals was studied, evaluating the role of different initial pH and chemicals concentration. Afterwards, the efficiency of two different Advanced Oxidation Processes for leachate remediation was assessed. Fenton and solar photo-Fenton processes were applied alone and in combination with a coagulation/flocculation pre-treatment. This physicochemical conditioning step, with 2 g L<sup>-1</sup> of FeCl<sub>3</sub>·6H<sub>2</sub>O at pH 5, allowed removing 63% of COD, 80% of turbidity and 74% of total polyphenols. Combining the coagulation/flocculation pre-treatment with Fenton reagent, it was possible to reach 89% of COD removal in 96 hours. Moreover, coagulation/flocculation combined with solar photo-Fenton revealed higher DOC (75%) reductions than single solar photo-Fenton (54%). In the combined treatment (coagulation/flocculation and solar photo-Fenton), it was reached a DOC reduction of 50% after the chemical oxidation, with 110 kJ L<sup>-1</sup> of accumulated UV energy and a H<sub>2</sub>O<sub>2</sub> consumption of 116 mM. Toxicity and biodegradability assays were performed to evaluate possible variations along the oxidation processes. After the combined treatment, the leachate under study presented non-toxicity but biodegradability increased.

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\* Adapted from: Amor, C., Torres-Socías, E.D., Peres, J.A., Maldonado, M.I., Oller, I., Malato, S., Lucas, M.S. *Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes*. Journal of Hazardous Materials. **2015**, 286, 261–268.



### **3.1. Introduction**

Human activities have always contributed to waste generation. This fact has not been considered as a major issue while human population has been relatively small, but became a serious problem with industrialisation and growth of urban areas<sup>[1]</sup>.

Landfill waste disposal represents a key management strategy in most developed countries, mainly due to its economic advantages<sup>[2,3]</sup>. The landfill leachate generated by the decomposition of organic wastes and rainfall percolation through the waste material<sup>[4]</sup> is nowadays one of the most pressing issues surrounding the operation of sanitary landfills. The composition of leachate, a complex and high-strength wastewater, is featured by the presence of large amounts of organic matter, ammonia, heavy metals and toxic materials<sup>[5]</sup>. Several factors influence leachate's characteristics: waste age, climatic conditions, waste composition, landfill design and operational practice. The specific composition of leachates determines their relative treatability, which is evaluated as a function of landfill's age and/or by its BOD<sub>5</sub>/COD ratio<sup>[6]</sup>.

As a landfill becomes older, it goes through the successive degradation stages of organic waste, ranging from initial aerobic to a longer anaerobic decomposition period in which properties, such as COD, BOD<sub>5</sub>/COD ratio, ammonium nitrogen (NH<sub>3</sub>-N) and pH, widely vary<sup>[5]</sup>.

Young landfill leachate (<5 years) is usually characterized by high concentrations of biochemical oxygen demand (BOD) (4000 – 15 000 mg O<sub>2</sub> L<sup>-1</sup>) and COD (25 000 – 60 000 mg O<sub>2</sub> L<sup>-1</sup>), moderately high strength of ammonium nitrogen (500 – 2000 mg L<sup>-1</sup>), high BOD<sub>5</sub>/COD ratio (0.15 to 0.25) and pH around 4<sup>[7]</sup>. An intermediate leachate (from 5 to 10 years) is characterized by the presence of substantial loads of recalcitrant COD, volatile fatty acids and pH greater than 7<sup>[8, 9]</sup>. A mature or stabilized leachate (> 10 years) is featured by high molecular weight contaminants (compounds which are not easily biodegradable), high strength of ammonium nitrogen (3000 – 5000 mg L<sup>-1</sup>), moderately high strength of COD (5000 – 20 000 mg L<sup>-1</sup>) and a BOD<sub>5</sub>/COD ratio lower than 0.1<sup>[8]</sup>.

When leachates from young landfills exhibit BOD/COD ratios around 0.25, they can be subjected to standard biological treatment processes<sup>[10]</sup>. However, landfills

ageing make waste decomposition difficult to be biologically treated, due to the presence of toxic and/or biorecalcitrant substances. Therefore, the application of physicochemical treatment processes in older landfills is compulsory<sup>[6]</sup>.

The most common physicochemical processes used for leachate remediation are coagulation/flocculation<sup>[11-13]</sup>, reverse osmosis<sup>[14]</sup> activated carbon adsorption<sup>[6]</sup> and advanced oxidation processes (AOPs)<sup>[15,16]</sup>.

Coagulation/flocculation is a relatively simple technique that can be successfully employed in the remediation of old landfill leachates. Selection of appropriate coagulant, determination of best experimental conditions, assessment of pH effect and investigation of optimal reagents dosage are required for performance optimization<sup>[12,17]</sup>.

AOPs are considered feasible technologies for the treatment of effluents containing refractory compounds similar to leachate<sup>[3]</sup>. Fenton's oxidation and solar photo-Fenton are examples of AOPs which can degrade organic recalcitrant pollutants by the action of hydroxyl radicals ( $\text{HO}^\bullet$ )<sup>[18]</sup>. Hydroxyl radicals effectively mineralize refractory organic matter (OM) into more biodegradable compounds and so it could be subsequently treated by using more economic biological-based methods<sup>[19]</sup>. Fenton process uses  $\text{H}_2\text{O}_2$  as an oxidizing agent and the reduced form of iron ( $\text{Fe}^{2+}$ ) as a catalyst to generate  $\text{HO}^\bullet$  in acidic conditions<sup>[20, 21]</sup>. Solar photo-Fenton is based on Fenton process and the use of UV-visible radiation to improve reaction through regeneration of  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$  produced in Fenton, as well as the generation of photoactive complexes and more hydroxyl radicals<sup>[22-24]</sup>. This process is considered as one of the most promising AOPs for recalcitrant organic compounds removal from wastewater though they involve high investment and operating costs. Using sunlight as a source of irradiation in AOPs can reduce processing costs and makes it more affordable for commercial use as a complex water treatment technology<sup>[25]</sup>.

The aim of this study is to treat a mature landfill leachate trying to reach the legal limits of release in natural waters. In a first stage the leachate was submitted to a coagulation/flocculation process and subsequently the efficiency of Fenton and solar photo-Fenton techniques were evaluated, taking into account toxicity and biodegradability evolution during the oxidation processes.

## 3.2. Material and methods

### 3.2.1. Landfill leachate

Leachate under study was collected in a municipal landfill located in the north of Portugal, Vila Real. This landfill is in operation since 2000, receiving approximately 75 000 tonnes of household wastes per year. The landfill has a leachate recirculation system which operates mainly in the summer period (May - September). The leachate was taken directly from a collection box at the exit of the landfill cell, just before the wastewater treatment facilities (stabilization pond and coagulation/flocculation process). Due to the landfill characteristics the generated leachate can be classified as stabilized. The landfill leachate's main physicochemical characteristics are shown in Table 3.1.

**Table 3.1** - Characterization of landfill leachate.

<i>Parameters</i>	<i>Value</i>
<b>pH</b>	7.8
<b>Turbidity</b> (NTU)	140
<b>COD</b> (mg O <sub>2</sub> L <sup>-1</sup> )	5700
<b>BOD<sub>5</sub></b> (mg O <sub>2</sub> L <sup>-1</sup> )	400
<b>BOD<sub>5</sub>/COD</b>	0.07
<b>DOC</b> (mg C L <sup>-1</sup> )	2400
<b>Total polyphenols</b> (mg gallic acid L <sup>-1</sup> )	750
<b>Total Suspended Solids</b> (mg L <sup>-1</sup> )	130
<b>Total iron</b> (mg Fe L <sup>-1</sup> )	4.1
<b>Zinc</b> (mg Zn <sup>2+</sup> L <sup>-1</sup> )	0.7
<b>Arsenic</b> (µg As <sup>2+</sup> L <sup>-1</sup> )	37.0
<b>Lead</b> (µg Pb <sup>2+</sup> L <sup>-1</sup> )	28.5
<b>Cadmium</b> (µg Cd <sup>2+</sup> L <sup>-1</sup> )	1.1
<b>Copper</b> (µg Cu <sup>2+</sup> L <sup>-1</sup> )	46.9
<b>Total chromium</b> (mg Cr L <sup>-1</sup> )	2.2
<b>Nickel</b> (µg Ni <sup>2+</sup> L <sup>-1</sup> )	3.0

Attending to presented data, it can be stated that this landfill leachate is a complex wastewater which can be designated as mature leachate, since it has a

BOD<sub>5</sub>/COD ratio lower than 0.1. This very low BOD<sub>5</sub>/COD ratio implies that the application of a biological treatment process will be inappropriate. Therefore, alternative treatment processes must be considered, particularly physicochemical conditioning and advanced oxidation technologies.

### **3.2.2. Chemicals**

In coagulation/flocculation trials, calcium hydroxide, Ca(OH)<sub>2</sub>; aluminium sulphate, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O; ferrous sulphate, FeSO<sub>4</sub>·7H<sub>2</sub>O and ferric chloride, FeCl<sub>3</sub>·6H<sub>2</sub>O, all purchased from Panreac, were used. Hydrogen peroxide (30% w/w), sulphuric acid and sodium hydroxide were supplied by Sigma Aldrich. Ultra-pure distilled-deionised water was collected from a Milli-Q (Millipore Co.) system.

### **3.2.3. Analytical determinations**

COD analysis was performed using Merck Spectroquant<sup>®</sup> cuvette tests (HACH Co.). Samples were pre-filtered through 0.20-μm syringe nylon filters (25 mm, Millex<sup>®</sup> GN, Millipore). Turbidity was determined in a HACH 2100N turbidimeter. Organic matter concentration and mineralisation were monitored by DOC, through direct injection of filtered samples into a Shimadzu TOC-V CSN analyser, equipped with an ASI-V autosampler and calibrated with standard solutions of potassium phthalate. BOD<sub>5</sub> was determined according to Standard Methods using an OXITOP<sup>®</sup> system. Total iron and hydrogen peroxide concentrations were monitored using a PerkinElmer UV/VIS spectrophotometer lambda 25 and UNICAM 2 spectrophotometer. Colorimetric determination of total iron concentration was performed with 1,10-phenantroline (510 nm) according to ISO 6332. Hydrogen peroxide concentration was followed using titanium (IV) oxysulfate (DIN 38 402 H15 method) at 410 nm. Total polyphenol content was measured by spectrophotometry at 765 nm using the Folin-Ciocalteu reagent (Merck)<sup>[26]</sup>. The total polyphenol content is expressed as mg gallic acid L<sup>-1</sup>. Total and volatile suspended solids were determined according to Standard Methods<sup>[27]</sup>.

### 3.2.4. Experimental setup

Solar photo-Fenton experiments were carried out in a CPC solar pilot plant located in Plataforma Solar de Almería (PSA), Spain (latitude 37°N, longitude 2.4°W). The pilot plant consists of a photocatalytic system constituted by a hydraulic circuit with four compound parabolic collectors (CPCs) with 4.16 m<sup>2</sup> of irradiated area, a recirculation tank, one centrifugal pump for water recirculation and a temperature control system. A diagram of this system has been published elsewhere<sup>[28]</sup>. The plant is operated in batch mode, and it is able to treat a total volume of 82 L ( $V_T$ ) but the total illuminated volume inside the absorber tubes is 44.6 L ( $V_i$ ). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, Model CUV 3) mounted on a platform tilted 37° (the same as the CPC reactor).

Eq. 3.1 allows calculating the amount of accumulated UV energy ( $Q_{UV}$  kJ/L) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval  $\Delta t$ :

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (E3.1)$$

where  $t_n$  is the time corresponding to  $n$ -water sample,  $V_t$  the total reactor volume,  $A_r$  the illuminated collector surface area and  $\overline{UV}_{G,n}$  the average solar ultraviolet radiation measured during the period  $\Delta t_n$ . Temperature inside the reactor was set and controlled at 35°C.

### 3.2.5. Experimental procedure

#### i. Coagulation/flocculation

Coagulation/flocculation tests were performed in a jar-test apparatus (ISCO) using calcium hydroxide, aluminium sulphate, ferrous sulphate and ferric chloride, as chemical coagulants at 0.8, 2 and 4 g/L. These concentrations were selected on the basis of previous studies<sup>[11]</sup> and adapted to this specific effluent. Experiments were performed in order to determine the most convenient operational conditions for organic matter removal, e.g. pH value and coagulant/flocculant dosages were evaluated. In each test, 250 mL sample was poured into the beakers and pH was adjusted to different values

within the optimal range of each coagulant:  $\text{Ca}(\text{OH})_2$  from 7 to 10;  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  from 6 to 9;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  from 8 to 11 and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  from 5 to 8. Afterwards, a specified dosage of coagulant/flocculant was added to the effluent and appropriate contact times were applied: 3 min of rapid mixing at 120 rpm for coagulation, 20 min of slow mixing at 20 rpm for flocculation and 60 min of settling to promote solids sedimentation. After sedimentation, the supernatant was withdrawn from a point located about 2 cm below the top of the liquid level for COD and total polyphenols content measurement, thus it was possible to ensure that no flock or foam was removed with the sample.

#### ii. Fenton's reagent

Fenton's treatment was carried out at ambient temperature according to the following sequential steps. Initially, 500 mL of leachate was put in a 1000 mL beaker and magnetically stirred; pH was adjusted to fixed values (2.9 - 3.1) by adding  $\text{H}_2\text{SO}_4$  95-97% (w/w). Then, 20 mg  $\text{Fe}^{2+} \text{ L}^{-1}$  was dosed by adding the necessary amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Finally, to initiate Fenton process, an initial amount of  $\text{H}_2\text{O}_2$  (17.6 mM) was added. Afterwards, this reagent was successively added in order to maintain a  $\text{H}_2\text{O}_2$  concentration around 8.8 mM during the process. Samples were withdrawn at specified reaction times and ferrous iron concentration, hydrogen peroxide and COD were immediately analysed.

#### iii. Solar photo-Fenton

Solar photo-Fenton experiments were performed using the CPC photoreactor described in section 3.2.4. Initially, and with the collector still covered, pH was adjusted to 2.8 – 3.0 and ferric iron salt ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was added. Tests were performed with an initial concentration of 20 mg  $\text{Fe}^{3+} \text{ L}^{-1}$  in solution. After reagents addition, the wastewater was well homogenised by recirculation for at least 15 min. Then, a first sample was taken (time zero), after that, an initial dosage of hydrogen peroxide (23.5 mM) was added and the CPC was uncovered (RAD-ON). Such dosage of hydrogen peroxide was higher than that used for Fenton process in order to avoid an initial shortage of this reagent, given that solar photo-Fenton's reactions are faster. The



concentration of hydrogen peroxide was monitored and restored throughout the experiment in order to keep always a value around 8.8 mM in solution (which is high enough for avoiding this reagent being a limiting factor during the chemical oxidation).

#### iv. Biocompatibility assays

In order to assess the leachate's toxicity and biodegradability, bioassays were carried out at different stages of solar photo-Fenton treatment. The photo-treated samples were evaluated after H<sub>2</sub>O<sub>2</sub> total elimination by adjusting the pH between 6.5-7.5 and adding catalase solution (2500 U/mg bovine liver). Toxicity and biodegradability were analysed by respirometric techniques using a BM-T Advance Respirometer (SURCIS S.L, Spain), which consists in a 1 L capacity vessel, provided with an oxygen probe (Hamilton), pH and temperature control system. The activated sludge used in the bioassays was collected from a conventional municipal wastewater treatment plant and subjected to characterization through DOC, ammonium, nitrate concentration, TSS and VSS measurements. The respirometer was loaded with the required amount of activated sludge according to the manufacturer specifications. Afterwards, in order to inhibit the nitrification process and measure the sample effect only on the heterotrophic bacteria, 3 mg of N-allylthiourea per gram of volatile suspended solids (VSS) was added to the activated sludge half an hour before the beginning of each trial. Continuous aeration and agitation were applied to ensure air saturation conditions. Temperature was maintained at 20° C during the tests.

#### v. Toxicity analysis

For toxicity analyses, respirometer was loaded with 1 L of endogenous activated sludge. Temperature was controlled at 20 °C and the system was continuously aerated and agitated. This analysis compares maximum bacterial oxygen uptake rate (OUR<sub>max</sub>) in a reference with that of the target sample. The reference was 30 mL of distilled water with 0.5 g of sodium acetate g<sup>-1</sup> VSS. Moreover, 30 mL of sample was added to obtain the OUR<sub>max-sample</sub>. Tests were extended until the biomass reached the maximum respiration rate and the inhibition percentage of each sample is expressed quantitatively according to the following equation:

$$Inhibition(\%) = 100 \times \left( 1 - \frac{OUR_{\max-sample}}{OUR_{\max-reference}} \right) \quad (E3.2)$$

where  $OUR_{\max-sample}$  and  $OUR_{\max-reference}$  are expressed in terms of  $\text{mg O}_2 \text{ L}^{-1} \text{ h}^{-1}$ .

#### vi. Biodegradability

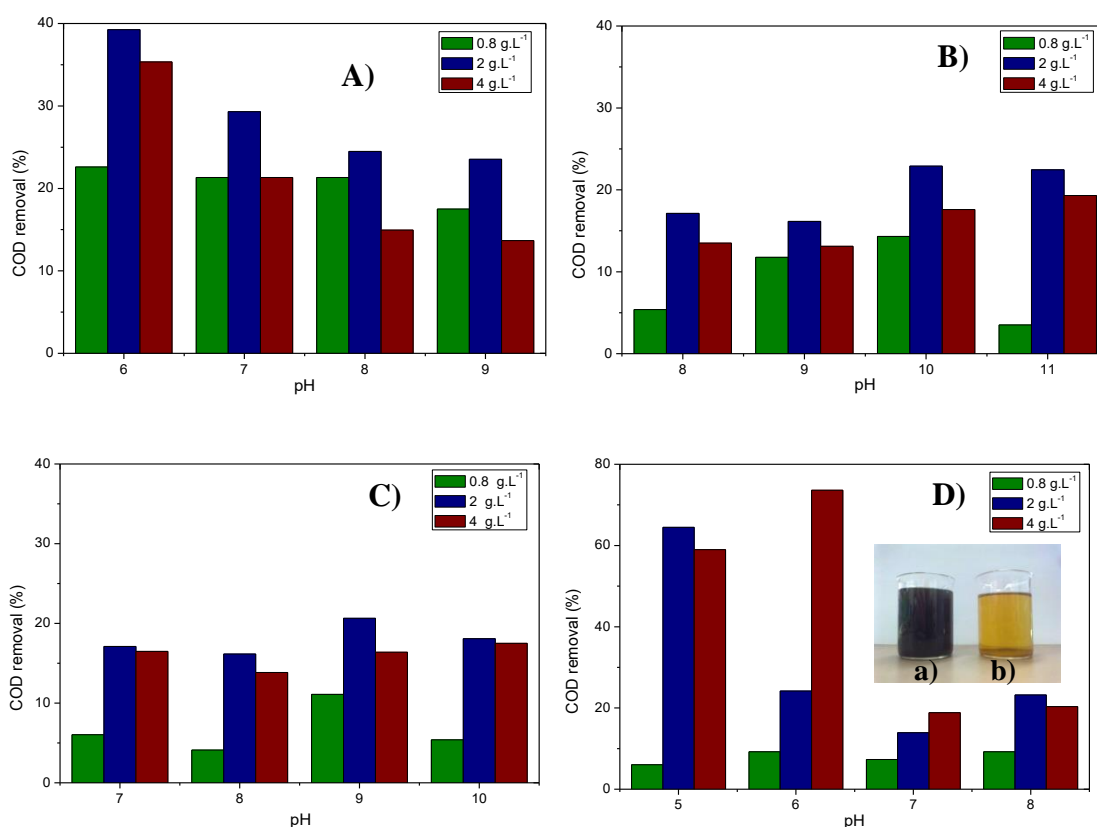
In these assays, 700 mL of endogenous activated sludge were introduced in the respirometer and aerated until saturation. At that moment, 300 mL of oxygen-saturated target sample were added and the test started. The ratio  $\text{COD}_{\text{rb}}/\text{COD}$  (ready biodegradable COD/total COD) allows establishing the biodegradable character of the sample. A sample is considered to be highly biodegradable when  $\text{COD}_{\text{rb}}/\text{COD}$  is greater than 0.8; biodegradable, when it is comprised between 0.7 and 0.8; slowly biodegradable when the ratio is 0.3 – 0.7, slightly biodegradable when the ratio is between 0.1 and 0.3 and non-biodegradable when it is lower than 0.1 (according to instructions given by the respirometer's manufacturer, SURCIS S.L.).

### 3.3. Results and Discussion

#### 3.3.1. *Coagulation/flocculation stage*

Coagulation/flocculation stage is essential to reduce total suspended solids, organic content and colour in order to improve later treatment's efficiency. Leachate's dark colour is mainly due to the presence of high concentrations of humic substances which represent the majority of organic compounds in the leachate<sup>[29]</sup>. Additionally, these substances are considered to be hydroxyl radical scavengers. Furthermore, without suspended solids and dark colour, light can better penetrate through the solution to trigger the photo-Fenton reaction. In addition, lower turbidity values favour Fenton performance, too.

The efficiency of these physicochemical methods depends on many factors including the presence of inorganic and organic substances in the leachate, pH, stirring velocity and reaction time. The stability of colloidal aggregates results from intermolecular forces that keep the particles in suspension. These pollutants cannot agglomerate unless the pH is adjusted to the isoelectric point.



**Figure 3.1** - Effect of pH and coagulant dosage in COD removal from raw landfill leachate by coagulation/flocculation: (A) aluminium sulphate, (B) ferrous sulphate, (C) calcium hydroxide and (D) ferric chloride. Inset: (a) raw landfill leachate and (b) after ferric chloride coagulation using 2 g L<sup>-1</sup> and pH=5.

From data in Figure 3.1 and Table 3.2 it is possible to say that the highest COD removal was obtained at pH 6 using 4 g L<sup>-1</sup> of FeCl<sub>3</sub>. Calcium hydroxide revealed low COD removal capacity although, by adding 2 g L<sup>-1</sup> at pH 9, it was improved attaining 21% of COD removal. Noticeably, it cannot be observed further COD reduction through the increase of the coagulant dosage to 4 g L<sup>-1</sup>. This behaviour can be explained by the charge neutralization theory. When coagulants were added to the leachate, cations and its hydrolysed products interacted with negative colloids and neutralized their charges which promoted the colloids destabilization. Over the appropriate dosage, colloids can absorb the cations and become positively charged, hence, may be stable again as a result of electrical repulsion, diminishing the capacity of organic matter removal. Adding aluminium sulphate allows reaching 39% of COD reduction, 26% of total polyphenols and 6% turbidity. Concerning the different dosages tested, it can be said that, in general, 4 g L<sup>-1</sup> of coagulant provides lower removal when compared with 2

$\text{g L}^{-1}$  and  $0.8 \text{ g L}^{-1}$ . Therefore, the most efficient experimental conditions of aluminium sulphate were at pH 6 for  $2 \text{ g L}^{-1}$ .

Regarding ferrous sulphate the best COD removal was obtained with high pH values. COD removals of around 20% were reached with  $2 \text{ g L}^{-1}$  of coagulant at pH 10 and 11. Regarding turbidity and total polyphenols, removals of 31% and 1%, respectively, were attained for those pH values.

**Table 3.2** - Effect of different coagulants/flocculants when applied to raw leachate under optimal pH range for each reagent and different concentrations (0.8, 2 and 4 g L<sup>-1</sup>). Results in % removal of (A) polyphenols and (B) turbidity.

(A)												
pH	<i>Ca(OH)<sub>2</sub></i>			<i>Al(SO<sub>4</sub>)<sub>3</sub></i>			<i>FeSO<sub>4</sub></i>			<i>FeCl<sub>3</sub></i>		
	0.8	2.0	4.0	0.8	2.0	4.0	0.8	2.0	4.0	0.8	2.0	4.0
<b>5</b>	-	-	-	-	-	-	-	-	-	10	<b>71</b>	63
<b>6</b>	-	-	-	21	<b>26</b>	22	-	-	-	6	24	<b>82</b>
<b>7</b>	7	11	<b>12</b>	5	6	6	-	-	-	11	7	45
<b>8</b>	4	7	6	3	13	11	0	0	4	0	5	38
<b>9</b>	0	3	3	3	5	7	7	<b>8</b>	<b>8</b>	-	-	-
<b>10</b>	0	2	3	-	-	-	6	0	0	-	-	-
<b>11</b>	-	-	-	-	-	-	1	1	1	-	-	-

(B)												
pH	<i>Ca(OH)<sub>2</sub></i>			<i>Al(SO<sub>4</sub>)<sub>3</sub></i>			<i>FeSO<sub>4</sub></i>			<i>FeCl<sub>3</sub></i>		
	0.8	2.0	4.0	0.8	2.0	4.0	0.8	2.0	4.0	0.8	2.0	4.0
<b>5</b>	-	-	-	-	-	-	-	-	-	13	<b>83</b>	80
<b>6</b>	-	-	-	5	6	33	-	-	-	6	18	67
<b>7</b>	<b>34</b>	22	21	20	28	28	-	-	-	1	22	0
<b>8</b>	32	8	9	16	26	25	36	17	16	0	0	0
<b>9</b>	31	6	8	17	32	<b>35</b>	49	<b>68</b>	51	-	-	-
<b>10</b>	0	0	1	-	-	-	32	31	29	-	-	-
<b>11</b>	-	-	-	-	-	-	0	24	26	-	-	-

In general, trials in which ferric chloride was used exhibited better results when a dosage of 4 g L<sup>-1</sup> was added. However, it is important to highlight those highly acceptable results in terms of removal of COD (63%) and polyphenols (71%) were also

obtained when adding 2 g L<sup>-1</sup> at pH 5 (closer to the optimal pH for photo-Fenton better performance). The photo inset Figure 3.1 (D) confirms the high removals of colour and turbidity by ferric chloride. Table 3.3 presents the main characteristics of the leachate before and after each coagulation/flocculation test under the best conditions, excluding calcium hydroxide due to its low efficiency.

**Table 3.3** - Evolution of leachate characteristics during coagulation/flocculation treatment processes.

<i>Parameter</i>	<i>Raw leachate</i>	<i>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (2 g L<sup>-1</sup>)</i>	<i>FeSO<sub>4</sub> (2 g L<sup>-1</sup>)</i>	<i>FeCl<sub>3</sub> (2 g L<sup>-1</sup>)</i>	<i>FeCl<sub>3</sub> (4 g L<sup>-1</sup>)</i>
<b>pH<sub>initial</sub></b>	7.8	6.0	10.0	5.0	6.0
<b>pH<sub>final</sub></b>	-	7.3	9.9	3.2	5.4
<b>Turbidity (NTU)</b>	140	132	97	24	45
<b>COD (mg O<sub>2</sub> L<sup>-1</sup>)</b>	5700	3460	4395	2100	1480
<b>Total Polyphenols (mg gallic acid L<sup>-1</sup>)</b>	750	552	815	216	134

A global analysis of these coagulation/flocculation experiments performed within the optimal pH range for each reagent reveals that lower pH values are most suitable to treat a mature landfill leachate. Additionally, high removals of COD and total polyphenols were obtained with aluminium sulphate (pH 6) and ferric chloride (pH 5 and 6).

Consequently, it is possible to say that Fe<sup>3+</sup> and Al<sup>3+</sup> cations are the most indicated coagulant/flocculant agents to reduce landfill leachate's organic load, turbidity and colour. In the case of FeCl<sub>3</sub>, this behaviour can be explained by the different hydrolysed species of ferric iron. In basic conditions, ferric iron (Fe<sup>3+</sup>) can react with hydroxyl (OH<sup>-</sup>) and form Fe(OH)<sub>3</sub> that promotes flocculation. It must be also mentioned that both reagents can act simultaneously as coagulant and flocculant, promoting the best destabilization and aggregation of colloids<sup>[12]</sup>. Recent works clearly reveal that iron salts are more efficient than aluminium ones, resulting in significant COD reductions (up to 50%), whereas the corresponding values in case of aluminium or lime addition achieve moderate reductions between 10 and 40%<sup>[3]</sup>. Daud *et al.*<sup>[11]</sup> also reports ferric

chloride as the most efficient chemical in their study which led to 84% of colour removal and 37% of COD elimination.

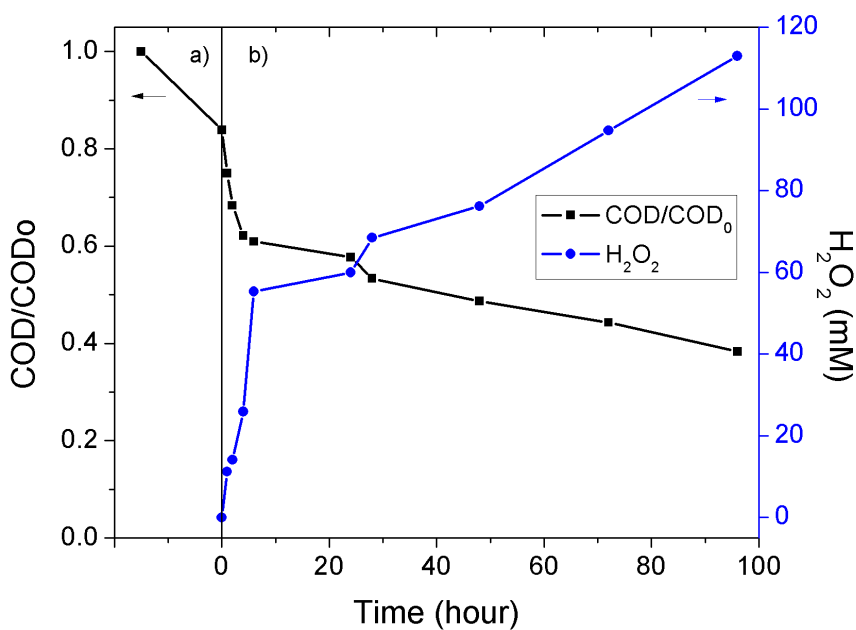
According to the discussion presented above, ferric chloride was selected as the most convenient coagulant agent under the following experimental conditions: pH 5 and a dose of 2 g L<sup>-1</sup>, achieving removals of 63% for COD and 71% for total polyphenols. Another important effect obtained with this coagulant was the highest reduction of turbidity, from 140 to 24 NTU.

Once the best conditions for leachate pre-treatment by coagulation/flocculation were determined, this physicochemical treatment was performed at pilot plant scale. Afterwards, the supernatant was transferred to the recirculation tank of the CPC pilot plant, once pH adjustment to 3 and sludge sedimentation had taken place.

### ***3.3.2. Chemical oxidation by Fenton Reagent***

After physico-chemical pre-treatment leachate remained non-toxic (11% of inhibition). However, biodegradability ratio worsened (COD<sub>rb</sub>/COD=0.09, very little biodegradable). This last fact points out that a biological oxidation cannot be performed just after the conditioning stage. Thus, a further chemical oxidation process must be carried out. The efficiency of the advanced oxidation process known as Fenton's reagent was evaluated for the treatment of the leachate under study. Initially, Fenton reagent was applied to the raw leachate without any pre-treatment, using 20 mg L<sup>-1</sup> of Fe<sup>3+</sup> at pH 3, and an initial dose of H<sub>2</sub>O<sub>2</sub> of 17.6 mM (with subsequent additions of this reagent to maintain a constant concentration of 8.8 mM) (Figure 3.2). In these experiments it was possible to reach a COD removal of 63%, reducing COD from 5700 mg L<sup>-1</sup> to 2100 mg L<sup>-1</sup> but requiring large quantities of hydrogen peroxide (113 mM). It was necessary a reaction time of 96 hours to achieve this removal which indicates a slow oxidation rate. In addition, previously to the beginning of Fenton process, pH adjustment to 3 originated foam, suspended solids sedimentation and subsequently sludge formation. In this step, a COD reduction of about 15% was verified and the leachate dark-brown colour became clearer. This acidifying step promoted an acid cracking that led to significant COD and phenol removals, as well as to significant amount of oil and grease reductions<sup>[30]</sup>. Considering the insufficient COD removal

obtained with the coagulation/flocculation step, a further treatment process must be applied. Therefore, it was decided to test the combination between coagulation/flocculation (using ferric chloride under the best operating conditions previously selected in section 3.3.1) and Fenton reagent.

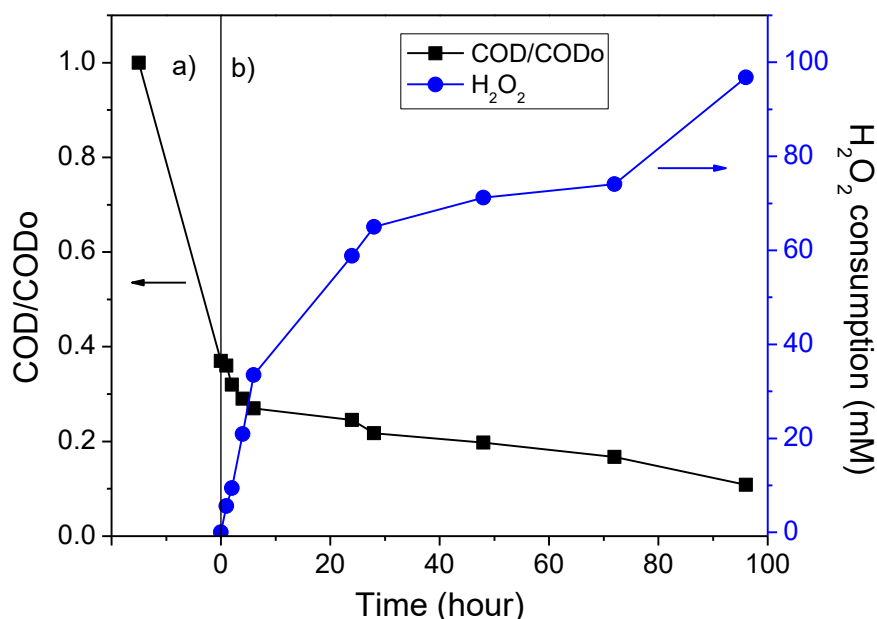


**Figure 3.2** - COD, H<sub>2</sub>O<sub>2</sub> and pH evolution in Fenton reagent process: (a) pH adjustment and (b) Fenton process. Experimental conditions: pH=3; [FeSO<sub>4</sub>]<sub>0</sub> = 200 mg L<sup>-1</sup>.

Figure 3.3 shows the evolution of COD and hydrogen peroxide consumption during Fenton process, after a pre-treatment step with ferric chloride (2 g L<sup>-1</sup>). As it can be observed, an initial coagulation/flocculation step with ferric chloride involved a 63% of COD removal.

Further combination with Fenton process allowed a total COD removal of 89% after 96 hours of reaction and 96.8 mM of H<sub>2</sub>O<sub>2</sub> consumption. As it can be seen in Figure 3.3, during the first three hours the removal rate was higher than for longer treatment times. The observed lower rate after the first hours could be explained by Fe<sup>3+</sup> complexation by carboxylic intermediates formed during oxidation that prevent the regeneration of Fe<sup>2+</sup> needed for Fenton process<sup>[22]</sup>. These complexes slow down the Fenton reaction, not allowing an efficient COD removal and so H<sub>2</sub>O<sub>2</sub> is inefficiently consumed. In any case, coagulation/flocculation with FeCl<sub>3</sub> at pH 5 highly improved the global removal efficiency of raw leachate's organic charge.





**Figure 3.3** - Coagulation/flocculation with  $\text{FeCl}_3$  ( $2 \text{ g L}^{-1}$ ; pH 5) combined with Fenton reagent: (a) coagulation step; (b) Fenton process (initial experimental conditions: pH=2.9-3.1,  $[\text{Fe}^{3+}]_0 = 20 \text{ mg L}^{-1}$  in solution,  $[\text{H}_2\text{O}_2]_0 = 17.6 \text{ mM}$ ).

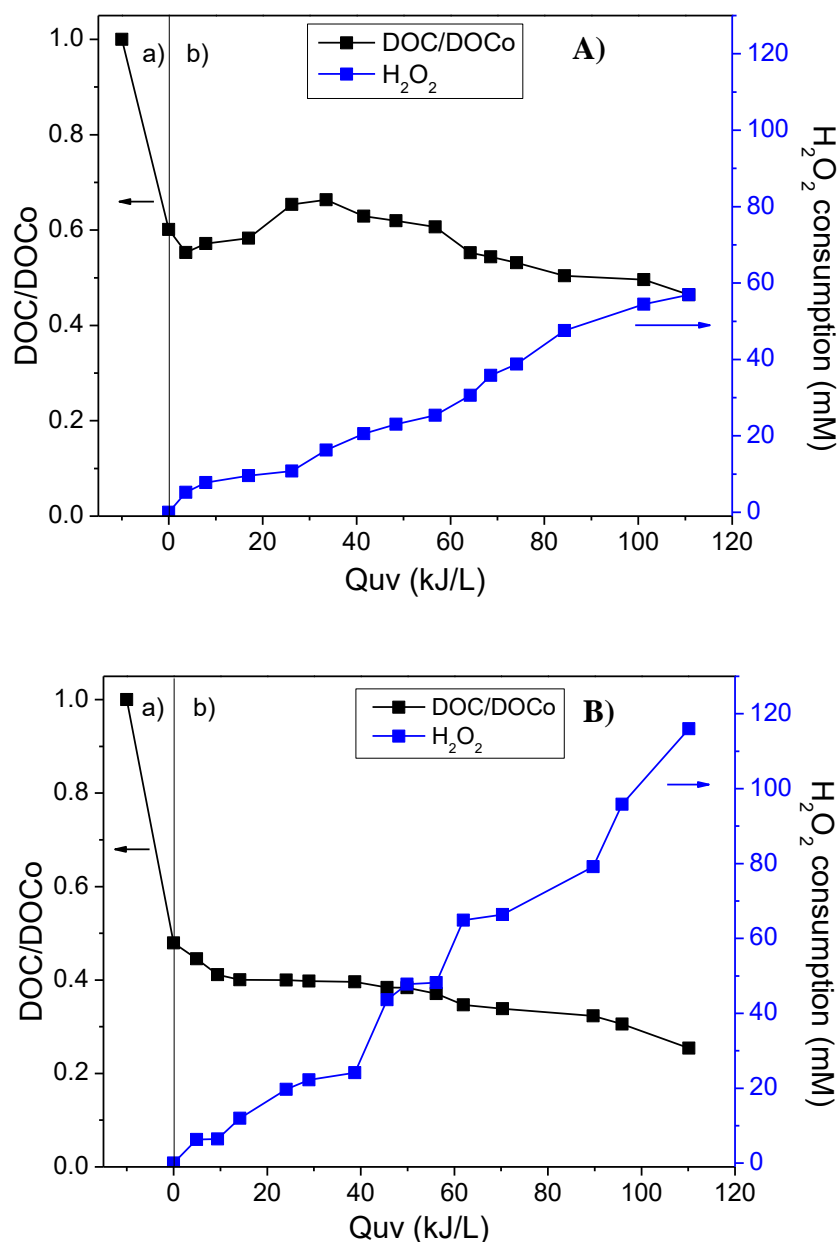
Both Fenton's reagent tests allowed reaching a significant removal of COD, although it is a very slow process. Regardless of high COD removals, Fenton process was not efficient enough to allow the direct release of treated leachate into natural water streams, even when coagulation/flocculation was combined with Fenton's reagent (final COD of  $620 \text{ mg L}^{-1}$  but the legal discharge limit is stated below  $150 \text{ mg L}^{-1}$ ).

### 3.3.3. Solar photo-Fenton process

Given that iron complexation by carboxylic intermediates generated during Fenton oxidation was one of the major drawbacks of that process, photo-Fenton process could be a good alternative. These complexes are usually photoactive<sup>[22]</sup>, and  $\text{Fe}^{2+}$  regeneration and additional  $\text{HO}^\bullet$  generation are also favoured. Therefore, solar photo-Fenton experiments were applied to leachate at a constant temperature of  $35^\circ\text{C}$ , pH between 2.9 – 3.1 and an initial  $\text{H}_2\text{O}_2$  dosage of 17.6 mM.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was used as iron ( $\text{Fe}^{3+}$ ) source. Direct solar photo-Fenton treatment of leachate and solar photo-Fenton in combination with coagulation/flocculation under the same experimental conditions were compared.

Solar photo-Fenton experiments were monitored by DOC measurement in order to get a deeper knowledge of the mineralization level reached with this AOP. COD was measured only for samples selected for toxicity and biodegradability analysis due to the special complexity of the wastewater and the presence of  $\text{H}_2\text{O}_2$ , which normally provokes low accurate COD values. In direct solar photo-Fenton, first step (pH adjustment of raw leachate to values around 3) promoted a DOC reduction of 42% (from  $2400 \text{ mg L}^{-1}$  of DOC to  $1400 \text{ mg L}^{-1}$ ) and after solar photo-Fenton direct treatment (see Figure 3.4 (A)) global DOC reduction of 54% was attained (after  $110 \text{ kJ L}^{-1}$  and 15.8 hours). Nevertheless, under solar photo-Fenton treatment after pre-coagulation step and pH adjustment, DOC was globally mineralized to 75% (see Figure 3.4 (B)) after  $110 \text{ kJ L}^{-1}$  of accumulative UV energy in approximately 11.5 hours. Pre-coagulation step and pH adjustment reduced 50% of initial DOC and solar photo-Fenton process 25%.

$\text{H}_2\text{O}_2$  consumption in direct photo-Fenton treatment of raw leachate was 55.9 mM but it was 116 mM when coagulation/flocculation was previously performed. This major difference can be explained by the higher mineralization attained during solar photo-Fenton process thanks to the coagulation/flocculation pre-treatment. Figure 3.4 (A) shows an initial DOC decay during pH adjustment and a later increase due to foam formation that retained DOC from leachate. This foam disappeared as photo-Fenton proceeded and DOC was released again into water. When coagulation/flocculation was applied, foam was not generated and DOC was continuously mineralized (Figure 3.4 (B)).



**Figure 3.4** - Solar photo-Fenton treatment of leachate (initial experimental conditions: pH=2.9-3.1,  $[\text{Fe}^{3+}] = 50 \text{ mg L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 23.5 \text{ mM}$ ). **A)** Direct treatment of raw leachate: (a) pH adjustment step and (b) solar photo-Fenton. **B)** Previous coagulation with  $\text{FeCl}_3$  at pH 5: (a) coagulation step and pH adjustment and (b) solar photo-Fenton process.

In both cases, before starting solar photo-Fenton process, a high DOC removal was verified due to the initial pH adjustment. During solar photo-Fenton treatment, registered pH values remained within the desired range (2.9 and 3.1).

Finally, in order to evaluate leachate's biocompatibility during the different treatment steps (coagulation/flocculation stage and solar photo-Fenton process,) toxicity

and biodegradability analysis were carried out by means of respirometric methods. Raw wastewater exhibits non-toxicity (0.5) and non-biodegradability (0.01), which agrees with the low BOD<sub>5</sub>/COD ratio (Table 3.1). Table 3.4 shows toxicity and short-term biodegradability results obtained from leachate subjected to solar photo-Fenton treatment combined with pre-coagulation using FeCl<sub>3</sub>·6H<sub>2</sub>O. Throughout the solar photo-Fenton experiment, wastewater's biodegradability increased until reaching a final low-biodegradability state (0.35 of COD<sub>rb</sub>/COD). Toxicity did not significantly change during the treatment as it was always maintained under quite low values (never higher than 20% of inhibition measured on the activated sludge's activity).

**Table 3.4** - Toxicity and short term biodegradability evolution during solar photo-Fenton process combined with coagulation/flocculation pre-treatment using FeCl<sub>3</sub>.

	<i>DOC</i> (mg L <sup>-1</sup> )	<i>COD</i> (mg L <sup>-1</sup> )	<i>Q<sub>UV</sub></i> (kJ L <sup>-1</sup> )	<i>Toxicity</i> (I%)	<i>Biodegradability</i> (COD <sub>rb</sub> /COD)*
Raw landfill leachate	2400	5700	-	0.5	0.07
Pre-treated landfill leachate	1200	3400	-	11	0.15
Solar photo-Fenton treatment	1200	3800	0	11	0.15
	950	3700	40	19	0.17
	770	2100	90	3	0.28
	420	980	110	9	0.35

Therefore, although the photo-Fenton process improved wastewater's biodegradability, it is not advisable to release the treated leachate into a biologic process as the DOC concentration was rather low when biodegradability threshold was attained. Ideally, the photo-Fenton process could be performed until legal discharge limits would be achieved or photo-Fenton could be carried out only until discharge limit into sewage (which is much higher than 150 mg L<sup>-1</sup>) would be attained.

### 3.4. Conclusions

This work presents a general protocol for identifying the best combined treatment line for the remediation of a specific landfill leachate. This protocol should

include preliminary coagulation/flocculation studies followed by application of advanced oxidation processes evaluated by both chemical analyses and bioassays.

In coagulation/flocculation process ferric chloride showed the best capacity to remove solids and colour, and reduced substantially COD from leachate. The selected conditions were pH 5 and coagulant dose of 2 g L<sup>-1</sup> of such reagent. The combination of coagulation/flocculation with Fenton led to high COD removal rates but so extended treatment time in the range of several days.

Solar photo-Fenton process combined with coagulation pre-treatment revealed a DOC reduction of 75% (final DOC of 420 mg L<sup>-1</sup> and COD of 980 mg L<sup>-1</sup>) with 110 kJ L<sup>-1</sup> of accumulated UV energy (around 11.5 hours) and a H<sub>2</sub>O<sub>2</sub> consumption of 115 mM. Under these conditions the leachate treated cannot be discharged in natural water bodies but it is improved enough to be released into public sewage where the COD legal limit is 1000 mg O<sub>2</sub> L<sup>-1</sup>.

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#### **4. COMBINED TREATMENT OF OLIVE MILL WASTEWATER BY FENTON'S REAGENT AND ANAEROBIC BIOLOGICAL PROCESS**

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#### **4. COMBINED TREATMENT OF OLIVE MILL WASTEWATER BY FENTON'S REAGENT AND ANAEROBIC BIOLOGICAL PROCESS<sup>§</sup>**

##### **Abstract**

This work presents the application of a Fenton's reagent pre-treatment combined with an anaerobic biological process to remove the olive mill wastewater (OMW) pollutant load. Initially, pre-treatment of OMW is promoted by chemical oxidation in a batch reactor, with Fenton's reagent, using a fixed weight ratio  $\text{H}_2\text{O}_2/\text{COD}$  of 0.20, a  $\text{pH} = 3.5$  and a  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio of 15 defined as optimal initial conditions. There was obtained therefore a reduction of 17.6% in COD and 82.5% in the total polyphenol content. A second phase was performed by anaerobic biodegradation assays in a batch reactor, containing microorganisms immobilized in *Sepiolite* and adapted previously to the substrate. The tests were carried out varying the substrate concentration provided to biological reactor, measured as COD. The anaerobic biological treatment itself allowed conversions from 52% to 74% of COD. The results obtained for the combined process (Fenton's reagent and anaerobic biological process) show reductions in COD ranging from 64 to 88% and allowed to calculate the yield of methane generation, ranging from 281  $\text{cm}^3$  to 322  $\text{cm}^3$  of  $\text{CH}_4/\text{g}$  COD removed. The kinetic study for the rate of methane generation was performed using the Monod model. The application of this model allowed observing an increase in the kinetic constant of the combined process ( $k_{\text{FN}} = 0.036 \text{ h}^{-1}$ ) when compared to the single anaerobic process ( $k_{\text{F}} = 0.017 \text{ h}^{-1}$ ).

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<sup>§</sup>Adapted from: Amor, C., Lucas, M.S., García, J., Dominguez, J.R., De Heredia, J.B., Peres, J.A. *Combined treatment of olive mill wastewater by Fenton's reagent and anaerobic biological process*. Journal of Environmental Science and Health, Part A. **2015**, 50, 161–168.



## **4.1. Introduction**

The olive oil industry uses some milling methods (traditional pressing, three-phase and two-phase decanting processes) that operate seasonally and produce a large volume of effluents<sup>[1]</sup>. The disposal of olive mill wastewater (OMW) is a problematic issue in the countries located in the edge of the Mediterranean. These effluents are characterized by large suspended solids content, dark red to black colour, foul-smelling, high turbidity and organic load (COD between 50 000 to 100 000 mg O<sub>2</sub> L<sup>-1</sup>). The pollution potential of these wastewaters is considerable, because their main constituent is organic matter which includes sugars, polyphenols, proteins, pectins, lipids, etc.<sup>[2]</sup> When released into the environment, OMW create serious deteriorations such as colouring of natural waters, changes in soil quality, antimicrobial characteristics and phytotoxicity. Due to these environmental problems and potential hazards caused by OMW many countries have restricted their discharge limits into natural waters and tried to develop new technologies for reducing its contaminant character.

Anaerobic digestion has been recognized in recent years as a viable form of treating effluents with high organic load. It is generally accepted that these processes have some advantages compared to aerobic treatment: low cost, reduced energy requirements and reduced amount of nutrients. Additionally these processes present the advantage of generating biogas with the corresponding energy saving<sup>[3]</sup>. However, several problems associated with OMW toxicity and biodegradability have been found during anaerobic treatments. This occurs as some microorganisms, like methanogenic bacteria, are particularly sensitive to the organic compounds present, especially polyphenols which limits application of anaerobic digestions<sup>[4]</sup>. Some pre-treatments which remove polyphenols and facilitate the anaerobic digestion were introduced. Among them, some chemical processes have been successfully investigated<sup>[5-8]</sup>.

Advanced oxidation processes (AOPs) are known for their capability to mineralize a wide range of organic compounds. AOPs applied to OMW include ozonation<sup>[9]</sup>, combination of ultrafiltration and UV/H<sub>2</sub>O<sub>2</sub><sup>[10]</sup>, combination of UV/H<sub>2</sub>O<sub>2</sub> and lime<sup>[11]</sup>, conductive diamond electro-oxidation<sup>[12]</sup>, wet air oxidation<sup>[13]</sup>, catalytic wet air oxidation<sup>[14]</sup>, supercritical water oxidation, UV/TiO<sub>2</sub><sup>[16]</sup>, solar photocatalysis with

TiO<sub>2</sub> and solar photo Fenton<sup>[17]</sup> Justino *et al.*<sup>[18]</sup> and Duarte *et al.*<sup>[19]</sup> presented the OMW potential treatment by biocomposites of silica-alginate–fungi (*Pleurotus sajor caju* and *Trametes versicolor*).

Rivas *et al.*<sup>[20]</sup> reported Fenton's treatment of OMW diluted with a synthetic urban wastewater. Gomec *et al.*<sup>[21]</sup> applied Fenton's oxidation to OMW after acid cracking and cationic polyelectrolyte treatment while Beltran-Heredia *et al.*<sup>[9]</sup> and Lucas *et al.*<sup>[22]</sup> combine Fenton's reagent with aerobic biological treatment. Treatment of olive mill wastewater was also studied by Fenton reagent<sup>[23]</sup> and by a combined process: Fenton's reagent and chemical coagulation<sup>[24]</sup>. El-Gohary *et al.*<sup>[25]</sup> used an integrated treatment scheme consisting of wet hydrogen peroxide catalytic oxidation (WHPCO) followed by two-stage upflow anaerobic sludge blanket (UASB) reactor for the treatment of OMW.

Fenton's reagent, a catalytic oxidation process based on the homogeneous reaction of hydrogen peroxide with ferrous ions, presents several valuable features for the oxidation of organic compounds. The chemicals involved are commonly available, inexpensive, easy to handle and the final decay products after the oxidation reaction are significantly less contaminant than the original organic pollutants. The fundamental Fenton reaction generates hydroxyl radicals that have a high oxidation potential:<sup>[26]</sup>



The optimum performance of Fenton's reagent occurs in acidic medium at pH values between 3 and 4. In addition to main reaction above are several possible competitive reactions involving Fe<sup>2+</sup>, Fe<sup>3+</sup>, H<sub>2</sub>O<sub>2</sub>, hydroxyl radicals and superoxide radicals<sup>[27]</sup>.

Although the cost of COD removal through chemical oxidation processes is usually higher than the biological processes, there will be specific situations where its use can be justified. For instance, the elimination or partial degradation of pollutants present in highly toxic and recalcitrant wastewater.

This research work intends to present a viable treatment process to high load OMW. The study carried out the OMW treatment by the combination of Fenton's reagent and anaerobic digestion. Therefore, it is expected the degradation of complex

organic acids' by Fenton's reagent, allowing further OMW treatment by conventional anaerobic processes.

## **4.2. Materials and methods**

### ***4.2.1. Olive mill wastewater***

The original OMW used in this study was obtained from an olive oil production plant located at Extremadura Community (southwest of Spain) which uses the traditional mill and pressing process. Wastewater samples, with a dark red-brown colour, were collected from the tanks of the classical mills and stored at 4°C during the transport to the laboratory and immediately analysed.

Table 4.1 summarizes the main physico-chemical characteristics of OMW. After this characterization, and before experiments, OMW was stored at -20° C in plastic cans. For each experiment a new frozen sample was used in order to minimise discrepancies between experiments.

**Table 4.1** - Physico-chemical characteristics of olive mill wastewater.

<b>Parameter</b>	<b>Value</b>
pH	4.8
BOD <sub>5</sub> (g O <sub>2</sub> L <sup>-1</sup> )	32.1
COD (g O <sub>2</sub> L <sup>-1</sup> )	92.5
TKN (g NL <sup>-1</sup> )	0.37
Suspended solids (g L <sup>-1</sup> )	67.5
Volatile solids (g L <sup>-1</sup> )	40.2
Total polyphenols (g caffeic acid L <sup>-1</sup> )	2.10
Alkalinity (g CaCO <sub>3</sub> L <sup>-1</sup> )	2.26
Total phosphorous (g P L <sup>-1</sup> )	1.82
Biodegradability (BOD <sub>5</sub> /COD)	0.35

#### 4.2.2. Experiments

##### OMW pre-treatment with Fenton's reagent

The Fenton experiments with OMW were performed according to Lucas and Peres<sup>[23]</sup> in a stirred jacketed glass batch reactor (2 L capacity) with temperature control through a Julabo F25-MP thermostatic bath. The temperature was kept constant at 20°C. The pH adjustment was carried out with diluted sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (NaOH) solutions. Experiments were carried out with 1.5 L of OMW to which a weighted amount of FeSO<sub>4</sub>·7H<sub>2</sub>O was added and dissolved under continuous stirring. Fenton oxidation began with the addition of hydrogen peroxide (30% w/w).

Samples were withdrawn from the reactor at pre-determined times, to analyse COD and TP concentrations, and reaction was stopped by adding excess amount of Na<sub>2</sub>SO<sub>3</sub>, which instantaneously consumes the remaining hydrogen peroxide. When the experiments ended, a certain amount of the wastewater treated with Fenton (with a pH correction to 7) was loaded into the bioreactor of anaerobic degradation experiments.

##### Anaerobic biological treatment of OMW

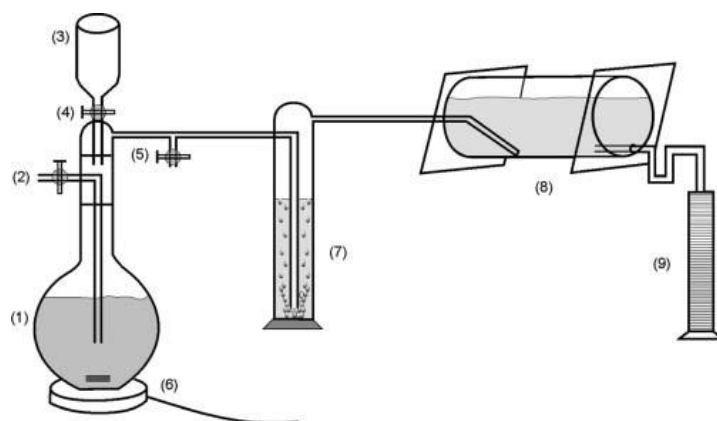
Biologic experiments were performed in a discontinuous anaerobic digestion reactor (Figure 4.1). This unit consisted of a glass container with 3 L of capacity, with a double function outlet side: output of the biogas formed and inert gas bubbling at the beginning of the experiment.

This unit, with magnetic stirring, was submerged in a thermostatic bath that ensured a constant temperature (35°C ± 0.2°C). Anaerobic biomass was collected from a municipal wastewater treatment plant and used as inoculum. This inoculum was adapted to OMW during a preliminary period of 12 weeks.

The microorganisms were supported on *Sepiolite* (magnesium silicate, Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O). Methane produced was measured using a deposit type Boyle Mariotte initially filled with water, coupled to the digester. Biogas passing in an intermediate position by a trap, containing a solution of sodium hydroxide, to retain the CO<sub>2</sub> produced during the fermentation. The amount of generated methane corresponds, in an indirect way, to the volume of water displaced.



Each experiment began with the feeding of a certain volume of wastewater, added to the reaction medium, replacing an equal volume to the feed. The extension of each experiment was equivalent to the time required to complete biomethanation of each load. The amount of methane produced was determined at regular times.



**Figure 4.1** - Schematic representation of batch anaerobic digestion unit: (1) standard round-bottom flask with a magnetic stirrer; (2) lateral outlet; (3) wastewater inlet; (4) clamp; (5) gas outlet; (6) adjustable stirrer; (7) gas trap with alkaline solution to remove carbon dioxide; (8) one litre Boyle-Mariotte container type; (9) graduate beaker.

#### **4.3.3. Reagents**

Research grade reagents used during experiments were:  $\text{H}_2\text{O}_2$  (30% w/w),  $\text{Na}_2\text{SO}_3$ ,  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$  from Merck (Portugal) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  from Panreac (Portugal). Ultrapure distilled-deionised water was collected from a Milli-Q (Millipore Co.) system. Other chemicals used in these experiments were reagent grade and they were used as received.

#### **4.3.4. Analytical methods**

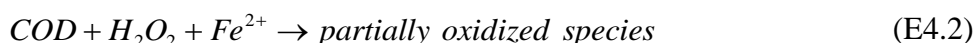
The COD analyses were performed by the dichromate closed reflux Colorimetric Method, using a Hach DR2010 Model spectrophotometer according with Standard Methods (for a COD range  $0\text{--}1500 \text{ mg O}_2 \text{ L}^{-1}$ ). Biological oxygen demand ( $\text{BOD}_5$ ) was evaluated by the respirometric method using an OXITOP system (OxiTop, WTW). Hydrogen peroxide concentration was determined using titanium (IV) oxysulfate (DIN 38 402 H15 method) at 410 nm. Total polyphenol content was measured in filtered

samples by spectrophotometry at 765 nm using the Folin-Ciocalteu reagent (Merck). The polyphenol content is expressed as mg L<sup>-1</sup> of caffeic acid. Other wastewater parameters were analysed according to Standard Methods. Experiments were performed in duplicate and the observed standard deviation was less than 5% of the reported value.

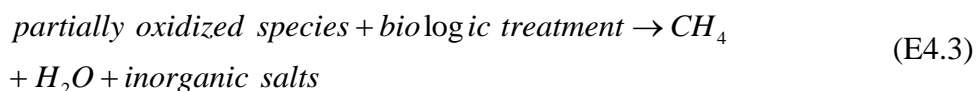
### 4.3. Results and discussion

Treatment of OMW has been investigated by the sequential combination of a Fenton's reagent (Eq. 4.2) followed by an anaerobic process (Eq. 4.3).

Step 1:



Step 2:



#### 4.3.1. Pre-treatment of OMW by Fenton's reagent

Chemical oxidation of OMW with Fenton's reagent was studied in order to minimize the impact of OMW discharge in a biologic reactor. The low BOD<sub>5</sub>/COD ratio of the OMW (Table 4.1) suggests a difficult treatment of this effluent by biological means. In that way, Fenton's reagent was applied as a pre-treatment trying to increase the OMW biodegradability.

The extension of OMW oxidation and the cost of Fenton's reagent application are depending upon the H<sub>2</sub>O<sub>2</sub> amount used. However, sometimes it is not necessary to achieve the complete mineralization of the organic compounds in carbon dioxide and water. The partial oxidation in intermediate compounds minimizes the consumption of chemicals reagents and often results in substantial reductions of COD and toxicity. Therefore, organic load and toxicity decrease and a biological treatment can be successfully applied.

Preliminary experiments were performed in order to determine the influence of pH, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> dosages on the Fenton' reagent treatment efficiency. A fixed

H<sub>2</sub>O<sub>2</sub>/COD ratio of 0.20, a pH = 3.5 and a H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> molar ratio of 15 were defined as optimal conditions to treat the OMW studied by Fenton's oxidation. Table 4.2 lists the Fenton's reagent results obtained under the selected optimal experimental conditions to treat OMW.

**Table 4.2 - Pre-oxidation of OMW with Fenton's reagent.**

T	[H <sub>2</sub> O <sub>2</sub> ]	[Fe <sup>2+</sup> ]	COD <sub>0</sub>	COD <sub>f</sub>	TP <sub>0</sub>	TP <sub>f</sub>	X <sub>COD</sub>	X <sub>TP</sub>
(°C)	(mol L <sup>-1</sup> )	(mol L <sup>-1</sup> )	(g L <sup>-1</sup> )	(g L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(%)	(%)
30	0.55	0.0367	92.5	76.2	2 095	366	17.6	82.5

Where: COD<sub>0</sub> and COD<sub>f</sub> = initial and final values of COD, TP = total polyphenol index; TP<sub>0</sub> and TP<sub>f</sub> = initial and final values of TP; X<sub>COD</sub> = percentage reduction of COD; X<sub>TP</sub> = percentage reduction of TP.

Table 4.2 shows that Fenton experiments allowed a COD conversion of only 17.6%. This low conversion can be explained by the fact that, although the organic compounds are very reactive towards hydroxyl radicals, numerous intermediates made of smaller molecules with less pollutant character are often generated. However, as these intermediates still demand oxygen to reach their final stage of oxidation, the reduction of COD is low.

On the other hand, Table 4.2 also depicts the initial and final values of the total phenolic compounds (TP<sub>0</sub> and TP<sub>f</sub>) and its conversion (X<sub>TP</sub>). As can be observed for this parameter, an important removal of 82.5% is reached after 8 hours of reaction. This phenolic fraction present in OMW is the main limiting factor to anaerobic digestion application, since they are refractory and even toxic to methanogenic bacteria. Their elimination will reduce the OMW toxicity allowing a later anaerobic treatment.

#### **4.3.2. Anaerobic biological degradation**

OMW pre-treated with Fenton's reagent was further submitted to an anaerobic biologic step (experiments FN-i). Simultaneously, there were performed anaerobic experiments with the raw OMW (experiments N-i).

Table 4.3 shows the initial and final values of COD present in the anaerobic reactor ( $COD_0$  and  $COD_f$  respectively) and the COD value corresponding to the volume of wastewater fed to the reactor at the beginning of each experiment (defined as  $COD_{al}$ ).

**Table 4.3** - Anaerobic digestion of OMW (Ni) and pre-oxidized with Fenton (FN-i).

Exp.	$COD_{al}$ (g)	$COD_0$ (g L <sup>-1</sup> )	$COD_f$ (g L <sup>-1</sup> )	$X_{COD}$ (%)	$V_{CH_4}$ (mL)	$Y_{CH_4}$ (mL CH <sub>4</sub> /g COD)
N-1	1.0	3.45	3.08	74.0	209	282
N-2	2.0	4.20	3.49	71.0	420	296
N-3	3.5	4.50	3.53	55.4	570	294
N-4	7.0	6.16	4.32	52.6	1022	278
FN-1	1.0	4.85	4.41	88.0	263	299
FN-2	3.5	6.39	5.10	73.7	650	322
FN-3	5.0	6.66	5.07	63.6	1025	322
FN-4	7.0	7.55	5.22	66.6	1310	281

The degradation level reached at the end of each test was measured as the conversion of COD ( $X_{COD}$ ) which in this specific case is determined by the following equation:

$$X_{COD} = \frac{(COD_0 - COD_f) \times V}{COD_{al}} \times 100 \quad (E4.4)$$

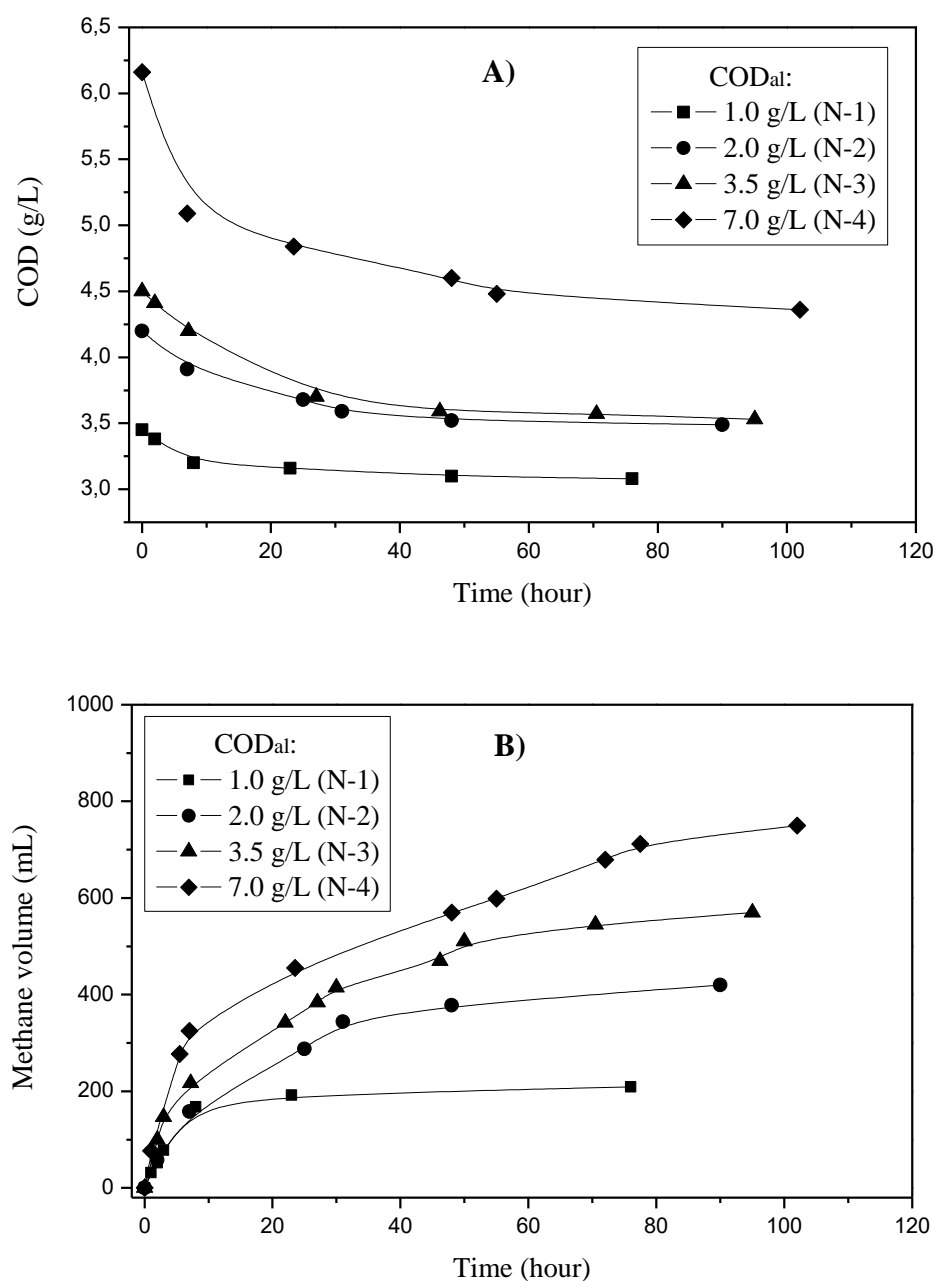
V is the volume of the anaerobic bioreactor. In Table 4.3  $V_{CH_4}$  represents the volume of methane accumulated at the end of each experiment and  $Y_{CH_4}$  represents the coefficient of methane generation (mL of CH<sub>4</sub>/g of substrate consumed). This parameter is defined as the amount of methane produced per unit of COD degraded, so that can be determined by the equation:

$$Y_{CH_4} = \frac{V_{CH_4}}{(COD_0 - COD_f) \cdot V} \quad (E4.5)$$

As it can be seen in Table 4.3, the conversion of COD values for anaerobic digestion of OMW experiments (N-i) are between 52.6% and 74.0%, indicating that much of the substrate fed to the reactor at the beginning of each experiment is degraded. These results demonstrate a reasonable behavior of anaerobic microorganisms in the

degradation of olive mill wastewater and in the range of initial concentrations used in this investigation.

Figure 4.2 (A) presents the results obtained with the anaerobic digestion treatment, after 120 h.



**Figure 4.2 - A)** Evolution of substrate concentration (COD) in the anaerobic digestion of OMW; **B)** Evolution of methane volume generated in the anaerobic digestion of OMW for experiments where  $COD_0$  was varied.

The COD concentration decreased continuously with degradation time in all experiments until a constant value was reached corresponding to the non-biodegradable substrate fraction. This remaining non-biodegradable organic matter is due to the presence of components like phenols and polyphenols which are very refractory to microbial flora breakdown. On the other hand the volume of methane produced ( $V_{CH_4}$ ) was measured through each experiment. Figure 4.2 (B) shows the  $V_{CH_4}$  values versus time: it can be observed that the highest production rate at initial times of reaction is obtained in experiments where the  $COD_{al}$  was highest. The final values of methane formed in every experiment  $V_{CH_4}$  are given in Table 4.3.

It is worth highlighting that increasing the load of the COD fed to the reactor 1.0 g to 7.0 g, decreases the final conversion of COD. This observation may be attributed to the toxic nature and inhibition effect of some compounds present in olive mill wastewater<sup>[28,29]</sup> which are present in equivalent amounts proportional to the load of effluent fed to the anaerobic reactor.

Indeed, the anaerobic digestion of olive mill wastewater is not easy due to the fact that although it has readily biodegradable compounds, as the carbohydrates, it also has aromatic and fatty acids of difficult degradation.<sup>[28]</sup> The methane formation, which represents the rate limiting step in the anaerobic digestion of soluble compounds, is inhibited by the presence of high concentrations of aromatic compounds, fatty acids and high amounts of volatile acids formed during the acidogenic step<sup>[29]</sup>. It is well known that concentrations of 2 g L<sup>-1</sup> of tannin and concentrations of 1 g L<sup>-1</sup> of phenolic compounds are toxic to methanogenic bacteria,<sup>[29]</sup> since these compounds lead to an accumulation of hydrogen and acetate in the reaction medium.

According to the Monod model is possible to establish an empirical relation between  $\mu$  (the specific growth rate of biomass) and the concentration of substrate S, as follows:

$$\mu = \frac{\mu_{\max} S}{k_s + S} \quad (E4.6)$$

where  $\mu_{\max}$  is the maximum specific growth of microorganisms and  $k_s$  (g COD L<sup>-1</sup>) is the Monod constant saturation. This equation for low concentrations of substrate, where  $k_s \gg S$ , can be reduced to:

$$\mu = \frac{\mu_{\max} S}{k_s} \quad (\text{E4.7})$$

An additional kinetic parameter that has an interest in the draft of biological treatment plants is the cell yield. Is defined as the mass of microorganisms which occur per unit weight of substrate consumption and is represented by the mathematical expression:

$$Y_{X/S} = -\frac{\Delta X}{\Delta S} \quad (\text{E4.8})$$

where  $Y_{X/S}$  is the cell yield (g microorganisms/g of substrate). The negative signal is due to the fact that while the substrate is consumed, the microorganisms are generated. For differential variations this equation can be expressed as:

$$Y_{X/S} = -\frac{dX}{dS} \quad (\text{E4.9})$$

where  $X$  is the concentration of microorganisms in the digester, measured as g VSS/L. From this equation can be deduced that:

$$-Y_{X/S} \frac{dS}{dt} = \frac{dX}{dt} \quad (\text{E4.10})$$

The rate of biomass production is proportional to the cell mass present (first order kinetics):

$$\frac{dX}{dt} = \mu X \quad (\text{E4.11})$$

$\mu$  representing the specific growth rate of biomass.

Introducing this equality in in Eq. 4.10 and matching Eq. 4.7:

$$-\frac{Y_{X/S} dS}{dt} = \frac{\mu_{\max} X}{K_s} S \quad (\text{E4.12})$$

That can be transformed into:

$$-\frac{dS}{S} = \frac{\mu_{\max} X}{Y_{X/S} k_s} dt = k_N dt \quad (\text{E4.13})$$

The constant  $k_N$  includes biomass concentration  $X$ , which remains almost constant throughout all experiments, at a value of  $12 \pm 0.2$  g VSS/L. Integrating this expression with the initial condition  $S = S_0$  at  $t = 0$  leads to

$$\ln \frac{S_0}{S} = k_N t \quad (\text{E4.14})$$

In another approach, the amount of methane produced in an anaerobic reactor can also be expressed as follows:<sup>[30]</sup>

$$V_{\text{CH}_4} = Y_{\text{CH}_4}(S_0 - S)V \quad (\text{E4.15})$$

where  $S_0$  and  $S$  represent respectively the biodegradable substrate concentration at the beginning of the experiment and at any moment and  $V$  the volume of the anaerobic bioreactor.

From Eq. 4.14,  $S$  can be defined as:

$$S = S_0 e^{-k_N t} \quad (\text{E4.16})$$

Substituting into Eq. 4.15 gives:

$$V_{\text{CH}_4} = Y_{\text{CH}_4} S_0 (1 - e^{-k_N t}) V \quad (\text{E4.17})$$

After applying logarithms, can be deduced the following expression:[27]

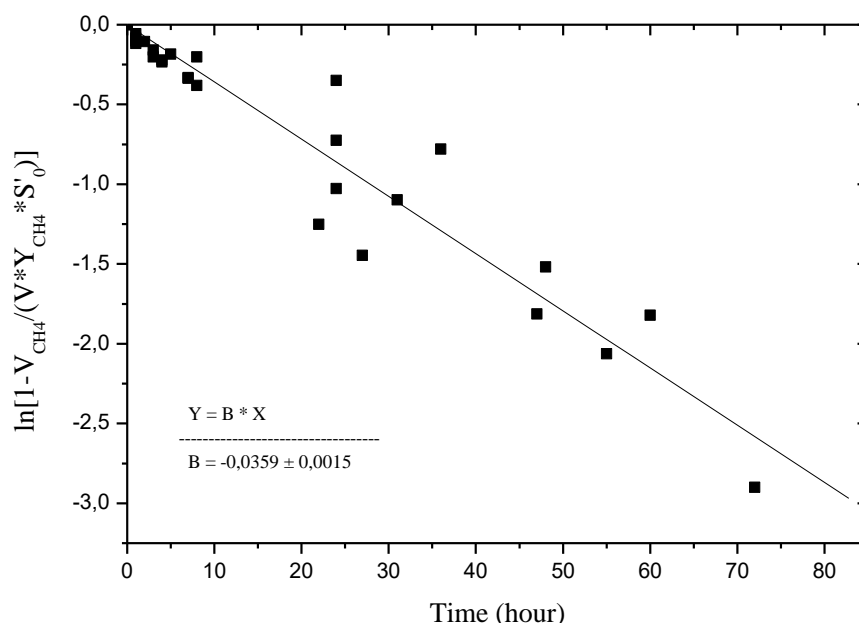
$$\ln \left[ 1 - \frac{V_{\text{CH}_4}}{V Y_{\text{CH}_4} S'_0} \right] = -k_N t \quad (\text{E4.18})$$

In this equation  $k_N$  is the first order rate constant observed of the olive mill wastewater anaerobic digestion process,  $V_{\text{CH}_4}$  the volume of methane generated,  $Y_{\text{CH}_4}$  the coefficient of generation of methane and  $V$  the volume of the reactor (in this case 2 L). In view of experimental results obtained in this work it is considered that the concentration (COD) of biodegradable substrate ( $S'_0$ ) is about 30% of the initial concentration ( $S_0$ ).

According to Eq. 4.18, a representation of the values of the first term as a function of time  $t$  for each experiment, should lead to a straight line whose slope is negative  $-k$ . Figure 4.3 shows this representation and it demonstrates a satisfactory fit of the experimental points to the equation. From the slope of the line obtained  $k_{\text{FN}} = 0.036 \text{ h}^{-1}$  (the designation  $k_{\text{FN}}$  instead of  $k_N$  to best explain the observed first order



kinetic constant of olive mill wastewater anaerobic digestion process pre-treated with Fenton's reagent).



**Figure 4.3** - Kinetic constant determination (k) in olive mill wastewater anaerobic digestion process pre-oxidized with Fenton's reagent (experiments FN-1 to FN-4).

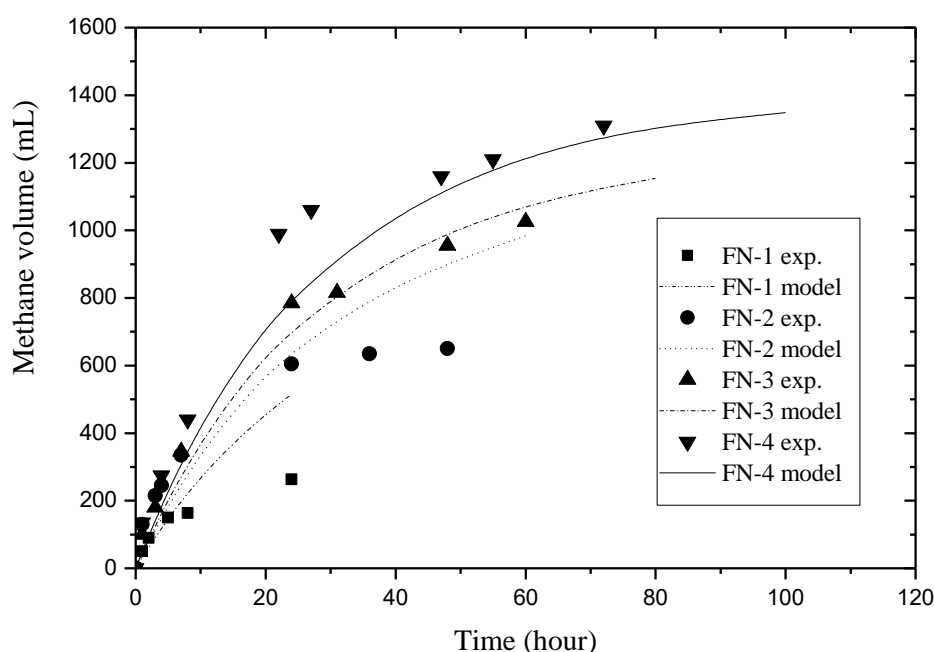
Knowing  $k_{FN}$  value is now possible to check the adequacy of the model. Figure 4.4 compares the experimental values obtained (represented by dots) with the theoretical values calculated (represented by lines). It can be noted that although some deviations associated with experimental errors, the model based on Eq. 4.18 allows us to describe the experimental results satisfactorily.

The comparison between the results obtained in the combined process (Fenton oxidation + anaerobic digestion) with those obtained in simple anaerobic degradation, using the same strategy of plotting the results, reveals some significant features:

- A steady increase in overall biokinetics of the combined process ( $k_{FN} = 0.036 \text{ h}^{-1}$ ) compared to the simple anaerobic process ( $k_N = 0.017 \text{ h}^{-1}$ ).
- An increase in the organic matter conversion ( $X_{COD}$ ). For example, in experiments starting COD of about  $3.5 \text{ g L}^{-1}$  (N-3 and FN-2) gave a value of  $X_{COD}$  of 55.4% and

73.7% respectively, for original olive mill wastewater and for chemical pre-treated with Fenton's reagent olive mill wastewater.

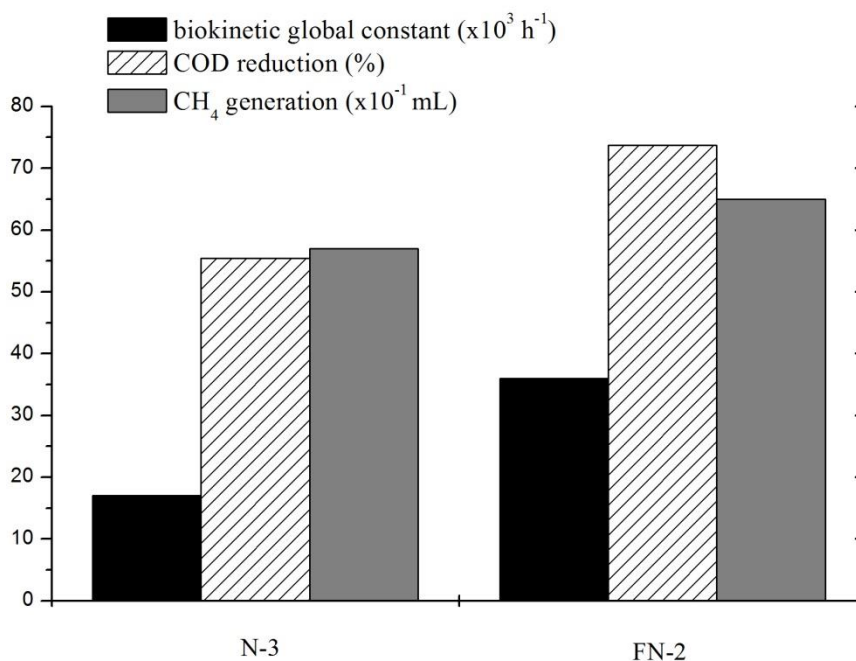
- An increase in the yield of methane  $Y_{CH_4}$ . For the experiments in Table 4.3 (FN-i) can propose an average of 306 mL of  $CH_4$ /g COD degraded to the combined process, higher than that of 288 mL of  $CH_4$ /g COD, obtained in the anaerobic degradation of olive mill wastewater without prior chemical treatment (N-i).



**Figure 4.4** - Comparison between the estimated values of biodegradable substrate ( $S'$ ) obtained by the adopted model (lines) and experimental values (points) for the anaerobic biological degradation experiments performed (FN-1 to FN-4).

Figure 4.5 presents, for two similar experiments (N-3 and FN-2), the final methane generation and the COD conversion obtained, as well as the global biokinetic constant.

These results could be explained by the reduction in phenolic compounds concentration, which occur in the chemical pre-treatment and reflected in total polyphenols (TP) reduction. This fact will provide better performance in the anaerobic degradation of organic matter and that converts into a biogas increase. This will improve the organic matter anaerobic degradation and consequently yield a higher production of biogas.



**Figure 4.5** - Comparison of COD reduction (%), volume of methane generated ( $\times 10^{-1} \text{ mL}$ ) and biokinetic global constants ( $\times 10^3 \text{ h}^{-1}$ ) in the system: (1) direct treatment by anaerobic digestion, (2) treatment of olive mill wastewater by anaerobic digestion pre-treated by Fenton's reagent.

The oxidation system used in the chemical pre-treatment of OMW defines the intermediate compounds generated, influencing the subsequent biodegradation of the remaining products. Regarding Fenton's reagent, although a powerful oxidizing agent, there are some species that are resistant to oxidation, such as chlorinated alkanes (tetrachloroethane, trichloroethane, chloroform, carbon tetrachloride), n-paraffins and short-chain carboxylic acids (fatty maleic, oxalic acid, malonic acid))<sup>[31]</sup>.

These latter compounds are typical by-products from the oxidation of larger molecules after fragmentation. That is, after Fenton's reagent application will be in solution some organic species partially oxidized because the oxidation complete is difficult. In this case, the final products of olive mill wastewater oxidation with Fenton's reagent include low molecular weight organic acids such as acetic, formic and succinic acids. These short chain carboxylic acids resulting from the process are coincidentally also Fenton primary metabolites which act on the energy cycles of most living organisms especially in anaerobic processes and are therefore biodegradable<sup>[29]</sup>.

#### **4.4. Conclusion**

The overall results of this study indicate that, under the range of the variables tested, the combination of Fenton's reagent with the anaerobic biological treatment leads to a better performance. The comparison between the results obtained in the combined process (Fenton oxidation + anaerobic digestion) with those obtained in simple anaerobic degradation, reveals some significant features:

1. An increase in the organic matter conversion ( $X_{\text{COD}}$ ).
2. A constant increase in the biokinetics combined process ( $k_{\text{FN}} = 0.036 \text{ h}^{-1}$ ) comparatively to the simple anaerobic process ( $k_{\text{N}} = 0.017 \text{ h}^{-1}$ ).
3. An increase in methane yield  $Y_{\text{CH}_4}$ : for the experiments FN-i we can propose an average of 306 mL of  $\text{CH}_4/\text{g}$  COD degraded, exceeding the value of 288 mL of  $\text{CH}_4/\text{g}$  COD obtained in the tests of anaerobic degradation of olive mill wastewater (experiments N-i).

It can be established that before olive mill wastewater treatment by anaerobic digestion is advisable to perform an oxidative treatment to partially remove some inhibiting compounds. Therefore, the combined treatment Fenton reagent-anaerobic digestion can be an effective solution for OMW. The anaerobic digestion has small energy consumption, reduced sludge generation, lower nutrients requirement, potential energy recovery from wastewater (biogas) and reduced issues with bad odours. Nonetheless, it also has some drawbacks such as the slow kinetics (since it requires to be operated at least under mesophilic conditions), the permanent operational conditions control and the high sensitivity to inhibitory substances. On the other hand, Fenton's reagent allows a fast and effective oxidation of the pollutant load (especially phenolic compounds); however, the high investment and running costs associated with the chemical reactor and the reactants can be pointed out as less positive assets.

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**5. TREATMENT OF CRYSTALLIZED FRUIT  
WASTEWATER BY UV-A LED PHOTO-FENTON  
AND COAGULATION-FLOCCULATION**

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## **5. TREATMENT OF CRYSTALLIZED FRUIT WASTEWATER BY UV-A LED PHOTO-FENTON AND COAGULATION-FLOCCULATION\***

### **Abstract**

This work reports the treatment of crystallized fruit effluents, characterized by a very low biodegradability ( $BOD_5/COD < 0.19$ ), through the application of a UV-A LED photo-Fenton process. Firstly, a Box-Behnken design of Response Surface Methodology (RSM) was applied to achieve the optimal conditions to the UV-A LED photo-Fenton process, trying to maximize the efficiency by saving chemicals and time. Under the optimal conditions ( $[H_2O_2] = 5459$  mg/L;  $[Fe^{3+}] = 286$  mg/L; time >180 minutes), it was achieved a COD removal of 45, 64 and 74% after 360 minutes using an irradiance of 23, 70 and 85 W/m<sup>2</sup> respectively. Finally, the combination of UV-A LED photo-Fenton with coagulation-flocculation-decantation (CFD) reached a higher COD removal (80%), as well as almost total removal of turbidity (99%) and total suspended solids (95%). Biodegradability of treated effluents increased, allowing the application of a biological treatment step after the photochemical/CFD with 85 W/m<sup>2</sup>.

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\*Adapted from: Rodriguez-Chueca, J., Amor, C., Fernandes, J.R., Tavares, P.B., Lucas M.S., Peres J.A. *Treatment of crystallized fruit wastewater by UV-A LED photo-Fenton and coagulation-flocculation*. Chemosphere. **2016**, 145, 351 – 359.



## **5.1. Introduction**

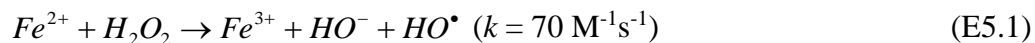
Crystallized fruit industry annually generates large volumes of wastewater, mainly from several washing and cooking operations of fresh fruits in syrup (water and sugar) as well as the rinsing of tanks, barrels and other equipment. This industrial effluent is characterized by a high seasonal variability, organic strength and unpleasant odour. Conventional treatments available in Municipal Wastewater Treatment Plants (MWWTP), such as biological processes, are susceptible to undergo several constraints due to the low biodegradability and high organic load of this wastewater.

In order to overcome the limitations enclosed to biological processes, physical-chemical treatments has been envisaged as promising alternatives to remove efficiently organic matter, suspended solids and turbidity<sup>[1]</sup>. In this connection, Advanced Oxidation Processes (AOPs), like  $\text{H}_2\text{O}_2/\text{UV-C}$ , heterogeneous photocatalysis, photo-Fenton and  $\text{H}_2\text{O}_2/\text{O}_3$ , are being proposed as valuable approaches for water and wastewater treatment<sup>[2-5]</sup> due to their efficiency in the generation of hydroxyl radicals ( $\text{HO}^\bullet$ ). These highly oxidant species can oxidize almost all organic compounds and inactivate a wide range of microorganisms. AOPs have been reported to be used in a successful way in the treatment of paper industry<sup>[6]</sup>, dyes and pigments<sup>[7]</sup>, landfill leachates<sup>[1,8]</sup>, fresh surface water and drinking water<sup>[9,10]</sup>, cork industry<sup>[11]</sup>, urban wastewater effluents<sup>[12]</sup> and agri-food industries<sup>[13-15]</sup>.

Fenton's reagent oxidation is a homogeneous catalytic oxidation process that uses a mixture of hydrogen peroxide and ferrous ions. In acid environment, the addition of hydrogen peroxide to an aqueous system containing an organic substrate and ferrous ions produces a complex redox reaction<sup>[16-18]</sup>. The ferrous ions initiate and catalyze the decomposition of  $\text{H}_2\text{O}_2$ , resulting in the generation of hydroxyl radicals,  $\text{HO}^\bullet$ <sup>[19]</sup>.

The production of  $\text{HO}^\bullet$  is greatly increased by UV-vis radiation up to a wavelength of 600 nm. Photo-Fenton produces hydroxyl radicals via a series of catalytic cycle reactions with iron ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ),  $\text{H}_2\text{O}_2$ , and UV radiation. The highest photo-Fenton efficiency is found at pH 2.8<sup>[20]</sup>, since iron salts precipitate above this pH value.

These reactions can be summarized as follows:



Different UV radiation sources have been reported in the last years in order to assist photo-Fenton treatments, but especially low and medium pressure mercury lamps. However, their high operational cost associated with large energy consumption and their toxicity are important drawbacks. In this connection, UV-light-emitting diodes (LEDs) lamps, more efficient and eco-friendly, are a serious alternative to mercury lamps and solar radiation. Semiconductor LEDs technology are a directional light source with maximum intensity at an angle almost perpendicular to the surface emission. Although at a relatively high cost, LEDs lamps have several advantages when compared to traditional UV lamps, such as a longer lifetime, not overheating, lower energy consumption and higher efficiency<sup>[21,22]</sup>.

When LEDs lamps are activated, the electrons and holes are directed to *p-n* junctions, suffering a recombination and emitting light (electroluminescence). This recombination compromises that couple of electrons and holes become more stable to release excess energy by photon emission. In fact, almost all the electrical energy is converted into light energy<sup>[22]</sup>. As all emitted photons have approximately the same frequency, this implies that the light is monochromatic, thus the wavelength depends on the semiconductor material used. UV LEDs have been increasingly used as they can be applied in several different processes, such as the degradation of chemicals and inactivation of microorganisms<sup>[22]</sup>.

The main purpose of this research was to optimize the experimental conditions (reaction time,  $Fe^{3+}$ , and  $H_2O_2$  dosages) of UV-A LED photo-Fenton treatments by means of a Response Surface Methodology (RSM) model. Afterwards, it was evaluated the combination of a UV-A LED photo-Fenton treatment with a CFD in crystallized fruit industry wastewater degradation.

## **5.2. Material and methods**

### ***5.2.1. Samples***

Crystallized fruit wastewater samples were collected in a company located at the North of Portugal. This company is the market leader of crystallized fruit production in Portugal for baking, jam and quince jelly. The production of these products requires a high amount of water to carry out the washing and cooking of the fruits. The main fruits used in the industrial process are pumpkins, carrots, pears, oranges, quinces, apples, cherries and figs. These fruits are conserved in baths of sodium bisulphite solutions before their handling. This processing stage promotes the generation of a high reducer wastewater. The physicochemical characteristics of the crystallized fruit wastewater are summarized in Table 5.1. The large differences observed in the physicochemical parameters, mainly in terms of pH, oxidation potential, COD and BOD<sub>5</sub>, of the three different samples are consequence of: i) the different productive process in each sample time; ii) the elementary operation of the WWTP of the factory just based on pH correction with NaOH and aeration of samples in order to remove the sodium bisulfite used to preserve the fruits.

**Table 5.1** - Physicochemical characteristics of crystallized fruit wastewater.

Parameter	Values		
	Sample A	Sample B	Sample C
	(02/2014)	(05/2014)	(07/2014)
pH (Sorensen scale)	9.78	3.50	6.95
E° (mV)	-140	212	17
Conductivity (µS/cm)	3820	8304	8578
Turbidity (NTU)	410	359	633
Total Suspended Solids (mg/L)	1100	1420	1850
Volatile Suspended Solids (mg/L)	125	265	-
COD (mg O <sub>2</sub> /L)	22 932	20 902	35 369
BOD <sub>5</sub> (mg O <sub>2</sub> /L)	1400	3300	6600
Biodegradability (BOD <sub>5</sub> /COD)	0.06	0.16	0.19
Polyphenols (mg gallic acid/L)	142	403	384
Absorbance at 254 nm (diluted 1:25)	0.265	0.323	0.409
Absorbance at 254 nm (diluted 1:10)	0.539	0.708	0.927
Hardness (mg CaCO <sub>3</sub> /L)	135	219	228
Chloride (mg Cl <sup>-</sup> /L)	824	1073	1281
Nitrite (mg NO <sub>2</sub> <sup>-</sup> /L)	453	0.07	0.01
Nitrate (mg NO <sub>3</sub> <sup>-</sup> /L)	168	49.3	88.8
Phosphates (mg PO <sub>4</sub> <sup>3-</sup> /L)	143	n.d.	n.d.
Sulphates (mg SO <sub>4</sub> <sup>2-</sup> /L)	80.5	272.5	n.d.
Calcium (mg Ca <sup>2+</sup> /L)	36.1	48.6	39.2
Iron (mg Fe <sup>2+</sup> /L)	87	3.0	2.2
Magnesium (mg Mg <sup>2+</sup> /L)	10.8	23.8	31.6
Potassium (mg K <sup>+</sup> /L)	2850	222	224
Sodium (mg Na <sup>+</sup> /L)	901	2766	2632
Aluminium (mg Al <sup>3+</sup> /L)	7.2	28.9	37.1
Arsenic (µg As /L)	7	46	62
Copper (µg Cu <sup>2+</sup> /L)	81	21	25
Manganese (mg Mn <sup>2+</sup> /L)	46	0.16	0.08



### **5.2.2. Analytical determinations**

Different physicochemical parameters such as pH, conductivity, redox potential, turbidity, Total Suspended Solids (TSS), Volatile Suspended Solids, Chemical Oxygen Demand (COD), Total Polyphenols (TP) and Cationic and Anionic concentration were analyzed for the samples characterization. In addition, values of COD, TSS and Turbidity were analyzed during the treatments in order to assess the efficiency of the treatments.

Chemical Oxygen Demand was measured according to 410.4 Method of Environmental Protection Agency of USA (EPA, 1993), using a HACH DR/2400 portable spectrophotometer. BOD<sub>5</sub> was checked and measured according to 5-Day BOD Test (Standard Method 5210B) using OxiTop<sup>®</sup> Control respirometer. The pH and redox potential were determined by a HANNA pH 209 laboratory meter following the Standard Method 4500-H<sup>+</sup>-B and 2580 respectively, while conductivity was measured by a Crison Basic as indicated in ISO 7888:1985. Turbidity was measured according ISO 7027:1999 using a HACH 2100 IS Turbidimeter. Total Suspended Solids (TSS) were measured by spectrophotometry according to Standard Method 2540D using a HACH DR/2400 portable spectrophotometer, while Volatile Suspended Solids (VSS) were measured through Standard Method 2540-E. In addition, Total Polyphenols concentration (TP), (mg gallic acid/L), was determined by spectrophotometry using the Folin-Ciocalteu reagent (Merck) (Singleton and Rossi, 1965). UV-vis measurements were carried out using a Jasco V-530 UV/VIS spectrophotometer. Finally, the anionic analysis was carried out according to D4327 and D6919-09 ASTM International Standards for anions and cations respectively, using a Dionex AS model ICS-3000 Detector Chromatography for anions determination, while for cationic determination it was used a Thermo Scientific Ice 3000 Series AA Spectrometer and an ATI Unicam Solaar 939 Atomic Absorption Spectrometer for the concentrations of mg/L and µg/L respectively.

### **5.2.3. Reagents**

Fenton and photo-Fenton treatments were carried out with different dosages of FeCl<sub>3</sub>·6H<sub>2</sub>O (Merck) and H<sub>2</sub>O<sub>2</sub> (30% w/w, Panreac) used as reagent grade. In addition,

H<sub>2</sub>SO<sub>4</sub> (Scharlau) and NaOH (BDH Prolabo®) aqueous solutions were applied for pH adjustment. Na<sub>2</sub>SO<sub>3</sub> (Merck) was used to quench the hydroxyl radicals action before analyses. The titanium (IV) oxysulfate solution (Riedel-de Haën, Germany) was used as received in order to analyse the concentration of H<sub>2</sub>O<sub>2</sub>. Finally, different inorganic (FeSO<sub>4</sub>·7H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ca(OH)<sub>2</sub> and aluminium chlorohydrate (Kemira Ibérica) and organics (QT100 and QTH100 (Grove Chemicals)) coagulants were used in coagulation-flocculation processes.

#### **5.2.4. Radiation source**

All experiments were carried out in batch mode lab-scale prototype reactor and illuminated with two different UV-A LED systems. The first UV LED photo-system applied was a matrix of 96 Indium Gallium Nitride (InGaN) LEDs lamps (Roithner RLS-UV370E), with an illuminated area of 11x7 cm<sup>2</sup>. These LED lamps had a light peak emission wavelength at 370 nm, and the nominal consumption of each LED lamp was 80 mW operating at 20 mA. The total optical power emitted was of approximately 100 mW, depending on the root mean square (RMS) current intensity supplied. The system irradiance was measured using a UV enhanced Si-photodetector (ThorLabs PDA155) in a configuration that replicates the one used in the photoreactor. In this system the output optical power is controlled using a pulse width modulation (PWM) circuit. The RMS current intensity was measured with a multimeter (UniVolt DT-64).

The second UV LED system was developed with 12 InGaN LED lamps (Roithner APG2C1-365E LEDS) with a light peak emission wavelength at 365 nm. The nominal consumption of each LED lamp was 1.4 W, for an applied current of 350 mA. The output optical power was controlled by maintaining the forward current constant using a power MOSFET in six different current settings.

The treatments were carried out in two UV-A LED photo-systems. The first one used a RMS current intensity of 240 mA, corresponding to a UV irradiance of 23 W/m<sup>2</sup> and a photon flux of 5.53×10<sup>-7</sup> Einstein/s. In the second photo-system were applied current intensities of 262 and 327 mA, corresponding to an UV irradiance of 70 and 85 W/m<sup>2</sup>, respectively, and a photon flux of 1.68×10<sup>-6</sup> and 2.04×10<sup>-6</sup>, respectively.

Figure S5.1 (Supplementary Material) shows the two UV-A LED photosystem and a diagram of the setup experiments.

#### **5.2.5. Experimental procedure**

The different experiments were carried out in a batch UV-A LED photoreactor. The pH was adjusted to 3, using  $\text{H}_2\text{SO}_4$  and a 209 pH Meter from Hanna Instruments. Then, the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  dosage (60 – 300 mg/L) was added to the effluent. Hydrogen peroxide (200 – 5500 mg/L) was directly added to the photoreactor at the beginning of each experiment. During each experiment the samples were withdrawn at different periodic times and analysed. The  $\text{H}_2\text{O}_2$  concentration was measured in a spectrophotometer (Jasco V-530) at 410 nm according to DIN 38409 H15, based on the formation of a yellow complex from the reaction of titanium (IV) oxysulphate with  $\text{H}_2\text{O}_2$ . The titanium (IV) oxysulphate method displays a detection limit of 0.1 mg/L. The signal was read after 5 min incubation time against a  $\text{H}_2\text{O}_2$  standard curve from 0.1–100 mg/L  $\text{H}_2\text{O}_2$ . The  $\text{Na}_2\text{SO}_3$  was added to water samples for the elimination of residual hydrogen peroxide. Temperature and pH were also monitored. Total polyphenols were followed using the Folin-Ciocalteu method<sup>[23]</sup>. The chemical oxygen demand (COD), biochemical oxygen demand ( $\text{BOD}_5$ ) and total and volatile solids were monitored according to the Standard Methods<sup>[24]</sup>. Moreover, the total iron concentration was measured through the phenanthroline method. Each sample was mixed with 1 mL of 1,10-phenanthroline (1 g/L) and 1 mL of buffer solution according to ISO 6332 regarding the assessment of dissolved  $\text{Fe}^{2+}$  and total iron ( $\text{Fe}_{\text{total}}$ ) concentrations. The coloured complex formed was measured with a spectrophotometer (Jasco V-530) at 510 nm. The concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}_{\text{total}}$  were determined using dedicated calibration curves. The temperature remained constant around 21°C. All assays were carried out in duplicates, results are presented as mean  $\pm$  standard deviation. Previous studies of coagulation-flocculation-decantation optimization carried out in our research work (data not shown) demonstrated that the best coagulant was  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at neutral pH (pH 7). In addition, it was observed as the best yields mainly in terms of suspended solids and turbidity removal were reached when CFD was performed after photo-Fenton treatments, because of in that way is removed the sludge generated (mainly composed by ferric hydroxides) after the Fenton treatments. Therefore, the CFD processes were

carried out at pH 7, after the photo-Fenton treatment and using the remaining iron. A Jar-Test (ISCO) was used to first produce a rapid agitation (200 rpm) for 3 minutes, where destabilization of the colloids occurred. After that, a slow agitation period (40 rpm) took place during 15 minutes. At the end, to promote the formation and precipitation of flocs a decantation period of 60 minutes was carried out.

#### **5.2.6. Experimental design**

A Box-Behnken design was employed to evaluate the effect of different parameters, such as concentration of  $\text{H}_2\text{O}_2$  (mg/L,  $X_1$ ), concentration of  $\text{Fe}^{3+}$  (mg/L,  $X_2$ ) and reaction time (min,  $X_3$ ) in the UV-A LED photo-Fenton treatment of crystallized fruit effluents. For this study, 15 UV-LED photo-Fenton experiments were performed. The levels considered for the Box-Behnken design are listed in Table 5.2 (a). The treatment schedule (Table 5.2 (b)) was arranged to allow an appropriate regression model. All experiments were carried out in triplicate. Three replicates at the center of the design were used (Experiments 1, 4, and 15). Experiments were randomized to maximize the efforts of unexplained variability in the observed response due to external factors.

#### **5.2.7. Statistical analysis**

The coefficients corresponding to the model equation were obtained using Statgraphics Centurion XV.I. (StatPoint Technologies Inc., Warrenton, VA, US). The analysis of variance (ANOVA) was carried out using the SPSS 21.0 software package (LEAD Technologies, Inc., Chicago, USA) in order to determine any significant difference ( $P < 0.05$ ).

**Table 5.2** - (a) Symbols and coded factor levels for the considered variables. (b) Box-Benken design: effect of operational variables on COD removal yield ( $[\text{H}_2\text{O}_2] = 1100 - 5500$  mg/L;  $[\text{Fe}^{3+}] = 60 - 300$  mg/L; reaction time = 30 – 180 minutes).

Independent Variables	Coded	Levels		
		-1	0	1
$[\text{H}_2\text{O}_2]$ (mg/L)	$X_1$	1100	3300	5500
$[\text{Fe}^{3+}]$ (mg/L)	$X_2$	60	180	300
Reaction time (min)	$X_3$	30	105	180

Assay	Coded level			Response values	
	$[\text{H}_2\text{O}_2]$ (mg/L)	$[\text{Fe}^{3+}]$ (mg/L)	Time (min)	COD removal (%)	
	$X_1$	$X_2$	$X_3$	Observed	Predicted
1*	3300	180	105	24.45	22.40
2	3300	60	180	26.27	24.22
3	5500	180	30	10.23	7.88
4*	3300	180	105	20.36	22.40
5	5500	60	105	16.59	19.03
6	5500	180	180	42.05	41.66
7	1100	300	105	23.86	21.42
8	5500	300	105	31.12	31.42
9	3300	60	30	0.86	0.77
10	1100	180	30	14.01	14.40
11	3300	300	30	6.74	8.79
12	1100	60	105	19.90	19.60
13	1100	180	180	23.35	25.70
14	3300	300	180	30.33	30.42
15*	3300	180	105	22.40	22.40

\*Central points

### 5.3. Results and Discussion

#### 5.3.1. UV-A LED photo-Fenton optimization by Response Surface Methodology

The present study was conducted to evaluate the optimal conditions for the COD removal present in a crystallized fruit effluent (Table 5.1, sample C) through photo-Fenton treatment assisted with UV-A LED radiation (23 W/m<sup>2</sup>). Nowadays, it is well known the high number of variables that affect photo-Fenton treatments, such as pH, temperature, radiation source, reaction time or dosages of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup>/Fe<sup>2+</sup>[20]. Similarly, it is widely accepted that pH the optimal pH for Fenton and photo-Fenton reactions ranges from 2.5 to 3.5, since all iron added to water is dissolved at this value, increasing the formation of hydroxyl radicals[20]. Thus, all treatments were carried out at pH 3 to obtain the higher yield in terms of COD removal.

The assessment of the percentage of COD removal was performed throughout panel of UV-A LED photo-Fenton conditions (n = 15) based on distinct combinations of H<sub>2</sub>O<sub>2</sub> concentration, Fe<sup>3+</sup> concentration, and reaction time. The results of the 15 runs are shown in Table 5.2 (b). This table includes the experimental design, as well as the observed and predicted values for the considered response, percentage of COD removal. Two previous rounds of analytical assessment were performed in order to obtain the adequate range for the considered factors: H<sub>2</sub>O<sub>2</sub> concentration (X<sub>1</sub>: 1100 – 5500 mg/L), Fe<sup>3+</sup> concentration (X<sub>2</sub>: 60 – 300 mg/L) and reaction time (X<sub>3</sub>: 30 – 180 min). The lack of fitting of the ranges considered in the two first rounds, regarding the optimal values could be due to the conditioning effect exerted by each factor on others. This situation prompted us to enlarge the ranges to obtain the optimal values. The range of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> concentrations are consistent with those previously assayed in the treatment of agro-industrial effluents by other authors[25,26]. With respect to H<sub>2</sub>O<sub>2</sub> concentration, the reaction rate increases in parallel to the augment of hydrogen peroxide dosage because of the concentration of hydroxyl radicals. However, an excessive dosage of H<sub>2</sub>O<sub>2</sub> may cause an adverse effect[27,28]. Thus, the optimal dosage of H<sub>2</sub>O<sub>2</sub> depends on the physico-chemical characteristics of the effluent and the dosage of iron[8]. Additionally, Fenton and photo-Fenton reaction rate increases with high iron concentrations due to the higher generation of hydroxyl radicals[29], whilst from a certain concentration of iron the efficiency of the reaction decreases or scavenger effects can emerge. For this reason Fe/H<sub>2</sub>O<sub>2</sub> ratio is sought as small as possible, trying to avoid possible recombination

between both and thereby to reduce the production of iron complexes. Therefore, this interconnection between factors involved in the Fenton and photo-Fenton reaction encourages the evaluation of the optimal concentrations of  $\text{H}_2\text{O}_2$  and iron to maximize the COD removal.

The quadratic model achieved allowed to adjust theoretical values of COD removal to observed values with a low deviation (Table 5.2b), suggesting a successful application of the Response Surface Methodology as optimization procedure. In this case, the model employed was noticed as much useful to predict COD removal yields without any further experiment.

The regression coefficients of intercept, linear, quadratic, and interaction terms of the model were calculated using the least square method. The effect of the linear, quadratic or interaction coefficients on the response was studied by analysis of variance (ANOVA) (Table 5.3). The degree of significance of each factor is represented by its  $P$  value, which evidenced that the regression models for COD removal was statistically relevant with a level of significance ranging from  $P < 0.0001$  to  $P < 0.0165$ . The models did not display significant lack of fit ( $P > 0.05$ ). Thus, these statistical parameters indicated well-fitting models for the described variables. These statistical analyses revealed that the most important variable for COD was the reaction time ( $X_3$ ) ( $P < 0.001$ ), whilst secondary variation can be attributed to the  $\text{Fe}^{3+}$  concentration ( $X_2$ ) and the combination of  $\text{H}_2\text{O}_2$  and reaction time ( $X_1X_2$ ) (both  $P < 0.05$ ) (Table 5.3).

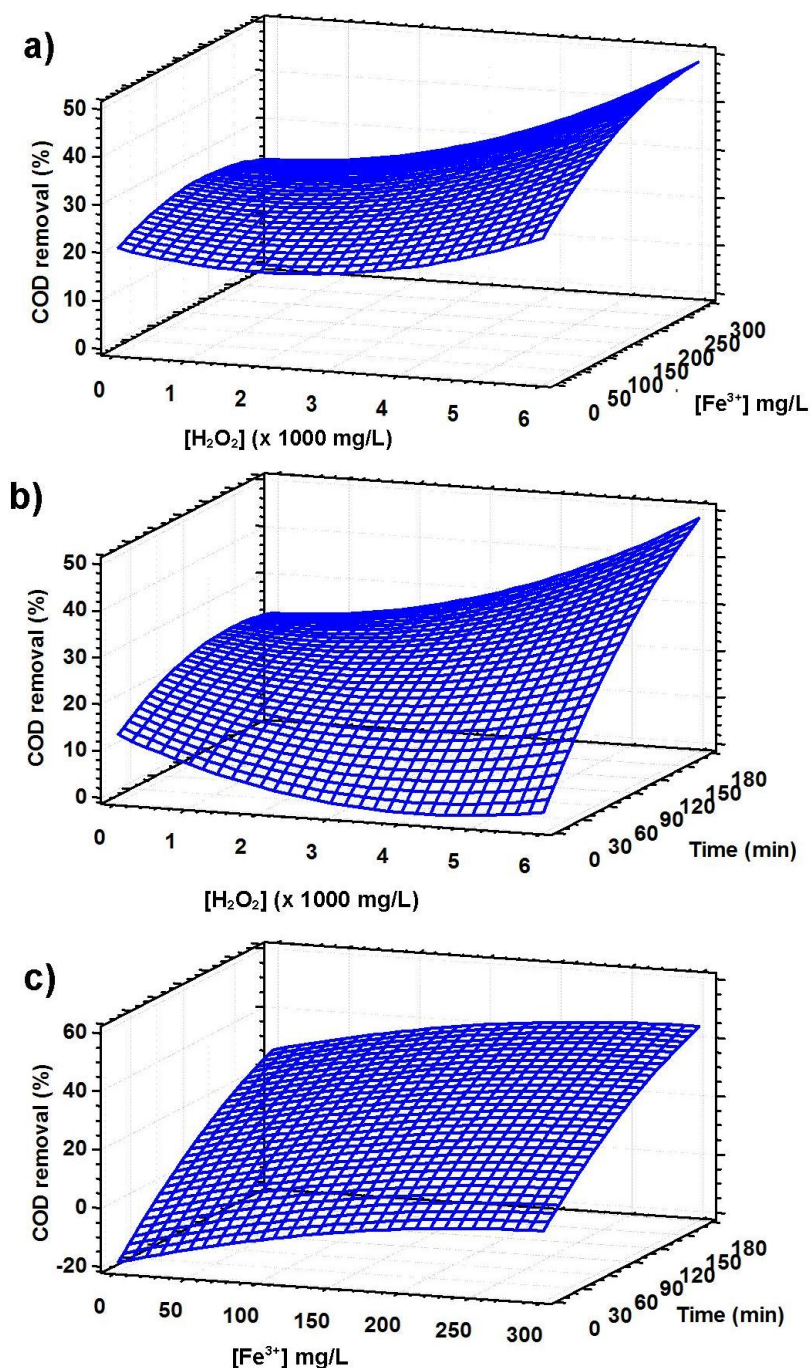
**Table 5.3** - Corresponding  $F$ -values and  $P$ -values for selected responses for each obtained coefficient.

Variable	$X_1$	$X_2$	$X_3$	$X_1X_1$	$X_1X_2$	$X_1X_3$	$X_2X_2$	$X_2X_3$	$X_3X_3$
$F$ -value	5.53	12.56	126.29	5.34	3.47	15.7	3.99	0.1	5.32
$P$ -value	n.s.	*	***	n.s.	n.s.	*	n.s.	n.s.	n.s.

$X_1$ :  $\text{H}_2\text{O}_2$  (mg/L);  $X_2$ :  $\text{Fe}^{3+}$  (mg/L);  $X_3$ : Reaction time (min). n.s.: Non-significant. Significant at \*  $P < 0.05$  and \*\*\*  $P < 0.001$ .

The response surface plots obtained further supported the relative contribution of each variable evaluated to the optimal condition for COD removal (Figure 5.1), which was confirmed by the value of the coefficient of each factor obtained in the polynomial

equation (Equation 5.3). Moreover, the regression coefficient ( $R^2$ ) for this method was of 0.973, which means that the model fits adequately the COD removal.



**Figure 5.1** - Response-surface plot showing the effect of  $H_2O_2$ ,  $Fe^{3+}$ , and reaction time on COD removal from crystallized fruit effluents.

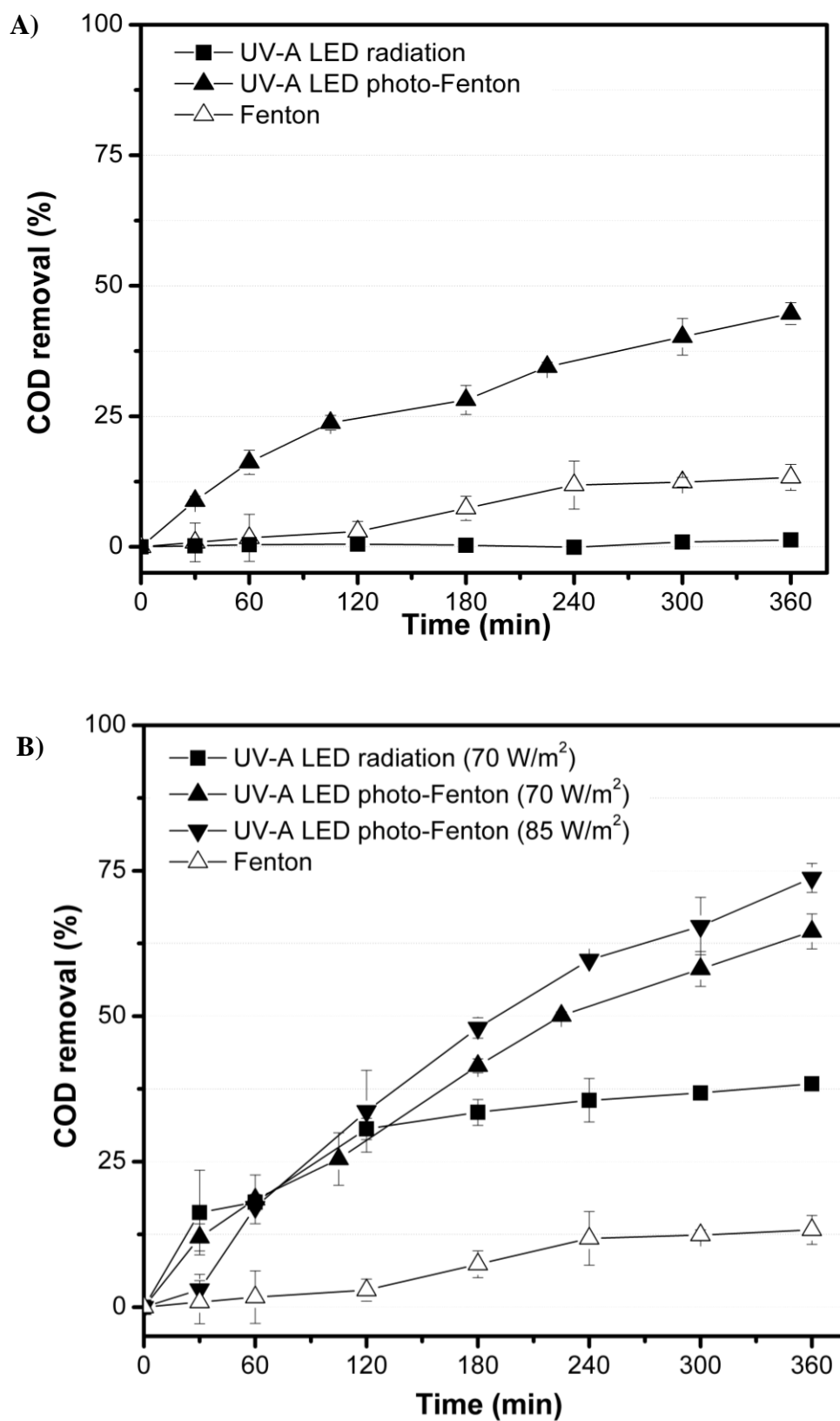


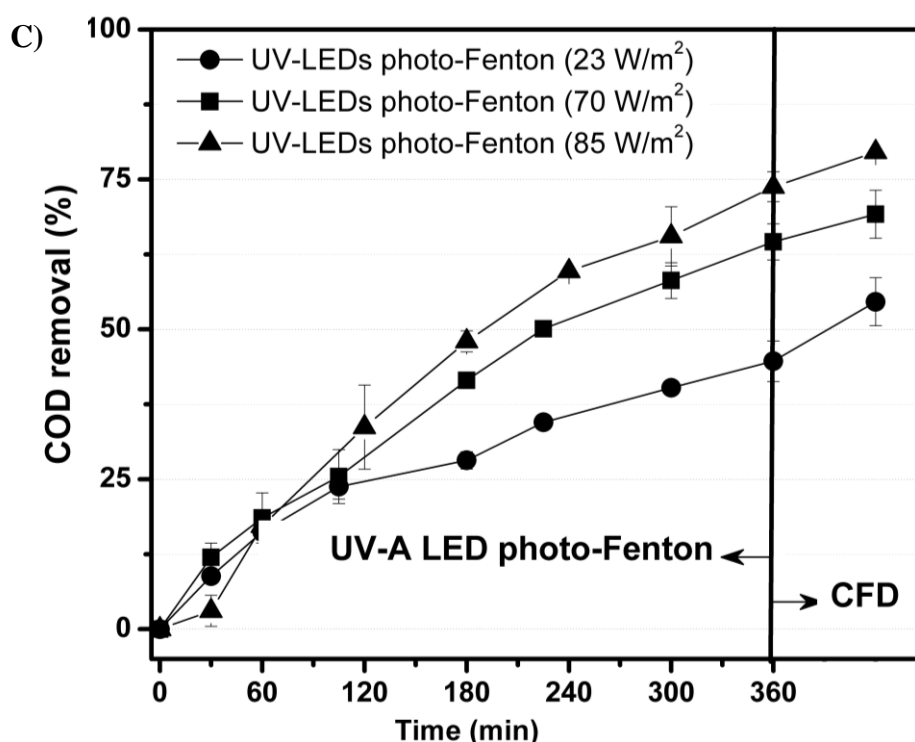
$$Y = 8.91847 - 0.00895875X_1 + 0.0755896X_2 + 0.174102X_3 + 7.04976 \cdot 10^{-7}X_1^2 + 0.0000100095X_1X_2 + 0.0000340606X_1X_3 - 0.000204716X_2^2 - 0.0000505556X_2X_3 - 0.000605407X_3^2 \quad (E5.3)$$

Optimal conditions concerning the three variables studied were achieved for the treatment of effluent C (Table 5.1). Thus, the optimal dosages of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> were 5459 and 286 mg/L, respectively. On the other hand, a reaction time higher than 180 minutes can be expected as optimal to obtain higher COD removal.

### 5.3.2. UV-A LED photo-Fenton

As mentioned in Table 5.1, due to the low BOD<sub>5</sub>/COD ratio and the reducer behavior of these effluents, there was a choice for a combination of photo-Fenton and CFD as the best alternative to increase the biodegradability of the effluent, suspended solids and turbidity removal. Different UV-A LED photo-Fenton treatments were carried out using the optimal conditions obtained through the RSM (H<sub>2</sub>O<sub>2</sub> = 5459 mg/L; Fe<sup>3+</sup> = 286 mg/L; time > 180 min). These optimal conditions were applied into the two UV-A LED photo-systems at pH 3 during 360 minutes. Figure 5.2 (A) shows the COD removal after the performance of Fenton and photo-Fenton treatment carried out in the first UV-A LED photo-system with an irradiance of 23 W/m<sup>2</sup>. As it can be observed in Figure 5.2 (A), photo-Fenton treatment reached a COD removal around 45% after 360 minutes. The COD removal reached contrasts with the results obtained by Fenton reagent, which only allowed a degradation of 13% at the end of the treatment. In addition, as it can be seen in Figure 5.2 (A), UV-A LED irradiation assays were also carried out. From data, it can be observed that no changes occurred after 360 minutes of irradiation.





**Figure 5.2** - COD removal with: (A) first UV-A LED photo-system; (B) with the second UV-A LED photo-system, using the optimal conditions reached in the RSM ( $[\text{H}_2\text{O}_2] = 5459 \text{ mg/L}$ ;  $[\text{Fe}^{3+}] = 286 \text{ mg/L}$ ; reaction time > 180 minutes); (C) combined UV-A LED photo-Fenton/CFD processes.

In order to increase the yield of COD removal in the effluents from crystallized fruit industry, a more powerful UV-A LED photo-system was applied. This second UV-LED photo-system is characterized by a higher irradiance under the same current intensity, with the same electric consumption. Therefore, with a current intensity of around 240 mA, an irradiance of  $70 \text{ W/m}^2$  was achieved. Additionally, in order to use the maximum capacity of the second UV-LED photo-system, a current intensity of  $85 \text{ W/m}^2$  was applied to the effluent. Figure 5.2 (B) shows the COD removal in the crystallized fruit effluent after the application of the photo-Fenton treatment with the second UV-A LED system using the optimal conditions reached in the RSM. As shown in Figure 5.2 (B), the higher COD removal (74%) was achieved with  $85 \text{ W/m}^2$ . This value is slightly higher than the obtained with an irradiance of  $70 \text{ W/m}^2$ , only 65%. Both values are much higher than the obtained in the Fenton treatment, thus in the absence of a UV-A LED irradiance (13%). On the other hand, control assays with UV-

A LED irradiation and H<sub>2</sub>O<sub>2</sub>/UV-A LED irradiation were carried out in order to check the effect of the different variables independently. In both cases, a final COD reduction of 38% was reached after 360 minutes. These results mean that the combination of hydrogen peroxide with UV-A irradiation does not have oxidation effect over the effluent since the degradation curve is similar to the obtained in the experiment performed in the absence of H<sub>2</sub>O<sub>2</sub>. Therefore, all the reduction of organic matter is consequence of UV-A LED irradiation. On the other hand, it is necessary to take into account the amount of consumed hydrogen peroxide in photo-Fenton treatments to compare with the blank assays. Thereby, in both photo-Fenton treatments (70 and 85 W/m<sup>2</sup>), hydrogen peroxide was totally consumed at 120 minutes, and for this reason this oxidant reagent was added again in the initial concentration in order to maintain a constant concentration until the end of the reaction. Thus, an approximate amount of 22 g/L of H<sub>2</sub>O<sub>2</sub> was consumed in the treatment carried out with 70 W/m<sup>2</sup>. Whilst, consumed hydrogen peroxide was increased in the treatment with a higher irradiance until 29 g/L approximately. As it can be observed in Figure 5.2 (B), there are small differences in the first 120 minutes of degradation curves both photo-Fenton assays and UV-A LED irradiation and H<sub>2</sub>O<sub>2</sub>/UV-A LED irradiation, coinciding this sampling point with the consumption of the initially added hydrogen peroxide (5.4 g/L of H<sub>2</sub>O<sub>2</sub>). This means that the first minutes of reaction, and due to the high organic load in the effluent the main effects in the degradation of organic matter are related to the effect of irradiation and to a lesser extent associated with the hydroxyl radicals generated in photo-Fenton treatment. As the reaction proceeds, the organic load decreases and a higher amount of hydroxyl radicals are formed, causing the consumption of hydrogen peroxide, thus the advance in the organic matter degradation.

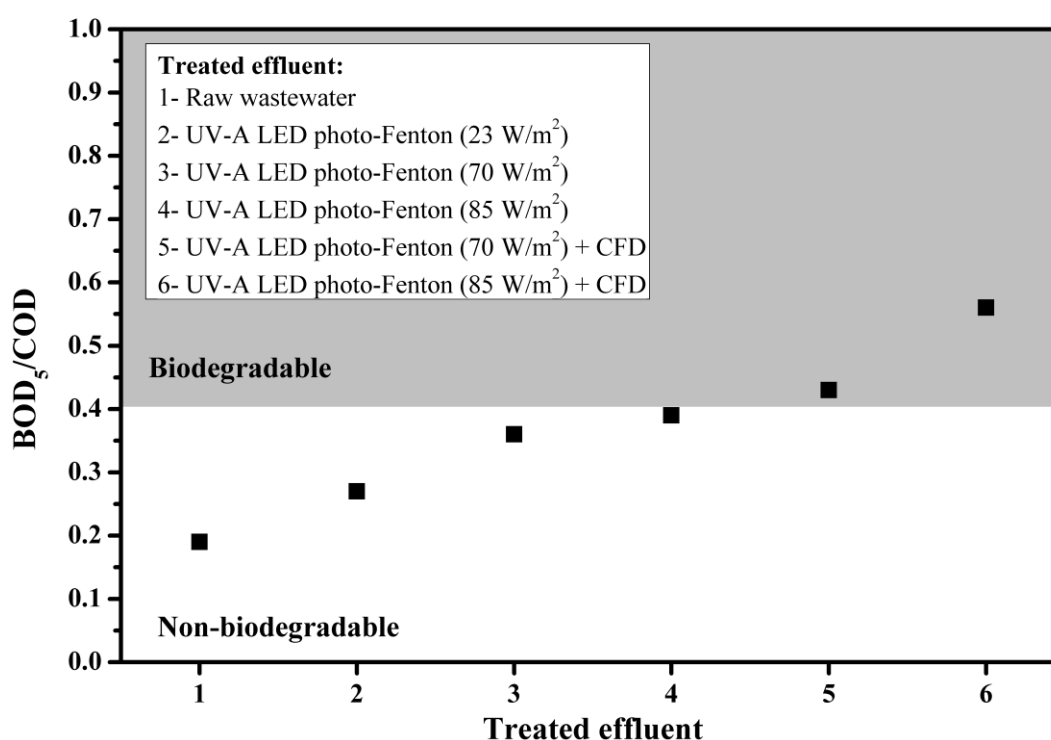
Durán *et al.*<sup>[26]</sup> reported values of COD removal of 59% after 120 minutes in juice effluents with 5800 mg/L of H<sub>2</sub>O<sub>2</sub> and 40 mg/L Fe<sup>3+</sup>. This result is considerably higher than the shown in Figure 5.2. However, it is necessary to take into account important differences between the two studies. Firstly, the effluent studied, had an initial COD value of 1260 mg O<sub>2</sub>/L, much lower than the studied in this research work (30 000 – 35 000 mgO<sub>2</sub>/L)<sup>[26]</sup>. Moreover, photo-Fenton treatments carried out were assisted with UV-C radiation (low pressure mercury lamp) emitting at  $\lambda = 190 - 280$  nm. In the meantime, UV-A radiation from LEDs lamps were used to assist photo-Fenton

treatments in the present research work<sup>[26]</sup>. Velegraki and Mantzavinos<sup>[15]</sup> reported a COD removal around 80% of winery effluents after 210 minutes, through solar photo-Fenton carried out in CPC reactors. To obtain this value was used a ratio  $\text{H}_2\text{O}_2$ :COD of 1.7. This ratio is almost three times higher than the ratio used to treat the crystallized fruit effluents present in this work (0.6). Thus, instead of the complexity of the water matrix treated in this work (higher COD concentration and reducer behaviour with negative values of redox potential), it was reached a similar COD removal than the obtained by Velegraki and Mantzavinos<sup>[15]</sup>, with a higher effectiveness of  $\text{H}_2\text{O}_2$ , able to treat higher amounts of COD with the same or lower doses of hydrogen peroxide.

After the UV-A LED photo-Fenton treatments, a coupled CFD stage was carried out in order to increase the COD removal and to reduce the amount of total suspended solids and the turbidity in the treated sample. With this objective, different inorganic and organic coagulants were tested (data not shown). After the study of the results obtained with the different coagulants, a coagulation-flocculation-decantation stage at pH 7 using the remaining iron ( $[\text{Fe}_{\text{total}}] \approx 325 \text{ mg/L}$ ) from photo-Fenton treatment was carried out. These conditions were selected regarding COD, total suspended solids and turbidity removal, and taking into account economic factors in order to transfer the studied treatment at laboratory scale to a real treatment plant inside the factory of crystallized fruit. Figure 5.2 (C) shows the results of COD removal after the coupled treatment UV-A LED photo-Fenton and CFD with different UV irradiances (23, 70 and  $85 \text{ W/m}^2$ ). As it can be observed in this figure, COD removal of treated effluents increases around 22% until a final value 54% in the combined treatment carried out with  $23 \text{ W/m}^2$ . Whilst, a slightly increase around 7% was observed in those treatments carried out in the second photo-system with 70 and  $85 \text{ W/m}^2$ , achieving a final removal of COD of 69 and 80% respectively. In addition, not only organic matter was removed, but also high removal of turbidity and suspended solids was achieved after the coagulation-flocculation stage. Therefore, maximum values of 99 and 95% were achieved for turbidity and total suspended solids removal after both combined treatments carried out in the second UV-A LED photo-system.

### 5.3.3. Biodegradability enhancement during coupled UV-A LED photo-Fenton and Coagulation Flocculation treatments

A good biodegradability index of treated wastewater is required for the application of a biological process as the last step in a crystallized fruit wastewater treatment system. The biodegradability index of all the treated samples (after UV-A LED photo-Fenton and photo-Fenton combined with CFD treatments) as well as raw wastewater, were evaluated according to the  $BOD_5/COD$  ratio. As shown in Figure 5.3, effluent biodegradability increases according to the requirement of treatment. As it can be observed in Figure 5.3 and Table 5.1, the biodegradability index of raw wastewater was ranging between 0.06 – 0.19, below 0.4 that is the value to consider an effluent as easily biodegradable, thus a non-biodegradable effluent<sup>[30; 31; 32]</sup>.



**Figure 5.3** - Evolution of biodegradability index of treated effluents.

The application of photo-Fenton treatment assisted with 23 W/m<sup>2</sup> of UV-A LED radiation increases slightly the biodegradability until 0.27. This value is still not enough to carry out a conventional biological treatment. However, the increase of the irradiance in the UV-A LED photo-Fenton treatments supposes the enhancement of the organic

matter removal and thus increase the biodegradability of the treated effluent. Therefore, after the photo-Fenton treatments with 70 and 85 W/m<sup>2</sup> the biodegradability index of the treated effluent rises to 0.36 and 0.39, respectively. Although the effluent is near to biodegradability, it only will be considered biodegradable when the ratio exceeds 0.4. This value is exceeded after the coupling of the UV-A LED photo-Fenton system and a coagulation-flocculation step. For instance, with an irradiance of 70 W/m<sup>2</sup> the treated effluent had a biodegradability ratio of 0.43, while the value is 0.56 after the combined treatment with irradiance of 85 W/m<sup>2</sup>. Therefore, treated effluents after UV-A LED photo-Fenton and subsequent CFD can be directed to a biological stage in order to continue the treatment to achieve the total degradation of organic matter. Similar coupling treatments have been reported in our research group and for other authors<sup>[33-35]</sup>.

In that way, the crystallized fruit wastewater treatment would be composed by a first tank of homogenization where after a pH adjustment, will be carried out the UV-A LED photo-Fenton treatment during enough time to degrade the organic matter until approximately 75%. Then, the effluent would be lead to a secondary tank where the CFD step would be carried out at pH 7 using the remaining iron from photo-Fenton step. In this stage, turbidity and suspended solids would be removed almost completely. Finally, the pre-treated effluent (5000 – 7000 mg O<sub>2</sub>/L) would be subjected to a biological treatment, for instance, with an activated sludge process. The retention time in the activated sludge tank would be dependent of the treatment goals. If the effluent will be discharged in a MWWTP the maximum admissible value of COD is 1000 mg O<sub>2</sub>/L, so a lower retention time should be enough. Alternatively, if the effluent will be discharged in a natural water course, a higher retention time in the biological treatment process will be necessary, since the maximum admissible value is 150 mg/L (Portuguese Decree Law no 236/98).

## **5.4. Conclusions**

A Box-Behnken design of Response Surface Methodology was employed to obtain the maximum yield in the organic matter removal of the crystallized wastewater through a UV-A LED photo-Fenton treatment. The experimental design was effective in estimating the influence of three independent variables: [Fe<sup>3+</sup>], [H<sub>2</sub>O<sub>2</sub>] and reaction

time, critically involved in the removal of COD. Additionally, a quadratic model was used to predict the response. The assessment of the best combination of variables to achieve the maximum COD removal ( $\text{Fe}^{3+} = 286 \text{ mg/L}$ ;  $\text{H}_2\text{O}_2 = 5459 \text{ mg/L}$  and reaction time  $> 180 \text{ min}$ ) was studied in two UV-A LED photo-systems. The two UV-A LED systems allowed evaluating the influence of increasing the irradiance from 23 to 85  $\text{W/m}^2$ .

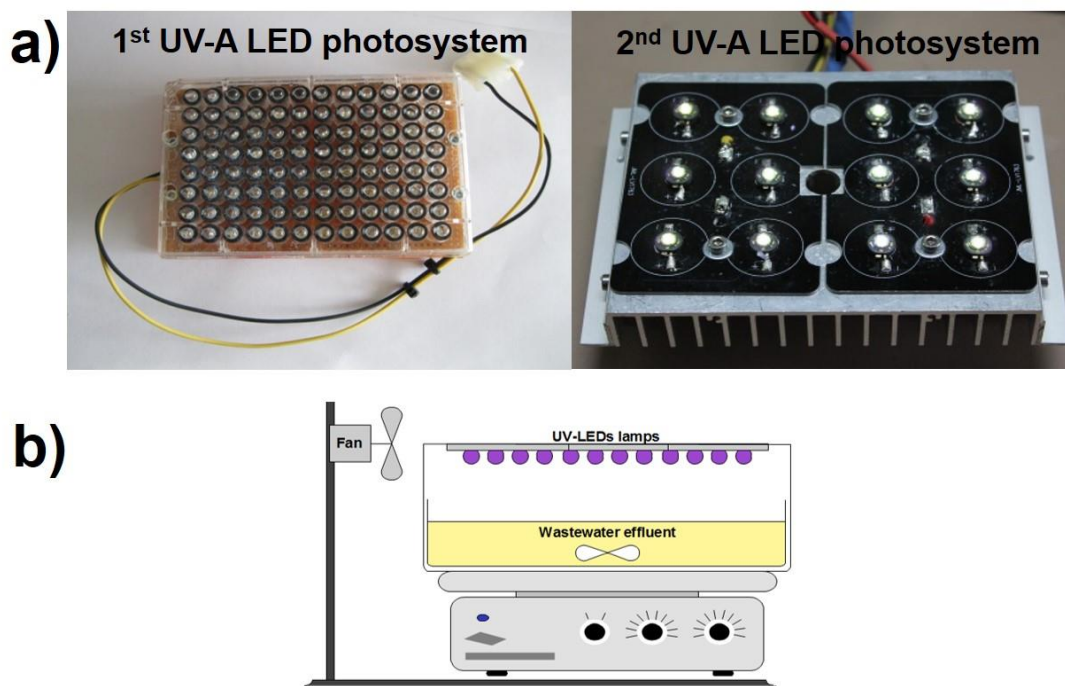
UV-A LED radiation is a serious alternative to conventional UV lamps, since they are eco-friendly, have a low operational cost and high energy efficiency. The yield of COD removal increases with the irradiance intensification in the photo-Fenton treatment. Therefore, 44.7% of organic matter was removed with a photo-Fenton with 23  $\text{W/m}^2$ . When the second UV-A LED system was used (with 70 and 85  $\text{W/m}^2$ ) the removal of COD reaches 65 and 74%, respectively.

The coupling of UV-A LED photo-Fenton and CFD allowed a slight increase in the removal of COD, up to 80%. Additionally, a higher removal of suspended solids (95%) and turbidity (99 %) was achieved.

This combined treatment increased the biodegradability index of the treated effluents, comparatively to the raw effluent. In that way, after a UV-A LED photo-Fenton/CFD treatment, the effluents can be subjected to conventional biological treatments such as activated sludge aiming at the complete degradation of the effluent's organic matter.



## SUPPLEMENTARY MATERIAL



**Figure S5.1** - a) Pictures of UV-A LED photosystems. b) Diagram of setup UV-A LED photo-Fenton experiment.

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**6. TREATMENT OF WINERY WASTEWATER BY  
SULPHATE RADICALS:  $\text{HSO}_5^-$ /METAL  
OXIDATION**

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## **6. TREATMENT OF WINERY WASTEWATER BY SULPHATE RADICALS: $\text{HSO}_5^-$ /METAL OXIDATION\***

### **Abstract**

In this study, the effectiveness of the  $\text{HSO}_5^-/\text{M}^{n+}/\text{UV}$  process on the treatment of winery wastewater (WW) was investigated. The optimal operating conditions were determined:  $[\text{HSO}_5^-] = 2.5 \text{ mM}$ ;  $[\text{M}_2(\text{SO}_4)_n] = 1.0 \text{ mM}$ ;  $\text{pH} = 6.5$  and reaction temperature = 323 K. Under the given conditions, 51%, 42% and 35% of COD removal was achieved using respectively Fe(II), Co(II) and Cu(II) as catalysts. Different UV sources were tested with the previously selected optimal conditions in order to increase the treatment efficiency. The highest COD removal (82%) was achieved using a UV-A LEDs system ( $70 \text{ W/m}^2$ ). These conditions were also promising for the treatment of WW with COD concentrations of 5000 mg  $\text{O}_2/\text{L}$ , reaching 79% and 64% of COD and TOC removal, respectively, after 180 minutes of treatment. At 323 K, the most effective treatment was obtained when Co(II) was used as catalyst (79% and 64% of COD and TOC removal), while at ambient temperature (293 K) the highest COD (65%) and TOC (52%) removals were obtained with Fe(II) catalyst. Moreover, it was demonstrated that the use of  $\text{HSO}_5^-/\text{M}^{n+}$  in several consecutive doses was more efficient than adding the reagents as a single dose at the beginning of the reaction. A comparison between the performance of the  $\text{HSO}_5^-/\text{Fe(II)}/\text{UV-A LED}$  process and the conventional photo-Fenton demonstrated important advantages associated with the  $\text{HSO}_5^-/\text{Fe(II)}/\text{UV-A LED}$  process, including the absence of the costly pH adjustment and of the hydroxide ferric sludge which characterize the photo-Fenton treatment process. The  $\text{HSO}_5^-/\text{M}^{n+}/\text{UV-A LED}$  process demonstrates a high COD and TOC removal efficiency, and it can be considered a promising technology for application in real scale agro-food wastewater treatment plants.

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\*\* Adapted from: Rodriguez-Chueca, J., Amor, C., Silva T., Li Puma, G., Lucas, M.S., Peres, J.A. *Treatment of winery wastewater by sulphate radicals:  $\text{HSO}_5^-$ /metal oxidation*. Chemical Engineering Journal. **2017**, 310, 473-483



## **6.1. Introduction**

The agricultural food industries produce large volumes of wastewater containing high concentrations of organic materials, which are occasionally discharged into municipal wastewater systems<sup>[1-3]</sup>. These effluents are mainly originated from various unit operations such as washing, crushing and pressing of food and grapes, as well as, the rinsing of fermentation tanks, barrels and other equipment<sup>[4, 5]</sup>.

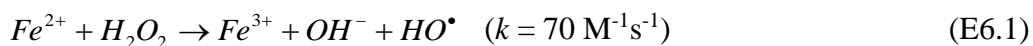
A winery typically produces around 1.3 – 1.5 kg of effluent per litre of wine produced. A high organic load of soluble sugars, organic acids, alcohols, polyphenols, tannins and structural polymers<sup>[6, 7]</sup> and an acidic pH characterize these effluents. In addition, these effluents present a seasonal variability and unpleasant odours, causing environmental and aesthetic problems in the wine producing countries.

The European Directive 91/271/EEC classifies these effluents as similar to urban wastewater<sup>[8]</sup>. For this reason, a high number of winery industries use wastewater treatments methods resembling those used in Municipal Wastewater Treatment Plants (MWWTP). However, conventional wastewater treatments do not work satisfactorily due to the seasonal variability and the high organic concentration of winery effluents. For these reasons, Advanced Oxidation Processes (AOPs) are gaining importance in the treatment of these effluents, due to the capacity of generating free radicals, which can attack and degrade the complex molecules found in winery wastewater.

AOPs can be classified on the basis of the radical species generated as hydroxyl based ( $\text{HO}^\bullet$ ; HR-AOPs) or sulphate based ( $\text{SO}_4^\bullet$ ; SR-AOPs). The most common HR-AOPs are based on the photolysis of hydrogen peroxide (UV- $\text{H}_2\text{O}_2$  process) or in the combination of a semiconductor photocatalyst (e.g.,  $\text{TiO}_2$  or iron oxides) with an oxidant (e.g., oxygen or hydrogen peroxide) and UV radiation; this is the case of  $\text{TiO}_2$ -photocatalysis and the photo-Fenton reaction. The powerful hydroxyl radical generated are able to oxidize a large variety of organic compounds<sup>[9, 10]</sup> and inactivate a wide range of microorganisms<sup>[11, 12]</sup>.

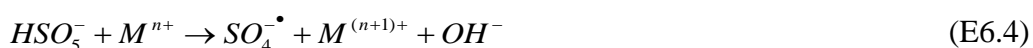
Fenton's reagents oxidation (HR-AOPs) is a homogeneous catalytic oxidation process based on the decomposition of hydrogen peroxide by ferrous ions resulting in the generation of hydroxyl radicals  $\text{HO}^\bullet$ <sup>[13-16]</sup>. The production of  $\text{HO}^\bullet$  is greatly

increased by UV-vis radiation of wavelength up to 600 nm (photo-Fenton process). Photo-Fenton produces hydroxyl radicals via a series of catalytic cycle reactions with iron [Fe(II) and Fe(III)],  $H_2O_2$  and UV radiation. The highest photo-Fenton efficiency is found at pH 2.8<sup>[17]</sup>, since iron salts precipitate far from this pH value. These reactions are summarized as follows:



Recently, sulphate radical-based AOPs (SR-AOPs) are gradually attracting attention as *in situ* chemical oxidation technologies, complementing HR-AOPs. Sulphate radicals processes are based in the addition of chemical oxidants as persulphate salts, such as  $Na_2S_2O_8$ ,  $K_2S_2O_8$  and  $KHSO_5$ <sup>[18]</sup>.

Peroxymonosulphate ( $HSO_5^-$ ; PMS) is the active ingredient of a triple potassium salt,  $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ . This salt has some advantages when compared to hydrogen peroxide. For instance, the oxidation potential of  $HSO_5^-$  ( $E^\circ_{HSO_5^-/HSO_4^-} = 1.82 \text{ V}$ ) is higher than hydrogen peroxide ( $E^\circ_{H_2O_2/H_2O} = 1.78 \text{ V}$ ), although lower than hydroxyl radical ( $E^\circ_{HO^\bullet} = 2.80 \text{ V}$ ). Moreover, PMS is relatively stable at ambient temperature and easy to handle since it is in a powder form. However, PMS presents some disadvantages such as that it reacts slowly with organic species at ambient temperature. PMS can be easily activated into highly reactive radicals by two different routes: i) through homolytic cleavage of the peroxide bond of  $HSO_5^-$  by photolysis or thermolysis (Eq. 6.3); ii) via one electron transfer by transition metal (Eq. 6.4 – 6.6)<sup>[19-21]</sup>.



$M = \text{Co(II), Fe(II) and Ru(II)}$



$M = \text{Ce(III), Mn(II) and Ni(II)}$



M = Ce(IV), Fe(III) and Mn(III)

The efficient activation of  $\text{HSO}_5^-$  through the use of different transition metals such as Fe(II), Co(II) Ni(II), and other metals, has been reported in literature<sup>[20, 22]</sup>. However, it is not clear which transition metal is the most effective for the activation of  $\text{HSO}_5^-$ . For instance, the coupling of  $\text{HSO}_5^-/\text{Fe(II)}$  is one of the most common combination, but it presents some disadvantages similar to the Fenton reaction, such as a slow regeneration of Fe(II) from Fe(III) and the production of a ferric hydroxide sludge<sup>[20]</sup>. In contrast, the coupling of  $\text{HSO}_5^-/\text{Co(II)}$  presents some advantages in comparison with Fenton reaction, including the possibility of applying the  $\text{HSO}_5^-/\text{Co(II)}$  process without pH adjustment<sup>[23, 24]</sup>.

Within this background, the main objective of this study was to evaluate the performance of SR-AOPs ( $\text{HSO}_5^-/\text{M}^{n+}/\text{UV}$ ) as a new and emerging process for the treatment of winery wastewater. In this study we determined the most effective operational conditions of the  $\text{HSO}_5^-/\text{M}^{n+}/\text{UV}$  oxidation process such as pH, temperature, dosage of  $\text{HSO}_5^-$ , the impact of transition metal salts ( $\text{M}_2(\text{SO}_4)_n$ ) and the influence of different artificial UV radiation sources. Finally, the  $\text{HSO}_5^-/\text{M}^{n+}/\text{UV}$  oxidation process performance was compared with the photo-Fenton treatment of winery wastewater performed under the same operational conditions, to determine the benefits of this new treatment process.

## **6.2. Materials and methods**

### **6.2.1. Winery wastewater**

Four different winery wastewater effluents were sourced. The pH of these effluents was in the range 3.6 to 4.0 and the COD load ranged from 513 to 5391 mg  $\text{O}_2/\text{L}$ . Table 6.1 summarizes the physico-chemical characteristics of the winery effluents.

**Table 6.1** - Physicochemical characteristics of simulated (SW) and real (RW) winery effluents

Parameter	Winery Wastewater			
	Effluent 1	Effluent 2	Effluent 3	Effluent 4
pH	4.0	3.8	3.7	3.6
Redox Potential (mV)	42	68	108	210
Conductivity ( $\mu\text{S}/\text{cm}$ )	180	192	201	213
Turbidity (NTU)	< 1	1	1	2
Suspended Solids (mg/L)	1	3	3	3
COD (mg $\text{O}_2/\text{L}$ )	513	864	1752	5391
TOC (mg/L)	143	252	500	1680
Total polyphenols (mg gallic acid/L)	33	47	84	175

### 6.2.2. Reagents

The SR-AOPs were carried out with different dosages of potassium peroxymonosulphate (PMS;  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ; Merck) coupled with different concentrations of transition metals ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{ZnSO}_4$ ;  $\text{NiSO}_4$ ;  $\text{CuSO}_4$ ;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{Ag}_2\text{SO}_4$ ;  $\text{MgSO}_4$  or  $\text{MnSO}_4$ ; Panreac). Sulphuric acid ( $\text{H}_2\text{SO}_4$ ; Scharlau) and sodium hydroxide ( $\text{NaOH}$ ; Panreac) were used for pH adjustment.  $\text{H}_2\text{O}_2$  (30% w/w, Scharlab) was used to carry out the Fenton and photo-Fenton treatments. All the reagents used were analytical grade.

### 6.2.3. Analytical determinations

Different physico-chemical parameters such as pH, conductivity, redox potential, turbidity, Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Polyphenols (TP) were analyzed for the samples characterization. In addition, values of COD and TOC were analyzed during the treatments in order to assess the efficiency of the treatments.

Chemical Oxygen Demand was measured according to 410.4 Method of Environmental Protection Agency of USA<sup>[25]</sup>, using a HACH DR/2400 portable spectrophotometer. Total Carbon (TC) and Total Inorganic Carbon (TIC) were separately determined by catalytic combustion at  $680^\circ\text{C}$  (Standard Methods 5310B<sup>[26]</sup>)

and acidification, respectively, both using a non-dispersive infrared detector (NDIR) in a TOC-L CSH/CSN analyzer equipped with an ASI-L autosampler (Shimadzu). Total organic carbon (TOC) was given by the difference between TC and TIC. The pH and redox potential were determined by a HANNA pH 209 laboratory meter following the Standard Method 4500-H<sup>+</sup>-B and 2580, respectively<sup>[26]</sup>, while conductivity was measured by a Crison Basic as indicated in ISO 7888:1985<sup>[27]</sup>. Turbidity was measured according ISO 7027:1999<sup>[28]</sup> using a HACH 2100 IS Turbidimeter, while Total Suspended Solids (TSS) were measured by spectrophotometry according to Standard Method 2540D using a HACH DR/2400 portable spectrophotometer<sup>[26]</sup>. Finally, the concentration of Total Polyphenols (TP), (mg gallic acid/L), was determined by spectrophotometry using the Folin-Ciocalteu reagent (Merck)<sup>[29]</sup>. UV-vis measurements were carried out using a Jasco V-530 UV/VIS spectrophotometer.

#### **6.2.4. UV radiation sources**

Three UV radiation sources were used: i) a *Heraeus* TNN-15/32 low pressure mercury vapour lamp and ii) two UV-A LEDs systems.

##### i) Heraeus TNN 15/32 mercury lamp

Batch experiments were performed in a *Heraeus* photoreactor (height 18 cm; diameter 8 cm). The cylindrical reactor of 800 mL capacity was made of borosilicate glass with ports, in the upper section, for sampling. The photoreactor was fitted with a *Heraeus* TNN 15/32 lamp (14.5 cm in length and 2.5 cm in diameter) mounted in the axial position inside the reactor. The spectral output of the low-pressure mercury vapour lamp emits mainly (85–90%) at 253.7 nm and about 7–10% at 184.9 nm. The reaction temperature in the reactor was kept at the desired value within  $\pm 0.5$  °C by using a thermostatically controlled outer water jacket. The reactor was loaded with 500 mL of winery wastewater and continuous mixing was maintained by means of a magnetic stirrer.

ii) UV-A LEDs radiation (365 and 370 nm)

The photo-assisted PMS/metal reactions were carried out in a lab-scale batch reactor which was illuminated with two different UV-A LED photo-systems<sup>[30, 31]</sup>. The applied UV radiation in the first photo-system was generated by a matrix of 96 Indium Gallium Nitride (InGaN) LEDs lamps (Roithner RLS-UV370E) which illuminated an area of 11 x 7 cm<sup>2</sup>. These LEDs have a light peak emission at 370 nm, and the nominal consumption of each LED lamp was 80 mW when the applied current was 20 mA. The maximum average optical power was, approximately, 100 mW. The array optical emission was controlled with a pulse width modulation (PWM) circuit that modulated the electric current supplied to each LED in the array. The current supplied had a square waveform with two states: 0 mA (LED emission OFF) and 30 mA (LED emission ON) and a frequency of 350 Hz. The PWM module allowed the configuration of the ON state time duration in each cycle between 0 and 100% of the cycle period and, consequently, the emitted average optical power was modulated between 0 and 100 mW depending on value of the root mean square (RMS) of the electric current intensity waveform supplied to the LED array by the PWM module. The system irradiance was measured using an UV enhanced Si-photodetector (ThorLabs PDA155) in a configuration that replicates the one used in the photoreactor. In this system, the output optical power was controlled using a pulse width modulation (PWM) circuit and the RMS current intensity was measured with a multimeter (UniVolt DT-64).

The second and more powerful photo-system consisted by a matrix of 12 InGaN LEDs lamps (Roithner APG2C1-365E LEDS) with a maximum emission wavelength at 365 nm. The nominal consumption of each LED lamp was 1.4 W at an applied current of 350 mA. The output optical power was controlled by maintaining the forward current constant using a power MOSFET with six different allowed current settings.

The photoirradiation treatments were carried out with a RMS current intensity of 240 mA in the first UV-A LED photo-system, corresponding to a UV irradiance of 23 W/m<sup>2</sup> and a photon flux of  $5.53 \times 10^{-7}$  Einstein/s. The second photo-system irradiance was 70 W/m<sup>2</sup> and the corresponding photon flux was  $1.64 \times 10^{-6}$  Einstein/s.



### 6.2.5. Electrical energy determination

The figure-of-merit electric energy per order ( $E_{EO}$ )<sup>[32]</sup> was used to evaluate the efficiency of the AOP used. This parameter refers to the electric energy in kilowatt hours (kWh) required to reduce the concentration of a pollutant C by one order of magnitude in a unit volume (1000 L) of contaminated water.  $E_{EO}$  can be calculated as follows (Equation 6.7):

$$E_{EO} = \frac{P \cdot t \cdot 1000}{V \cdot \log\left(\frac{C_i}{C_f}\right)} \quad \text{Batch mode} \quad (\text{E6.7})$$

where  $P$  is the rated power (kW) of the system,  $V$  is the volume (L) of water treated in the time  $t$  (h),  $C_i$  and  $C_f$  are the initial and final concentrations, and the factor of 1000 converts g to kg. Higher  $E_{EO}$  values correspond to lower removal efficiencies.

### 6.2.6. Experimental procedure

All the experiments were carried out in duplicate and values presented are the average of both results. The observed standard deviation was always less than 5% of the reported value.

#### i) PMS treatments (SR-AOPs)

Batch experiments were performed on 500 mL of winery wastewater. The pH of the winery wastewater was initially adjusted using  $H_2SO_4$  or NaOH and measured by a 209 pH meter from Hanna Instruments. Then, the effluent was heated to the operating temperature, which was in the range from 293 to 323 K. Finally, the assay started when the dosage of PMS (1 – 20 mM) and the metal sulphate catalyst (0.1 – 8 mM) were added to the effluent at the same time. In the photo-assisted experiments the assay started when the UV radiation system was switched on, also corresponding to the addition of PMS and catalyst. During the course of the reaction samples were withdrawn at periodic interval and analysed.

ii) Fenton and photo-Fenton treatments (HR-AOPs)

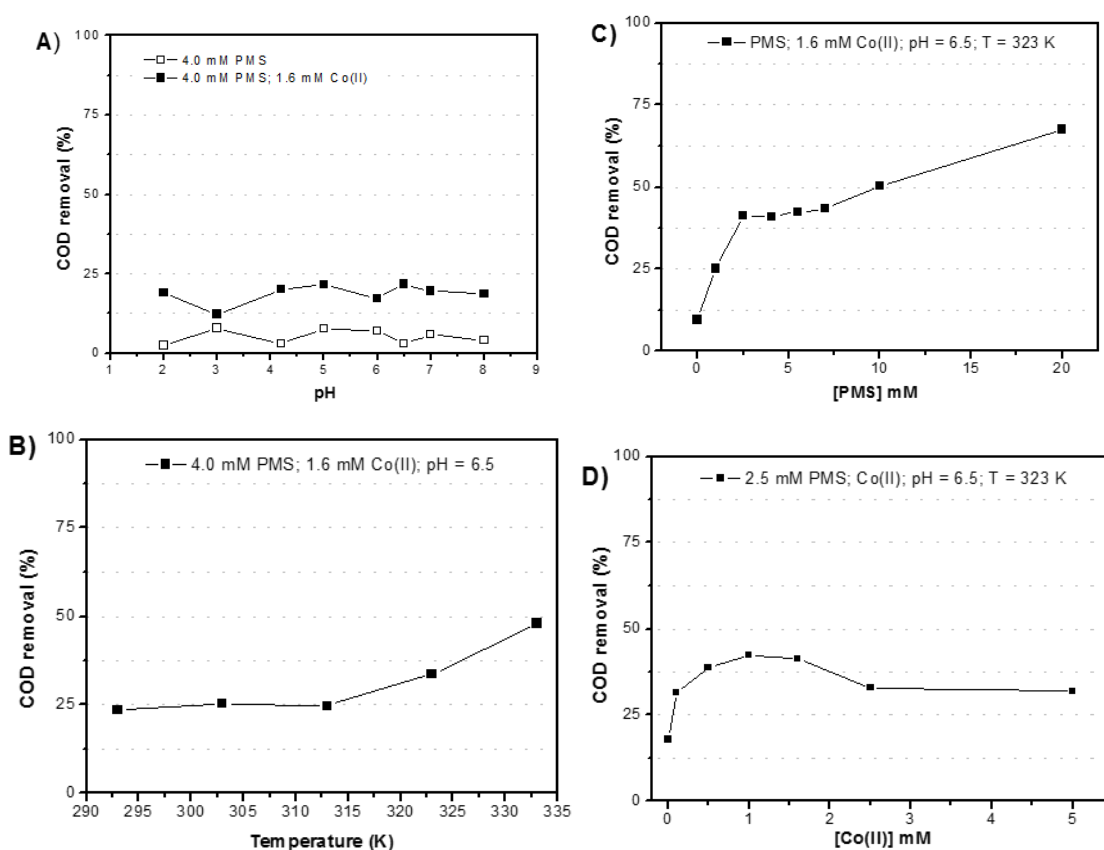
Batch experiments were performed on 500 mL of winery wastewater. The second UV-A LED system was used in the photo-Fenton experiments. The pH of the winery wastewater was initially adjusted to 3 or 6.5, using  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ . Then, the effluent was heated to the operating temperature, which was in the range from 293 to 323 K, and subsequently  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (1 – 8 mM) was added to the effluent. Finally, hydrogen peroxide (range 2.5 to 20 mM) was directly added to the photoreactor at the beginning of each experiment. Samples of the treated effluent were withdrawn during the course of the reaction, at predetermined time intervals and analysed. The concentration of  $\text{H}_2\text{O}_2$  was monitored via Merckoquant peroxide analytical test strips (Test Peroxides, Merck Merckoquant).  $\text{Na}_2\text{SO}_3$  (Panreac<sup>®</sup>) was added to water samples to eliminate residual hydrogen peroxide in each sample. In addition, the temperature of the samples was monitored.

## **6.3. Results and discussion**

### **6.3.1. SR-AOPs**

i) Optimization of operational conditions

The role of different operating parameters such as pH, temperature, PMS concentration, type of transition metal and concentration, as well as the UV radiation source were investigated to establish the optimal operational conditions for the treatment of winery wastewater with the SR-AOPs. In these experiments, winery wastewater with a COD concentration of approximately 500 mg  $\text{O}_2/\text{L}$  was used. Initially, the pH was varied in the range 2 to 8 to determine the pH that achieved the fastest COD removal, with a PMS concentration of 4.0 mM, without metal catalyst, at 293 K and in the absence of UV radiation during the 90 minutes run. Subsequently, the same set of experiments was carried out by adding 1.6 mM of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  metal catalyst.



**Figure 6.1** - COD removal in the optimization of: **A)** pH; **B)** temperature; **C)** PMS concentration; **D)** Co(II) concentration. (Reaction time = 90 minutes).

Figure 6.1 (A) shows the COD removal obtained as a function of the initial pH. In the absence of the sulphate salt, the COD removal did not exceed 10%, while in the presence of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , 20% COD removal was reached. The highest removals were achieved at pH 5.0 and 6.5. The last one was chosen as optimal pH since it is nearer to neutral pH. These results are supported by those obtained by Sun *et al.* for the treatment of landfill leachate<sup>[33]</sup>. On the other hand, the optimal pH is a function of the chemical and physical nature of the effluent and some authors have reported acidic pH values as optimal for the removal of pharmaceuticals and dyes<sup>[34,35]</sup>. Nevertheless, this study suggests that the PMS can also be used at neutral pH obtaining relatively high COD removals in water and urban wastewater treatment thus avoiding the pre- and post-adjustment of pH of the effluents. In the case of the winery wastewater, a slight pre-adjustment of the pH is required, because of the acidic condition of this kind of effluents.

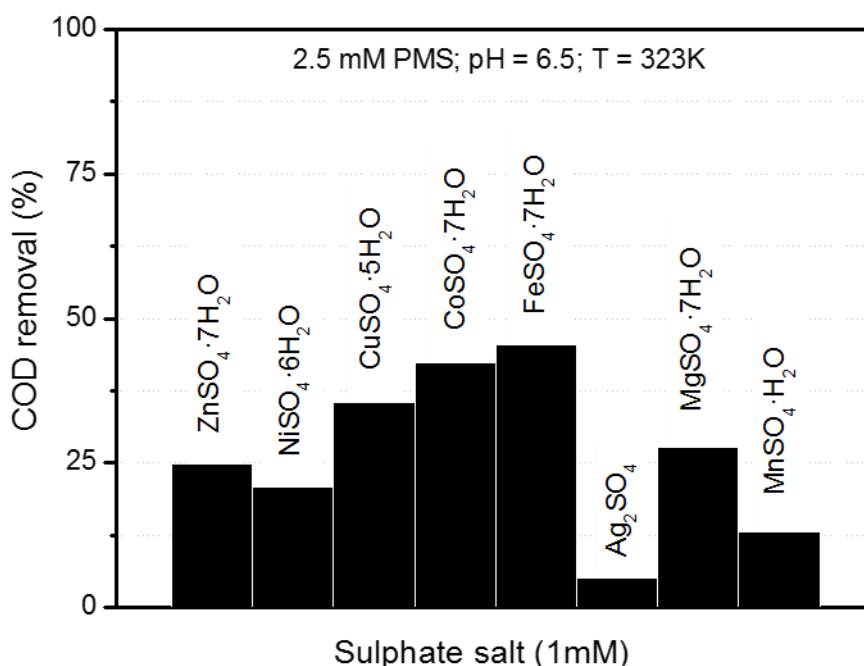
Some authors reported the need of thermal activation of PMS<sup>[21,36]</sup>. Figure 6.1 (B) shows the COD removal as a function of temperature after 90 minutes of treatment, using the optimal pH (6.5) and 4.0 mM of PMS and 1.6 mM of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . The results show no differences between treatments carried out at ambient temperature (293 K) and 313 K, however, the COD removal increased significantly at temperatures above 313 K, doubling COD removal at 333 K. In further experiments, the operating temperature of 323 K was selected since higher temperatures result in an increase in the energy requirement to heat the water.

After pH and temperature optimization, several dosages of PMS were applied in the range from 0 to 20 mM. Figure 6.1 (C) shows the results after 90 minutes of treatment carried out at pH 6.5 and 323 K. A sharp increase in COD removal was observed up to 2.5 mM, followed by a plateau from 2.5 – 7.0 mM, with a COD removal around 42% and to a further increase in the COD removal at higher PMS dosages, such as 10 and 20 mM reporting 50% and 68% of COD removal, respectively. Taking into account economic factors related to the cost of reagents, 2.5 mM was chosen as an optimal PMS dosage.

Finally, the optimization of the concentration of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in the range 0 to 5 mM was carried out using the optimal conditions obtained previously. The COD removal after 90 minutes of treatment reached a maxima (Figure 6.1 (D)) at 1 mM of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . Thus the optimal ratio PMS:Co(II) was 2.5:1, which obtained 43% of COD removal after 90 minutes of treatment. Sun *et al.* also observed a reduction of the COD removal at high Co(II) dosages<sup>[33]</sup>. They reported an optimal ratio PMS:Co(II) of  $10^4$ , therefore being 4.5 mM and  $4.5 \cdot 10^{-4}$  the suitable dosages of PMS and Co(II), respectively, to mediate PMS decomposition in the treatment of landfill leachate (COD = 1116 mg/L). Wang and Chu observed that an excessive ferrous ion concentration will retard the process due to the  $\text{SO}_4^{\bullet-}$  scavenging effect by an excess of Fe(II)<sup>[21]</sup>. In the case of using Co(II), a similar behaviour could be considered.

In further experiments, the effect of the metal species in the sulphate catalysts ( $\text{ZnSO}_4$ ,  $\text{NiSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{MnSO}_4$ ) which is responsible for the activation of  $\text{HSO}_5^-$ , was investigated. These sulphate salts were tested in experiments lasting 90 min, carried out at pH 6.5, 323 K and using a PMS dosage of 2.5 mM over winery effluents with a COD concentration of 500  $\text{mO}_2/\text{L}$ .

Higher COD removals (Figure 6.2) were obtained with  $\text{CuSO}_4$ ,  $\text{CoSO}_4$  and  $\text{FeSO}_4$ , reaching 35, 43 and 51%, respectively. Co(II) has been reported as the most effective metal catalyst for the activation of  $\text{HSO}_5^-$ , which further promotes a radical sulphate cascade mechanism<sup>[33,37,38]</sup>. Anipsitakis and Dionysiou<sup>[19,22,39]</sup> investigated different transition metals as catalysts for the decomposition of PMS. The reduction of Co(III) to Co(II) mediated by the oxidation of PMS is thermodynamically feasible (0.82 V) and fast, and the process proceeds cyclically many times until PMS is totally consumed<sup>[22]</sup>. However, in this reaction the Co(II) product formed is toxic and represents a serious risk to the environment if discharged with the effluent. Therefore, in this study Fe(II) sulphate was investigated for the treatment of winery wastewater as a replacement for Co(II), especially since the combination PMS/Fe(II) achieved COD removals of the same order as those obtained with Co(II). The main advantage of using Fe(II) as PMS activator lies in the synergistic effect with UV radiation, which produces sulphate and hydroxyl radicals, both of which enhance the degradation of organic matter in the winery wastewater. In this case, the catalytic cycle Fe(III)/Fe(II) is accelerated by the photo-reduction of Fe(III)-complexes. Regarding the solution pH, Fe(III) can exist as ferric ions and/or Fe(III)-complexes which in some cases act as photosensitizers, such as  $\text{Fe}(\text{OH})^{2+}$  according to Eq. 2<sup>[21,37-42]</sup>. Besides, significant results of COD removal were achieved with the combination of PMS/Cu(II). Ji *et al.* described the activation of PMS through combination with CuO, demonstrating the efficiency of this catalyst<sup>[43]</sup>, and Madhavan *et al.* compared the coupled system Cu(II)/PMS and Fe(III)/PMS assisted by visible light<sup>[44]</sup>.



**Figure 6.2** - Influence of different sulphate salts in combination with PMS in the COD removal. Conditions: 2.5 mM PMS; 1 mM M<sup>n+</sup>; pH 6.5; T = 323 K; 90 minutes.

As observed, PMS can be activated through a high number of variables; nevertheless, other authors do not report the use of all of these activation agents. Besides, the operational conditions can vary with the chemical composition of each effluent. Sun *et al.* achieved optimal conditions to treat landfill leachate through the combination of PMS/Co(II)/heating<sup>[33]</sup>. These optimal conditions present certain similarities with those obtained in this work. Sun *et al.* established as optimal pH 6.5, dosages of PMS and Co(II) of 4.5 mM and  $4.5 \times 10^{-4}$  mM, respectively, and temperature of 303 K<sup>[33]</sup>. Under these conditions, a COD removal of 57.5% was achieved after 300 minutes of treatment. This COD removal is significantly lower than the removals reported in this thesis, using a lower dosage of PMS and during approximately half of the time.

## ii) PMS/M<sup>n+</sup>/UV radiation

In order to increase the rate of organic matter removal, different UV radiation sources, including low pressure UV mercury lamp and UV-A LEDs lamps, were applied in combination with the optimal experimental conditions obtained in previous

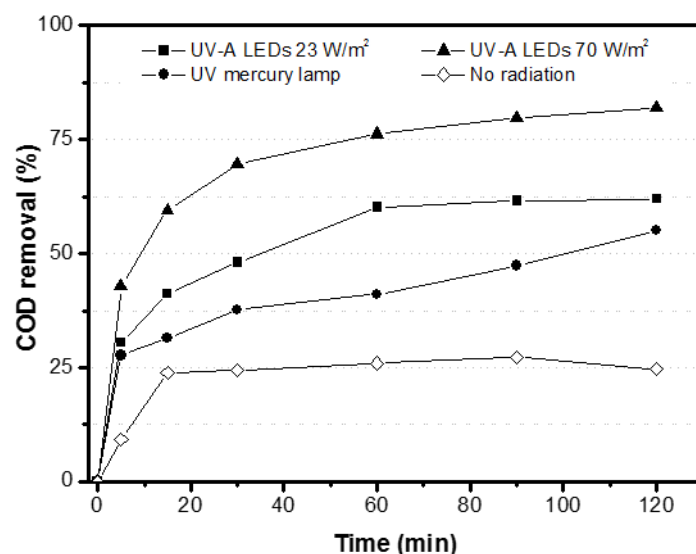
section (2.5 mM PMS; 1 mM  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ; pH = 6.5; T = 323 K). Figure 6.3 shows that most of the COD removal was obtained during the first 20 minutes of treatment. The highest values were achieved using the UV-A LEDs lamps with an irradiance of 70  $\text{W/m}^2$  (80%), followed by the UV-A LEDs lamps with 23  $\text{W/m}^2$  (62%) and the low pressure UV mercury lamp (55%) after a reaction time of 120 minutes, suggesting that the reaction is initially photon limited. As expected, the experiments performed without UV radiation reached a plateau at much lower COD removals (24%) due to the lack of sulphate radicals, after that Co(II) was totally consumed. A similar saturation kinetics was observed in the photo-assisted treatments, but the plateau is approached at much higher COD removals and much longer reaction times. Table 6.2 reports the values of the Electrical Energy per Order ( $E_{\text{EO}}$ ) for the different photo-assisted treatments. The low pressure mercury TNN 15/32 lamp returned a very large  $E_{\text{EO}}$  (173  $\text{kWh/m}^3/\text{order}$ ) in consequence of the high electrical consumption of these types of UV lamp. In contrast, the UV-A LED photo-systems (162 and 98  $\text{kWh/m}^3/\text{order}$ ) are more efficient than the TNN 15/32 lamp since most of the electrical energy applied is converted to UV radiation.

**Table 6.2** - Electrical energy per order ( $E_{\text{EO}}$ ) values of PMS/Co(II) treatments assisted with different UV radiation sources.

Radiation source	Power (kW)	[COD] <sub>f</sub> ( $\text{mgO}_2/\text{L}$ )	$E_{\text{EO}}$ ( $\text{kWh/m}^3/\text{order}$ )
TNN 15/32	0.150	225	1730
1 <sup>st</sup> UV-A LED (23 $\text{W/m}^2$ )	0.0103	190	98
2 <sup>nd</sup> UV-A LED (70 $\text{W/m}^2$ )	0.0301	90	162

The activation of PMS by UV radiation has been reported in the literature<sup>[21,42, 45-48]</sup>. The photolysis of PMS with visible light (419 nm) or near-UV radiation (350 nm) is negligible, however, at 254 nm becomes significant, as reported for the degradation of 2,4,5-trichlorophenoxyacetic acid<sup>[21]</sup>. The photolysis of PMS produces one mole of sulphate radical and one mole of hydroxyl radical per each mole of peroxymonosulphate (reaction 6.3). Thus, if the wavelength is higher than 260 nm, little or no photochemical decomposition of PMS was observed. However, the treatment of winery wastewater by the combination of PMS/ $\text{M}^{n+}$ /UV radiation, did not show significant differences when

the radiation wavelength was varied, and significant COD removal was achieved with UV-A LED radiation.



**Figure 6.3** - Influence of UV source in the PMS/Co(II)/UV treatment process. (▲) UV-A LEDs 70 W/m<sup>2</sup>; (■) UV-A LEDs 23 W/m<sup>2</sup>; (●) UV mercury lamp; (◇) No radiation. Conditions: 2.5 mM PMS; 1 mM Co(II); pH 6.5; T = 323 K; 120 minutes.

The treatment of winery wastewater by the PMS/M<sup>n+</sup>/UV process was performed at different COD concentrations (500, 900, 1900 and 5000 mg O<sub>2</sub>/L) to investigate the treatment efficiency in more concentrated effluents which are more difficult to treat. Table 6.3 shows the COD reduction after the application of the most effective operating conditions (2.5 mM PMS; 1 mM CoSO<sub>4</sub>·7H<sub>2</sub>O; pH = 6.5; T = 323 K; UV-A LEDs 70 W/m<sup>2</sup>).

**Table 6.3** - COD removal values in the PMS/Co(II)/UV-A LED treatment process with different initial COD concentration. Experimental conditions: 2.5 mM PMS; 1 mM Co(II); UV-A LEDs 70 W/m<sup>2</sup>; pH 6.5; T= 323 K; 180 min.

[COD] mg O <sub>2</sub> /L	COD removal (%)	COD removal rate (mg COD/min)
500	80	2.22
900	70	3.50
1900	75	7.92
5000	79	19.33

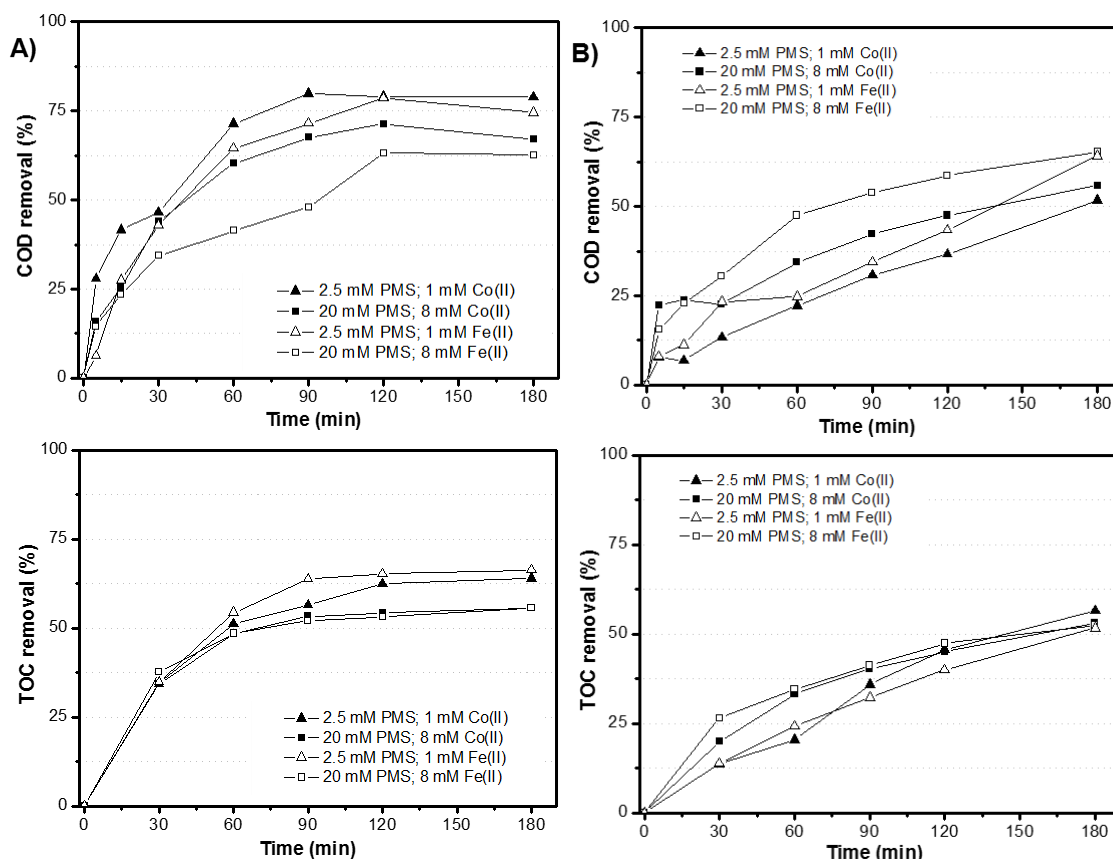
From Table 6.3, the COD removal it is almost the same independently of the initial COD concentration. Therefore, after 180 minutes, 3950 mg O<sub>2</sub>/L of COD were



removed from an initial concentration of 5000 mg O<sub>2</sub>/L. However, the COD removal rate (mg COD removed/min) increases accordingly with the concentration of organic matter. When treatments were applied over effluents with a COD load of 500 mg O<sub>2</sub>/L a removal rate 2.22 mg/min was obtained. Meanwhile, over more concentrated effluents, e.g. 5000 mg O<sub>2</sub>/L, a removal rate of 19.33 mg/min was observed. Thus, a higher amount of COD was removed per minute when the effluent presents a higher organic load. Further experiments were carried out using the effluent with the highest COD load, because such treatment process was able to remove a higher amount of organic matter with the same operating conditions. However, a pre-treatment step can be applied to reduce the COD load and consumption of reagents and energy during the photocatalytic PMS/M<sup>n+</sup>/UV process.

### iii) Application of most effective operational conditions

Different treatments were carried out in order to assess the influence of Co(II) and Fe(II) in combination with PMS, as well as, the influence of temperature when this was above ambient temperature, and the influence of an increase of PMS and transition metal concentration, keeping the molar ratio of PMS:M<sup>n+</sup> constant. Figure 6.4 (A) shows the results of COD and TOC reduction in treatments carried out at 323 K, while Figure 6.4 (B) shows the results obtained at ambient temperature. As it can be observed in Figure 6.4 (A), the experiments performed with Co(II) achieved slightly higher COD removal rate than those performed with Fe(II), but the plateau values achieved are approximately the same, suggesting the consumption of the limiting reactant [M<sup>n+</sup> = Fe(II) or Co(II)]. Moreover, it was observed that an increase in the concentrations of PMS and transition metal, at constant PMS:Metal molar ratio (2.5:1), resulted in a decrease in the final COD removal which was also observed in the TOC results. In terms of TOC removal, there was no difference in the removal rates observed with both metals. In all the treatments at 323 K it was observed that both the rates of removal of COD and TOC decreased after 90 minutes. The rate decrease might be a direct consequence of the decrease of concentration of reactant species in solution.



**Figure 6.4** - Influence of transition metal [Co(II) or Fe(II)] in COD and TOC removal at: (a) 323 K; (b) ambient temperature (293 K). Conditions: COD = 5000 mg O<sub>2</sub>/L; 2.5 mM PMS; 1 mM M<sup>n+</sup>; UV-A LEDs 70 W/m<sup>2</sup>; pH 6.5; 180 min.

On the other hand, the behaviour was opposite when the treatment was carried out at ambient temperature. Figure 6.4 (B) shows that the COD and TOC removals were considerably lower at ambient temperature than at 323 K. However, the most important difference lies in that the higher COD removals were obtained through the combination of PMS with Fe(II) and using the highest concentrations PMS:Fe(II) (20:8 mM). During the first 60 minutes of treatment, the COD removal with Fe(II) catalyst was 48% and with Co(II) catalyst was 34% at the same molar ratio. After 180 min of the treatment the COD removals were 65 and 56% with Fe(II) (0.0057 min<sup>-1</sup>) and Co(II) (0.0039 min<sup>-1</sup>) respectively. At lower concentration and same molar ratio (2.5:1 mM; PMS:Metal) the COD removal proceeded at slower rates although the final COD removals after 180 min were similar to those obtained with the highest dosage of reagents, 64 and 52% with Fe(II) (0.0051 min<sup>-1</sup>) and Co(II) (0.0038 min<sup>-1</sup>), respectively. The TOC removals

observed, which ranged from 50 to 60% (Figure 6.4 (B)), also agree with the general trend observed on the removal of COD.

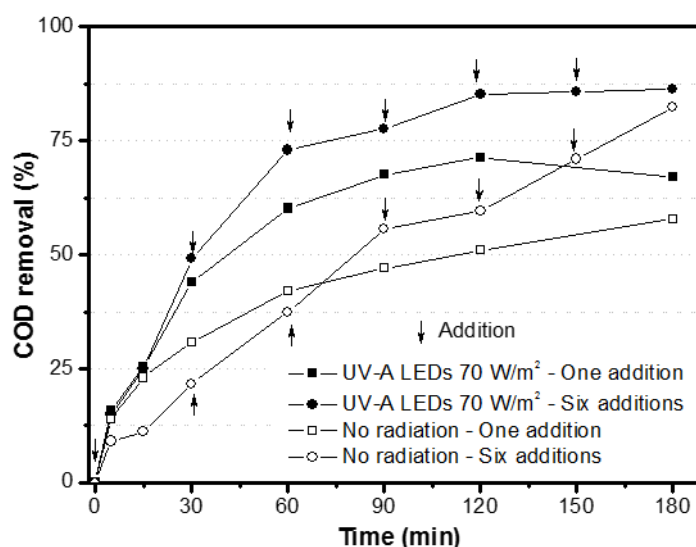
The removal of total polyphenols (TP) through the application of PMS/M<sup>n+</sup>/UV-A LED process at ambient temperature and 323 K is shown in Table 6.4 (TP removal results after 180 minutes of treatment). The highest TP removal was obtained at conditions of ambient temperature combining 2.5 mM of PMS and 1 mM of Co(II) reaching a value of 70%, which are different than the conditions that obtained the highest COD and TOC removal. A similar TP removal, 69%, was obtained but combining 8 mM of Fe(II) with 20 mM of PMS. The TP removal decreased with the increase of temperature until 323 K, reaching maximum removals of 56 and 55% using 8 mM of Co(II) and Fe(II), respectively, with 20 mM of PMS.

**Table 6.4** - Total polyphenols removal through PMS/M<sup>n+</sup>/UV-A LEDs treatments after 180 minutes at pH 6.5.

[PMS] mM	[Fe(II)] mM	[Co(II)] mM	Temperature (K)	TP removal (%)
2.5	1	-	293	27
2.5	1	-	323	19
2.5	-	1	293	70
2.5	-	1	323	47
20	8	-	293	69
20	8	-	323	55
20	-	8	293	57
20	-	8	323	56

Finally, the effect of the dosing procedure of the reagents was investigated using one dose or multiple dosing steps of PMS and CoSO<sub>4</sub>·7H<sub>2</sub>O. A higher dosage of PMS and CoSO<sub>4</sub>·7H<sub>2</sub>O (20 and 8 mM) using the same molar ratio (2.5:1) was selected and the solution was irradiated with UV-A LED radiation (70 W/m<sup>2</sup>) at pH 6.5 and 323 K. In the first set of experiments, the total amounts of PMS and Co(II) were added as a single dose at the beginning of the assay. Whilst, in the other set of the experiments, these reagents were added in six different dosing stages, every 30 minutes, so that in the last addition the total concentrations of PMS and Co(II) added to the solution were 20 and 8 mM, respectively. The results presented in Figure 6.5 show no significant

differences during the first 15 minutes of treatment, however thereafter, the COD removal increased when the reagents were added in stages. The final COD values after 180 min of treatment were 86% using multiple dosing and 70% using a single dose. In the absence of UV-A LED radiation a similar behaviour was observed, but at a reduced rate. In this case, the addition of reagents as a single dose, removed COD faster during the first 60 minutes of treatment, due to the faster generation of radical species at higher concentration of reagents.



**Figure 6.5** - The effect of different dosing steps on COD removal: one addition of 20/8 mM PMS/Co(II) or six additions of 3.33/1.33 mM PMS/Co(II). Conditions: COD = 5000 mg O<sub>2</sub>/L; UV-A LEDs 70 W/m<sup>2</sup>; pH 6.5; T = 323 K; 180 min.

The above behaviour can be understood by considering the scavenging reaction of hydroxyl (reactions 8-11<sup>[49]</sup>) and sulphate radicals (reaction 12<sup>[50]</sup>). At the beginning of the reaction the production of radicals is very rapid since the concentration of reagents is very high and the oxidation process is dominated by the production of radicals.

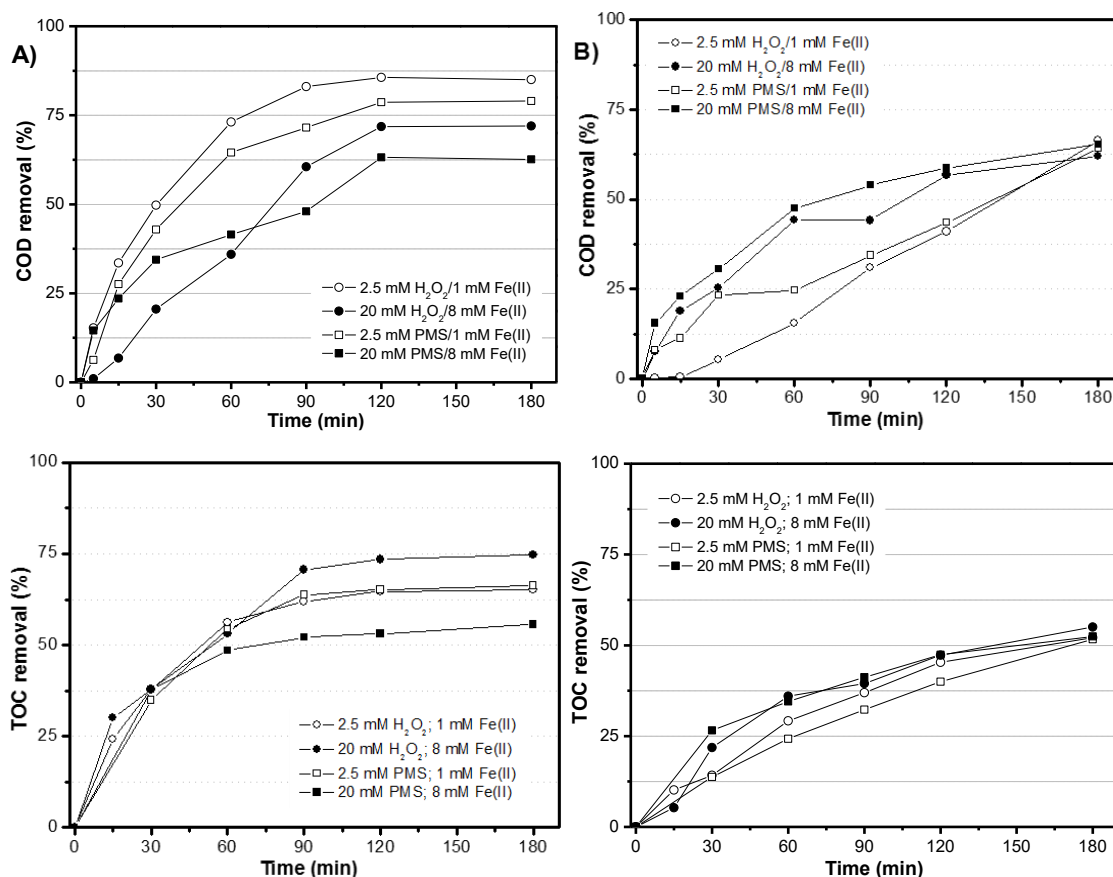




This results in a fast oxidation of the organic matter, however, in parallel the scavenging reactions also proceed at fast rate and the final COD removal does not reach its maximum value. In contrast, the addition of reagents in multiple doses keeps their concentration low in the reactor suppressing the rate of the scavenging reactions, and as a result a more gradual supply of radical species results in a significantly higher final COD removal (82%). This value approaches the same COD removal obtained at higher temperature (323 K) with a single dose of reagents, suggesting that it could be possible to reduce the operating costs, performing the treatment at ambient temperature and with a staged addition of reagents. The influence of number of dosing steps has also been reported by other authors both for the Fenton and the PMS/Co(II) oxidation. Deng and Englehard studied the behaviour in the treatment of landfill leachate by Fenton process, and considered that a single-step addition of the reagents may cause self-decomposition of oxidants due to high concentrations at the point of injection<sup>[51]</sup>. Sun *et al.* also tested various numbers of stepwise additions in the treatment of landfill leachate using Fenton and PMS/Co(II) oxidation processes<sup>[33]</sup> and reported that three and seven doses resulted in a faster treatment of the leachate.

### **6.3.2. HR-AOPs. Photo-Fenton treatments**

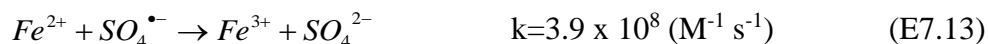
The efficiency of SR-AOPs in the treatment of winery wastewater was benchmarked against the photo-Fenton reaction process, which was applied using the same operational conditions in terms of pH, temperature, Fe(II) concentration and oxidant concentration, in this case H<sub>2</sub>O<sub>2</sub>. Figure 6.6 shows the COD and TOC removal at pH 6.5 at 323 K (Figure 6.6 (A)) and at ambient temperature (Figure 6.6(B)) comparing the treatment of winery wastewater with the SR-AOP and photo-Fenton processes.



**Figure 6.6** - Comparison of SR-AOPs and HR-AOPs on COD and TOC removal at: (a) 323 K; (b) ambient temperature (293 K). Conditions: COD = 5000 mg O<sub>2</sub>/L; 2.5 and 20 mM oxidant agent (PMS or H<sub>2</sub>O<sub>2</sub>); 1 and 8 mM Fe(II); UV-A LEDs 70 W/m<sup>2</sup>; pH 6.5; 180 min.

The photo-Fenton assays carried out at pH 6.5 using 2.5/1 mM H<sub>2</sub>O<sub>2</sub>/Fe(II) (Figure 6.6 (A)) achieved the highest COD removal (85%) and faster removal rate. The COD removal with photo-Fenton was slightly higher than that obtained with the same concentrations of PMS/Fe(II)/UV (79%), despite the photo-Fenton treatment was performed at neutral pH, which differs from the optimum conditions at acidic pH. In addition, at the higher reagents dose, at the same molar ratio, the COD removals decreased to 72 and 63% with the photo-Fenton reaction and PMS/Fe(II)/UV-A LED process. Although the rate of production of radical species may be considered the same at higher and lower dosages, since the molar ratio of the reagents remained unchanged, the scavenging effect of H<sub>2</sub>O<sub>2</sub> on the hydroxyl radicals generated may contribute to the decrease in COD removal. A similar behaviour has been observed with sulphate radicals when PMS was in excess in the reaction system<sup>[33]</sup>. Besides, an excess of Fe(II) would

also contribute to the scavenging of  $\text{SO}_4^{\bullet-}$  radicals<sup>[21, 50]</sup>, as can be observed in the equation 13<sup>[52]</sup>:

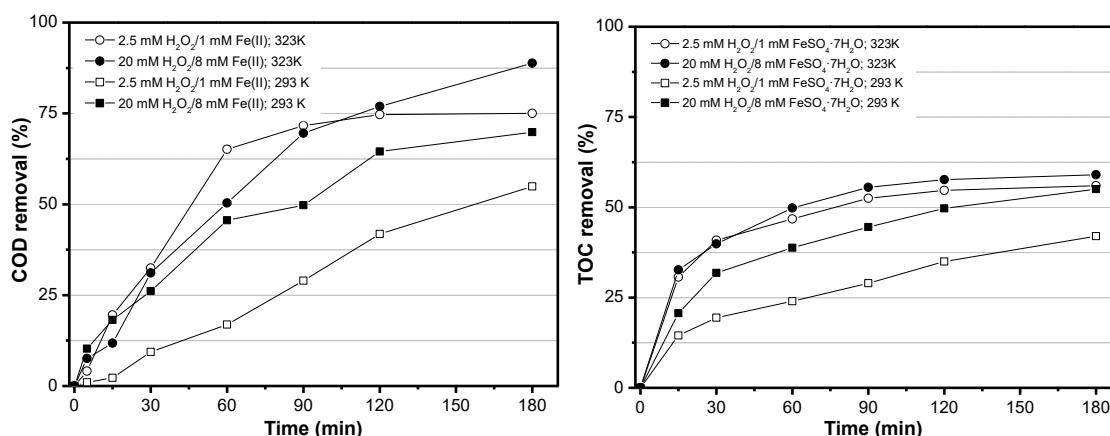


In terms of TOC removal, the highest mineralization of organic matter was obtained through the treatment 20:8 mM  $\text{H}_2\text{O}_2$ :Fe(II) in photo-Fenton treatments with a value of 74%, while at the same conditions the treatment PMS/Fe(II)/UV-A LED achieved 56%. On the other hand, the yields were similar in both treatments when the used concentrations were 2.5:1 mM oxidant:Fe(II), reaching 66% with PMS and 65% with  $\text{H}_2\text{O}_2$ . In conclusion, contaminant removal by the photo-Fenton process proceeded at faster rates than PMS/Fe(II)/UV-A LED treatments. However, it is necessary to take into account some aspects to distinguish both treatments, making difficult their comparison. Firstly, in the case of photo-Fenton assays, it was required to perform new additions of hydrogen peroxide when the concentration of this oxidant agent decreased to very low values in order to continue with the photo-Fenton process. Therefore, in those treatments carried out with 2.5 mM of  $\text{H}_2\text{O}_2$  a total amount of 10 mM hydrogen peroxide was consumed, while in the treatments with 20 mM of  $\text{H}_2\text{O}_2$  a final total amount of 100 mM was consumed, so 4 and 5  $\text{H}_2\text{O}_2$  doses were required respectively. These supplementary doses of oxidant reagent were not necessary in the PMS/Fe(II)/UV-A LED treatment process.

Figure 6.6 (B) shows the results obtained after the application of the same processes but at ambient temperature (293 K). The treatments with PMS were faster than photo-Fenton process both in COD and TOC removal. The final COD and TOC removal after 180 minutes were similar with values around 65% and 53%. In both cases the highest removal rate corresponded with the treatment 20 mM PMS and 8 mM of Fe(II). Again, in the photo-Fenton reactions it was necessary to carry out further doses (2 and 3, respectively) of  $\text{H}_2\text{O}_2$  when each one was consumed, reaching a total concentration of 5 and 60 mM in the treatments with 2.5 and 20 mM of hydrogen peroxide, respectively. Finally, one of the most important disadvantages of the photo-Fenton is the generation of sludge. For instance, in the treatments with 20 mM of  $\text{H}_2\text{O}_2$  and 8 mM of Fe(II), values of 600 mg/L and 717 NTU of total suspended solids and turbidity, respectively, were

observed at the end of the treatment. This situation was less significant in the experiments carried out with PMS/Fe(II) process, with values lower than 50 mg/L and 120 NTU for TSS and turbidity, respectively.

The above experiments were all carried out at near neutral pH of 6.5. However, the application of the photo-Fenton processes at pH 3, at both ambient temperature and 323 K yielded high COD removals (Figure 6.7) up to 89% at 323 K with the highest dosages of reagents (20/8 mM  $\text{H}_2\text{O}_2/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 70% at ambient temperature. Moreover, using eight times lower reactant concentrations (2.5:1 mM  $\text{H}_2\text{O}_2:\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), the difference in the COD removal was only 19% and 27% lower at 323 and 293 K, respectively.



**Figure 6.7** - The effect of temperature on COD and TOC removal through photo-Fenton treatments at pH 3. Conditions: COD = 5000 mg  $\text{O}_2/\text{L}$ ; 2.5 and 20 mM  $\text{H}_2\text{O}_2$ ; 1 and 8 mM Fe(II); UV-A LEDs 70  $\text{W}/\text{m}^2$ ; pH 3; 180 min.

In summary, the application of the  $\text{HSO}_5^-/\text{M}^{n+}/\text{UV-A}$  LED process presents some important advantages. First,  $\text{SO}_4^{\bullet-}$  possesses an oxidation potential (2.5–3.1 V) similar or even higher than  $\bullet\text{OH}$  depending on pH conditions<sup>[53]</sup>. In addition, the use of potassium peroxymonosulphate, as a good source of the oxidant PMS ( $\text{HSO}_5^-$ ), can be carried out without pre- and post-adjustment of pH previous to discharge of the treated effluents. Second, the combination of PMS with a transition metal does not generate ferric hydroxide sludge as in the case of Fenton's reagent, however it is necessary to take into account the residual metal concentration left in the treated effluent, as well as the accumulation of sulphates in the aqueous solution. Third, the activation of PMS



through the combination of a transition metal, heating or UV-A radiation, results in high rates of contaminant degradation during the first few minutes of treatment. Finally, PMS is much easier to store and handle in comparison to hydrogen peroxide. PMS/M<sup>n+</sup>/UV-A LED treatments could be a meaningful alternative for the treatment of winery wastewater, as a stand-alone process or as a pre- or post-treatment process in combination with a biological system. In the latter case a biodegradation study should be recommended.

## **6.4. Conclusions**

This study has focused on the degradation of the organic matter from a winery wastewater through the combined use of PMS/M<sup>n+</sup>/UV. The optimization of the operational conditions such as pH, temperature, PMS and transition metal concentrations was investigated.

Initially, different transition metals were studied in order to determine the most effective conditions for the PMS/M<sup>n+</sup>/UV process. From the results of this study, the following order of treatment efficiency was obtained for the PMS/M<sup>n+</sup>/UV ( $\lambda=365$  nm) technologies: PMS/Fe(II)/UV > PMS/Co(II)/UV > PMS/Cu(II)/UV > PMS/Mg(II)/UV > PMS/Zn(II)/UV > PMS/Ni(II)/UV > PMS/Ag(I)/UV > PMS/Mn(II)/UV.

Moreover, different UV sources were evaluated in terms of E<sub>EO</sub> values, resulting in clear advantages in using UV-A LED photo-systems rather than systems utilizing UV low pressure mercury lamps. These results were achieved considering the global power consumption (kW) of each UV source. To sum up, the optimal conditions were: pH = 6.5; temperature = 323 K; [PMS] = 2.5 mM; [M<sup>n+</sup>] = 1 mM (where M<sup>n+</sup> = Fe(II) or Co(II)) and UV-A LED radiation (365 nm; 70 W/m<sup>2</sup>) which achieved a COD and TOC removal of 75% and 56%, after 90 minutes in effluents with 5000 mg O<sub>2</sub>/L of COD. UV-A LED radiation sources also are eco-friendly, have a low operational cost, and exhibit a high energy efficiency in comparison to conventional mercury lamps.

When PMS/M<sup>n+</sup>/UV treatments were carried out at 323 K, higher COD and TOC removals were obtained through the catalysed decomposition of PMS with Co(II) (79 and 64% respectively) compared to PMS with Fe(II) (74 and 66% respectively) after 180 minutes using 2.5/1 mM PMS/M<sup>n+</sup>. However, the behaviour was the opposite at ambient temperature, reaching a 64 and 57% of COD and TOC removal with Fe(II) and

52% of COD and TOC removal with Co(II). This behaviour can be explained by the higher activation energy of the Co(II)/PMS system (34.3 kJ/M) comparatively to the Fe/PMS and also due to the higher photosensitivity of the Fe species in water as compared to those of Co.

Photo-Fenton treatments at pH 6.5 achieved higher COD removal than PMS/M<sup>n+</sup>/UV treatments at 323 K due to the high influence of heating and UV-A radiation absorption. Nevertheless, the behaviour was the opposite at ambient temperature both at pH 6.5 and pH 3.

The combined treatment PMS/M<sup>n+</sup>/UV-A LED presents some advantages over the photo-Fenton treatment, such as the application at neutral pH avoiding the pre- and post-adjustment of pH and no generation of ferric hydroxide sludge.

## SUPPLEMENTARY MATERIAL

**Table S6.1** - Analytical methodology: physicochemical parameters.

Parameter	Equipment	Method	Reference
pH	HANNA pH 209	SM 4500-H <sup>+</sup> -B	Standard Methods*
Conductivity	Crison Basic	7888:1985	ISO
Redox Potential	HANNA pH 209	SM 2580	Standard Methods*
Turbidity (NTU)	HACH 2100 IS Turbidimeter	7027:1999	ISO
Suspended Solids (mg/L)	HACH DR/2400	SM 2540D	Standard Methods*
COD	HACH DR/2400	410.4	EPA, 1993
TOC	Shimadzu TOC-L CSH/CSN	SM 5310 B	Standard Methods*
Polyphenols	Jasco V-530 UV/VIS	Folin-Ciocalteu	Singleton and Rossi, 1965

\* Eaton *et al.* 2005

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## **7. TREATMENT OF CONCENTRATED FRUIT JUICE WASTEWATER BY THE COMBINATION OF BIOLOGICAL AND CHEMICAL PROCESSES**

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## **7. TREATMENT OF CONCENTRATED FRUIT JUICE WASTEWATER BY THE COMBINATION OF BIOLOGICAL AND CHEMICAL PROCESSES\***

### **Abstract**

Concentrated fruit juice industries use a wide volume of water for washing and fruit processing, generating a large volume of wastewater. This work studied the combination of an aerobic biological process with a chemical coagulation/flocculation step to treat a high concentrated fruit juice wastewater. This wastewater presents a good biodegradability ( $BOD_5/COD=0.66$ ) allowing a chemical oxygen demand (COD) removal above 90% in most reactors. The best results in aerobic biological treatment were obtained in reactors initially loaded with 2 g VSS L<sup>-1</sup> of biomass concentration and 20 g COD L<sup>-1</sup> of organic matter concentration. Three different kinetic models were evaluated (Monod, Haldane and Contois). The Haldane-inhibition model was the one that best fitted the COD biodegradation. AQUASIM<sup>®</sup> software allowed calculate the following kinetic constants ranges for aerobic biodegradation:  $k_s$ : 6–20 g COD L<sup>-1</sup>;  $v_{max}$ : 2.0–5.1 g COD g<sup>-1</sup> VSS day<sup>-1</sup> and  $k_i$  values: 0.10–0.50 g COD L<sup>-1</sup>. These constants correspond to maximum removal rates ( $v^*$ ) between 0.11 and 0.26 g COD g<sup>-1</sup> VSS day<sup>-1</sup> for substrate concentrations ( $S^*$ ) from 0.77 to 3.16 g COD L<sup>-1</sup>. A tertiary coagulation/flocculation process improved the efficiency of the biological pre-treatment. Ferric chloride was selected as best compromise to treat this wastewater. Optimal conditions were 0.44 g L<sup>-1</sup> of coagulant at pH = 5.5, achieving 94.4% and 99.6% on turbidity and COD removal, respectively.

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\*Adapted from: Amor, C., Lucas M.S., Pirra A.J., Peres J.A. *Treatment of concentrated fruit juice wastewaters by the combination of biological and chemical processes*. Journal of Environmental Science and Health, Part A. **2012**, 47, 1809-1817.



## **7.1. Introduction**

Food and beverages processing industries transform agricultural raw materials into intermediate foods and edible products<sup>[1]</sup>. In the case of fruit juices, raw fruits are usually used through a series of sequential operations and processes to produce juice concentrates. During these operations large volumes of water are consumed with consequent wastewater generation, which are highly contaminated with organic matter and suspended solids<sup>[2,3]</sup>. Depending on the methods and equipment used wastewaters will present different physicochemical characteristics.

Fruit juice wastewaters (FJW), like all wastewaters, must be properly treated up to a necessary level to comply with the regulations of discharge into surface waters. Alternatively, it can be reused in agricultural practices<sup>[3,4]</sup>. Biological treatment methods have been recognized as a reasonable option to treat wastewaters with a high organic content<sup>[5–7]</sup> such as those coming from fruit juice processing industries. However, the presence of bio recalcitrant compounds frequently makes impossible to achieve an efficient treatment of these wastewaters. A possible solution to overpass this situation can be through the combination of biological and chemical processes<sup>[5,8,9]</sup>. Biological treatment mineralizes the large biodegradable portion, reducing effectively the COD of the wastewater. Finally, the chemical treatment degrades the remaining persistent compounds.

Physicochemical treatments such as coagulation/flocculation can be a suitable technique to reduce the polluting load of effluents and, particularly, the colloidal particles and natural organic matter. Colloidal particles typically have a negative surface charge. The size of colloids (from 0.01 to 1  $\mu\text{m}$ ) is such that the attractive body forces between particles are considerably less than the repelling forces of the electrical charge. Coagulation is a commonly used process in water/wastewater treatment, where compounds such as aluminium and iron salts are added into effluents to destabilize the colloidal material and agglomerate small particles into larger and settleable flocs<sup>[10]</sup>. Several studies have reported the application of coagulation/flocculation processes to treat industrial wastewaters, determining the optimal experimental conditions, such as pH, coagulant dosage and the influence of flocculant concentration<sup>[11–13]</sup>.

This research work intends to investigate a simple and low-cost treatment system, through the combination of an aerobic biological process and a coagulation/flocculation polishing. The main goal is to comply with the Portuguese legislation of wastewater discharge into natural water bodies. The aerobic biological step will evaluate the removal of dissolved organic matter using different aeration periods. The post-coagulation/flocculation process aims to improve the final characteristic of the biologically pre-treated effluent through the selection of the optimal coagulant dosage and pH. COD, total polyphenols (TP), total suspended solids (TSS), volatile suspended solids (VSS) and turbidity will be monitored.

## 7.2. Material and methods

### 7.2.1. Concentrate fruit juice processing wastewater

Wastewater samples were collected in a concentrated fruit juice industry, located in the centre of Portugal, where pear and apple concentrated syrups are produced. The effluent presents a dark colour and strong odour characteristic of the fruits used in the process. The main physical-chemical characteristics are presented in Table 7.1. From data it is possible to verify that these wastewaters present high COD, TOC and BOD<sub>5</sub> concentrations allied to a considerable amount of suspend and volatile solids. The BOD<sub>5</sub>/COD ratio (0.66) reveals a wastewater with high biodegradability.

**Table 7.1** - Characterization of the wastewater used in this study.

pH	Turbidity	COD	BOD <sub>5</sub>	BOD <sub>5</sub> /COD	TSS	VSS	TP	TOC
(-)	(NTU)	(mg O <sub>2</sub> /L)	(mg O <sub>2</sub> /L)	(-)	(mg O <sub>2</sub> /L)	(mg O <sub>2</sub> /L)	(mg gallic acid/L)	(mg/L)
3.45	719	21 040	13 900	0.66	3 130	1 360	512.4	6 770

### 7.2.2. Analytical determinations

The TSS and VSS were determined according to Standard Methods<sup>[14]</sup>. COD analysis was done in a COD reactor from HACH Co. and a HACH DR 2010 spectrophotometer was used for colorimetric determinations. Total polyphenols content was evaluated by the Folin-Ciocalteu method using a UV-Vis spectrophotometer

PerkinElmer  $\lambda 25$ . Turbidity was determined with a turbidimeter HACH 2100N. TOC was monitored with a Shimadzu TOC-VCSH. pH was followed using a CRISON 507 pH-meter. Biological oxygen demand ( $BOD_5$ ) was evaluated by the respirometric method using an OxiTop<sup>®</sup> device.

### ***7.2.3. Aerobic biodegradation***

Aerobic biodegradation experiments were carried out in 4 L cylindrical aerated biological batch reactors. These reactors, working at environmental temperature (20°C), were provided with covers containing inlets for feed bubbling atmospheric air and outlets for sampling and venting. The air flow was fed to the reacting medium through a bubble gas sparger at a constant flow rate of 125 L h<sup>-1</sup> with three different aeration periods 6, 12 and 18 h/day. The activated sludge used as inoculum was obtained from an aerobic stage of a full-scale urban wastewater treatment plant and previously acclimated to fruit juice wastewater for 3 days. Bioreactors were initially loaded with the fruit juice wastewater and the inoculum sludge. Experiments were performed varying the initial biomass concentration (X) and the initial COD load (S) in the reactor. Preliminary experiments showed that the best results for this kind of effluent were achieved with initial biomass concentration between 2 and 3 g L<sup>-1</sup> VSS, so the X value used ranged between 2 and 3 g L<sup>-1</sup> and the S content changed from 2.5 to 20 g O<sub>2</sub> L<sup>-1</sup>. Thus, in order to easily identify each experiment a simple designation can be used, as an example, the combination X2S2.5 means that such reactor has 2 gL<sup>-1</sup> of initial biomass and an initial COD load of 2.5 g O<sub>2</sub> L<sup>-1</sup>. Experiments were performed with a hydraulic retention time (HRT) of 21 days. During the experiments several samples were withdrawn at regular times to follow the COD, TSS, VSS and pH evolution.

### ***7.2.4. Chemical coagulation/flocculation***

Coagulation/flocculation studies were performed in a conventional model jar-test apparatus (ISCO JF-4, Milan, Italy), equipped with four 1 L beakers, using the effluent of the biological experiments. For each trial, 250 mL of wastewater was poured into the beakers. The calculated quantity of each coagulant/flocculant: Ca(OH)<sub>2</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O or FeSO<sub>4</sub>·7H<sub>2</sub>O was added to the wastewater and the pH

was adjusted to the required value. The mixture was stirred during the time fixed for each experiment. In a typical coagulation/flocculation experiment, the appropriate volume of coagulant was added directly to the sample while stirring during 3 min at 150 rpm. This step (fast stirring), is needed to destabilize the suspension and was followed by a slow stirring during 15 min at 20 rpm, to promote floc agglomeration. The end of sedimentation was set after 60 min when no additional settlement of flocs was observed. Supernatant samples were withdrawn from a point located about 2 cm below the top of the liquid level of the beaker to determine turbidity, COD, TSS, VSS and total polyphenols.

In each experiment the initial pH of the wastewater and the amount of coagulant used were optimized. The pH of the fruit juice wastewater was adjusted with sulphuric acid (1 M) or sodium hydroxide (1 M) solutions. All the experiments were carried out at environmental temperature (20°C). The coagulant solutions were prepared daily to avoid ageing phenomena and improve reproducibility.

#### **7.2.5. Kinetics models**

Several approaches are available in literature for representing the kinetics of bacterial growth and substrate consumption.<sup>[8,15]</sup> In this work the Monod, Haldane and Contois models were chosen to study the biological degradation. In order to evaluate the more suitable kinetic model for fruit juice wastewater biodegradation the AQUASIM<sup>®</sup> software (EAWAG, Dübendorf, Switzerland) was used to fit the experimental data.

If substrate is considered a non-inhibitory compound can be represented by Monod's non-inhibitory kinetics given by Eq. 7.1:

$$v = v_{\max} \frac{S}{k_s + S} \quad (\text{E7.1})$$

In this expression,  $S$  is the substrate concentration;  $v$  the specific growth rate;  $v_{\max}$  the maximum specific substrate utilization rate (gram COD per gram VSS per day) and  $k_s$  the saturation constant (gram of COD per litre).



The Contois model is also a non-inhibitory model commonly used, which usually gives good fits to experimental results<sup>[8]</sup>. The specific degradation rate ( $v$ ) provided by this model proposes Eq.7.2 as a function of substrate concentration:

$$v = v_{\max} \frac{S}{k * X + S} \quad (\text{E7.2})$$

where  $v_{\max}$  represents the maximum specific substrate utilization rate,  $X$  the biomass concentration and  $k$  the Contois saturation constant. Another approach considers the single substrate as a growth inhibitory compound, frequently observed in biological treatment of industrial wastewaters. An example of this approach is the Haldane's model. Haldane's inhibitory model was selected due to its mathematical simplicity and wide acceptance for representing the growth kinetics of inhibitory substrates. The Haldane's inhibitory growth kinetics equation is as follows:

$$v = v_{\max} \frac{1}{1 + \frac{k_s}{S} + \frac{S}{k_i}} \quad (\text{E7.3})$$

where  $v$  denotes the specific degradation rate,  $v_{\max}$  the theoretical maximum specific degradation rate,  $k_s$  the half-saturation constant and  $k_i$  the substrate inhibition constant.

In this model, in the real cases, the maximum growth rate actually observed is according to Eq. 7.4:

$$v^* = \frac{v_{\max}}{2 * \sqrt{\frac{k_s}{k_i}} + 1} \quad (\text{E7.4})$$

where  $v^*$  is the maximum real specific degradation rate observed (gram COD per gram VSS per day). The concentration at which  $v^*$  is observed is given by Eq. 7.5:

$$S^* = \sqrt{k_s \cdot k_i} \quad (\text{E7.5})$$

where  $S^*$  is the substrate concentration at which  $v^*$  is observed (gram per litre).

## 7.3. Results and Discussion

### 7.3.1. Aerobic biodegradation

In the first part of this study an aerobic biological treatment was applied to the concentrated fruit juice wastewater. This treatment process was selected taking into account the BOD<sub>5</sub>/COD ratio of the raw wastewater (0.66), which reveals the high wastewater biodegradability.

#### i) Effect of initial biomass and substrate concentration

Trying to evaluate the influence of biomass concentration (X), organic load (S) and aeration period in the aerobic biological treatment of the fruit juice wastewater, a matrix of experiments was designed. Table 7.2 shows the COD degradation achieved for those different combinations. COD conversion (X<sub>COD</sub>) obtained in each experiment was obtained as follow:

$$X_{\text{COD}} = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100 \quad (\text{E7.6})$$

where COD<sub>0</sub> and COD<sub>f</sub> are the initial and the COD concentration at time t, respectively.

From results, fruit juice wastewater can be successfully biologically degraded, as suggested by the BOD<sub>5</sub>/COD ratio. Because these effluents results from the processing of natural fruits (pear and apple), which contains a high content of nutrients favourable to microorganisms growth, this wastewater organic load can be effectively removed by biological means. Although results reveal different COD removals depending on the operational parameters applied. Aeration period, initial organic load and biomass influences were checked and showed an important role in treatment performance. Concerning to the aeration period, different air supply periods were tested: 6, 12 and 18 h/day. As expected, experiments performed with 6 h/day present the lowest degradation. For the same organic load and biomass (e.g., X2S5) the COD removal rises up with the increase of the aeration period to 12 and 18 h/day.

**Table 7.2** - COD removal rates for biological experiments along the specified days of treatment.

Aeration period	Reactor	$X_{COD}(\%)$			
		Time (days)			
		0.5	7	14	21
<b>6 h/day</b>	X3S2.5	2.5	93.5	96.4	96.7
	X3S5	1.2	30.7	83.9	96.5
	X3S10	0.8	17.5	76.9	94.4
	X3S15	0.5	5.0	29.0	39.9
	X2S2.5	10.2	65.8	96.2	97.0
	X2S5	6.5	31.0	96.0	96.6
	X2S10	1.1	4.7	55.1	78.9
	X2S15	0.3	3.4	28.7	44.4
<b>12 h/day</b>	X3S2.5	10.1	79.8	91.0	97.7
	X3S5	13.3	82.4	97.6	98.2
	X3S10	8.1	68.5	92.3	95.5
	X3S15	6.4	58.2	95.4	96.2
	X2S2.5	21.8	50.1	95.8	96.5
	X2S5	12.4	24.7	94.6	95.6
	X2S10	23.9	79.5	91.9	93.3
	X2S15	3.8	83.9	94.0	94.9
<b>18 h/day</b>	X3S2.5	47.5	95.0	95.4	96.0
	X3S5	40.7	98.4	98.4	98.6
	X3S10	2.4	97.5	97.8	98.4
	X3S20	1.6	28.9	47.6	98.3
	X2S2.5	69.8	92.0	95.2	96.0
	X2S5	7.8	90.0	97.9	98.4
	X2S10	6.0	70.0	97.1	97.8
	X2S20	1.2	35.7	98.5	98.5

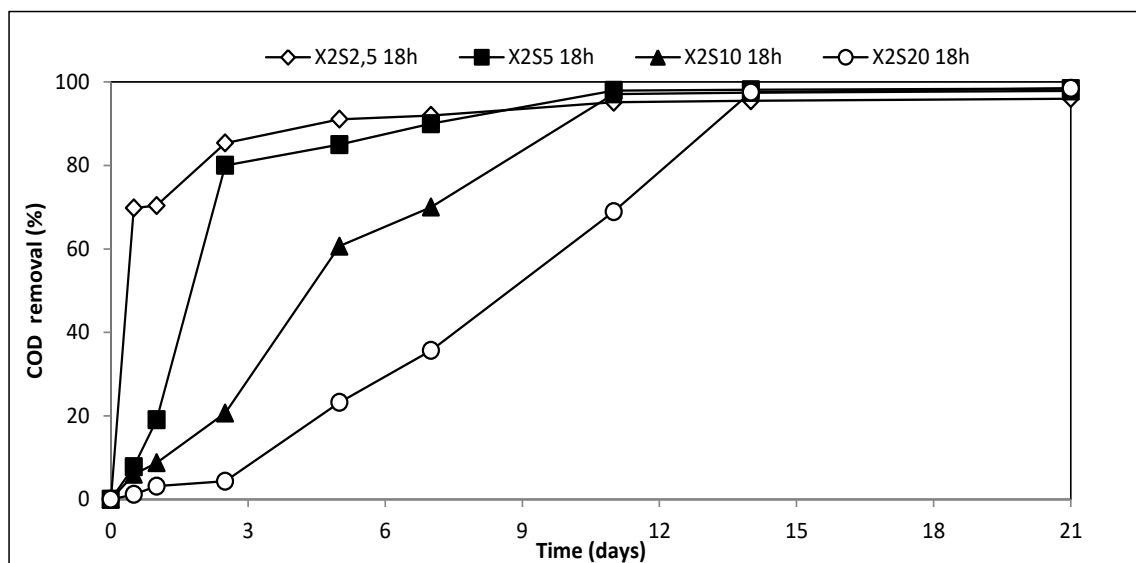
However, this positive influence diminishes with the HRT increase (to 14 and 21 days). This fact can be explained through the generation of facultative/anaerobic conditions in the experiments with 6 h/day of aeration, which allows the organic load degradation with the appearance of unpleasant odours. Thus, when small aeration periods are used the COD removal achieved after 21 days HRT is very similar to the

one obtained with 12 and 18 h aeration/day (around 97%) for low initial organic load applied. An increase in the organic load significantly reduces the depuration capacity of the biologic process, independently of using 2 or even 3 g L<sup>-1</sup> of biomass. Experiments with 6 h aeration/day show COD removals within a wide range (40 to 97%), for 21 days of HRT. On other hand, aerations of 12 and 18 h/day (after 21 days of HRT) present a very similar behaviour.

Assays performed with different initial organic load show that biologic processes are clearly affected, in terms of COD degradation, by this parameter. Increasing the S value from 2.5 to 15 or 20 g L<sup>-1</sup> the yield in terms of COD removal is significantly reduced. As an example, for an aeration period of 18 h/day and a HRT of 7 days, the X2S2.5 reactor reaches 92% of COD removal; alternatively the X2S20 reaches only 35.7% of COD removal. This behaviour shows significant microbial growth inhibition through the substrate.

Finally, the initial amount of biomass (X) added to each reactor was evaluated. Biomass influences the organic load removal in a positive way, particularly in the first 7 days of treatment. For example, with 18h aeration/day the assay X3S5 shows 98.4% of COD decrease, while X2S5 assay achieves only 90%. However, increasing the HRT to 14 or 21 days eliminates the positive effect of the biomass concentration.

Figure 7.1 shows the effect of the initial pollutant load (S) in concentrated fruit juice wastewater degradation with 2 g L<sup>-1</sup> of biomass (X) and an aeration period of 18 h/day. This figure highlights the pollutant load and HRT influences the COD removal rate. Experiments with high organic load achieve low COD degradations. However, increasing the reaction time the COD removed level increases, achieving the same COD degradation rate after 14 days.



**Figure 7.1** - Initial pollutant load applied (S) in concentrated fruit juice wastewater. Experimental conditions: 2 g L<sup>-1</sup> initial biomass (X2) and 18 h/day aeration period.

In a global analysis it is possible to point out that a significant COD removal occurs. Thus, aerobic biological degradation of concentrated fruit juice wastewater is an efficient treatment process, which allows COD removals higher than 96%, for HRT of 21 days and aeration periods of 12 or 18 h/day. However, even after this high degradation, the effluent of the aerobic reactors does not comply with the legal limits of discharge into natural water bodies. Therefore, another treatment process must be applied after the biologic treatment in order to achieve the proposed goal.

### 7.3.2. Kinetics

In order to deeply know the aerobic biologic process previously applied to the fruit juice wastewater, a brief kinetic evaluation will be performed. Thus, three kinetic models commonly used were fitted to the experimental data calculated from the batch experiments.

From the kinetic parameters and the  $\chi^2$  values obtained through AQUASIM<sup>®</sup> software, it was found that the model that best fits the experimental data was the Haldane's model.

Table 7.3 shows the kinetic constants obtained for the Haldane's model with the AQUASIM<sup>®</sup> software. As can be seen, the fruit juice processing wastewater

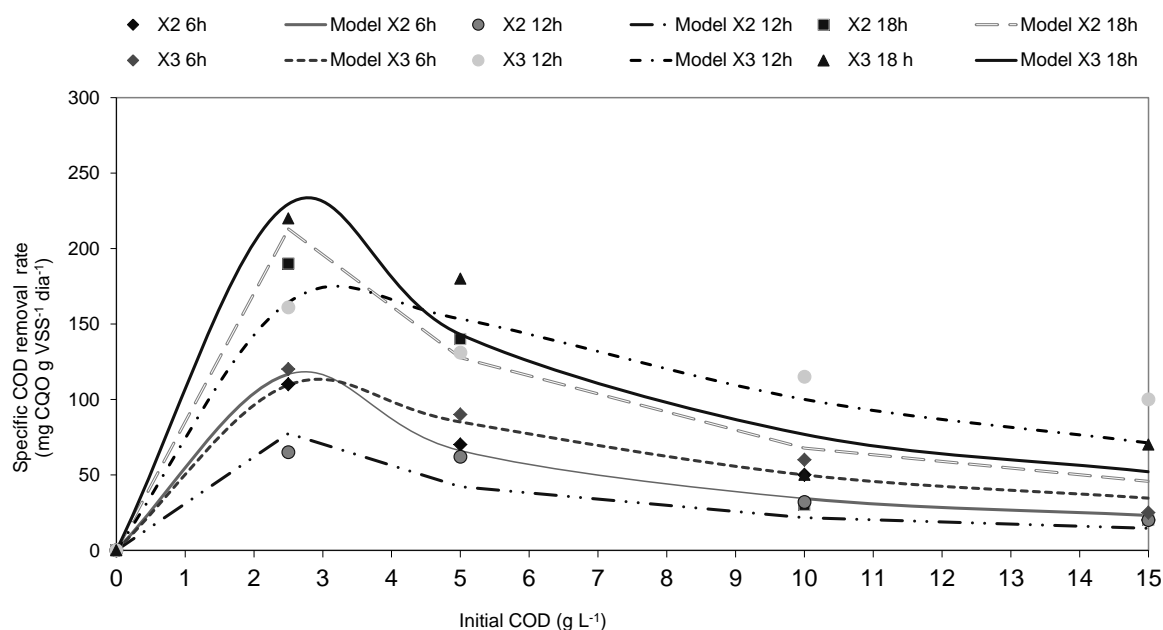
biodegradation presents  $k_s$  values from 6.0 to 20 g COD L<sup>-1</sup>,  $v_{max}$  from 2.0 to 5.1 g COD g<sup>-1</sup> VSS day<sup>-1</sup> and  $k_i$  values between 0.10 and 0.50 g COD L<sup>-1</sup>, which corresponds to maximum observable speeds ( $v^*$ ) from 0.11 to 0.26 g COD g<sup>-1</sup> VSS day<sup>-1</sup> and substrate concentrations ( $S^*$ ) among 0.77 and 3.16 g COD L<sup>-1</sup>.

**Table 7.3** - Haldane's model for fruit juice wastewater biodegradation using different initial biomass concentrations obtained with AQUASIM® software.

<i>Aeration period</i>	<i>Biomass X (g)</i>	<i>k (mg COD L<sup>-1</sup>)</i>	<i>v<sub>max</sub> (g COD g<sup>-1</sup> VSS<sup>-1</sup> day<sup>-1</sup>)</i>	<i>k<sub>i</sub> (mg COD L<sup>-1</sup>)</i>	<i>v* (g COD g<sup>-1</sup> VSS<sup>-1</sup> day<sup>-1</sup>)</i>	<i>S* (g COD L<sup>-1</sup>)</i>
<b>6h</b>	2	10	3.5	0.10	0.167	1.00
	3	20	2.0	0.27	0.110	2.32
<b>12h</b>	2	6.0	2.2	0.10	0.133	0.77
	3	20	2.3	0.50	0.169	3.16
<b>18h</b>	2	10	4.5	0.16	0.264	1.24
	3	13	5.1	0.16	0.265	1.42

From Table 7.3, and according to previous results, a maximum substrate removal rate ( $v^*$ ) is observed for an aeration period of 18 h/day, with similar values for 2 and 3 g of initial biomass content. For lower aeration periods (6 and 12 h/day) the maximum rate of substrate removal predicted by the model is minor, but a regular pattern (concerning the initial amount of biomass) cannot be established.

Figure 7.2 shows the COD removal rates to the different initial biomass concentrations ( $S$ ) (2 and 3 g L<sup>-1</sup>), obtained through the real data and those obtained by Haldane's model (Table 7.3). This figure allows a direct comparison between the different experiments performed, reflecting the specific COD removal rates achieved (g COD g<sup>-1</sup> VSS day<sup>-1</sup>). Regarding the influence of initial substrate concentration ( $S$ ) it appears that for all biomass concentrations tested  $X$  (2 and 3 g VSS L<sup>-1</sup>), the maximum organic matter degradation rate occurs for lower initial COD values. After this peak, a decrease in the maximum specific substrate degradation rate was observable, with the initial increase of COD concentration. This behaviour reveals a substrate inhibition on all the experiments.



**Figure 7.2** - Specific COD removal rate (real data and Haldane's model) as a function of different initial values of biomass, aeration period and COD load.

About the influence of initial biomass content, it can be stated that for 2 and 3 g VSS L<sup>-1</sup> the substrate removal rate is higher and very similar, particularly for 18 h aeration/day. Moreover, it was found that the maximum organic matter degradation rate achieved (approximately 2.2 g COD g<sup>-1</sup> VSS day<sup>-1</sup>) was obtained for 2 and 3 g VSS L<sup>-1</sup> of biomass (X2 and X3) and 2.5 g COD L<sup>-1</sup> of initial substrate concentration. The different initial COD loads showed a decrease in the degradation rates for the different initial S loads. Therefore, the maximum removal rates achieved were always lower, which is in agreement with our previous results.<sup>[8]</sup> After this optimal COD load values, the largest amount of microorganisms and initial COD load results in a lower degradation rate of the pollutant load, due to high substrate competition. Thus, it can be assumed that the removal rate decreases with the increase on initial COD concentration. This fact evidences a greater substrate inhibition, which sharply occurs when the substrate concentration increases.

### 7.3.3. Chemical treatment

Trying to reach the legal values of discharge into natural waters, the effluent of biological treatment needs to be properly managed to obey that objective. In that way,

and since wastewater is no longer biodegradable, a cheap and easy chemical treatment process<sup>[16,17]</sup> was selected to remove the remaining COD: coagulation/flocculation.

To determine the optimal coagulation/flocculation treatment conditions, a series of standard jar-tests were conducted. pH and coagulant dose were evaluated, since they influence the hydrolysis equilibrium of coagulant species. A first series of coagulation/flocculation experiments was conducted using the different chemical coagulants in wastewater solutions at different initial pH. The treatment efficiency was monitored after the mixing, coagulation and settling sequence. The degradation achieved significantly varies, depending on the different chemical coagulants characteristics.

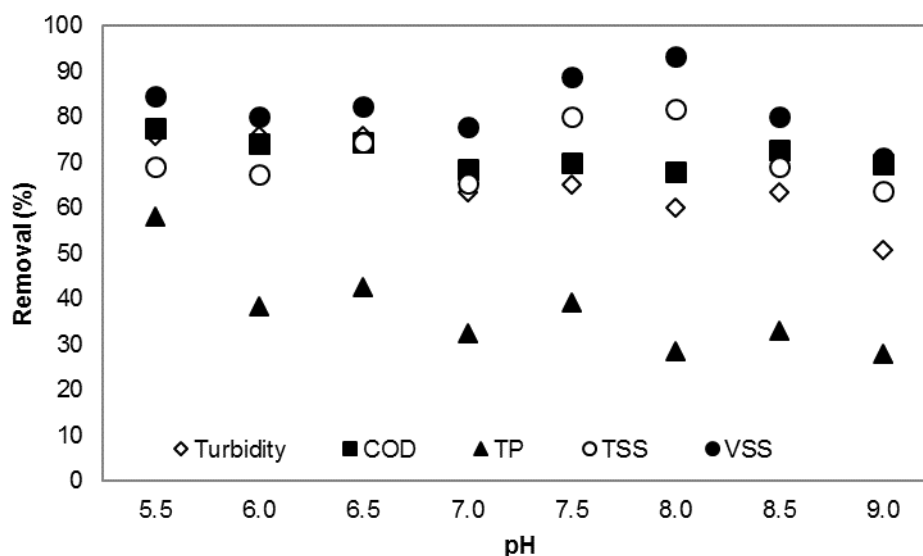
#### ***7.3.4. Influence of pH on coagulation process***

The coagulation-flocculation process depends on various physico-chemical characteristics of the wastewater, especially the pH. The stability of colloidal aggregates results from intermolecular forces that hold the particles in suspension. These pollutants cannot agglomerate unless the pH is adjusted to the isoelectric point. We can therefore assume that for a particular type of wastewater an optimal range of pH exists, where the coagulation process is most effective.

Aluminium sulphate. Alum is commonly used as coagulation agent in industrial wastewater treatment process. Figure 7.3 presents the pH effect in terms of turbidity, COD, total polyphenols, TSS and VSS removal in the coagulation/flocculation with aluminium sulphate. Experiments were performed with the same coagulant dosage ( $0.4 \text{ g L}^{-1}$ ) and within the pH range 5.5–9.0. From data it is possible to say that, in average, highest removals were obtained at pH 6.5. Adding aluminium sulphate at pH 6.5 allows reach reductions of 74.5% COD, 75.9% turbidity, 42.8% total polyphenols, 74.5% TSS and 82.2% VSS. To understand the process of colloidal particles destabilization and the removals achieved with hydrolysed metal ions, it is necessary considering the formation of metal ion hydrolysis products: adsorption and charge neutralization; adsorption and inter particle bridging and enmeshment in sweep flocs<sup>[10]</sup>. These results are according to the aluminium precipitation operational region, pH from 5 to 7, involving the formation of  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{AlOH}_4^-$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{AlOH}^{2+}$ <sup>[18]</sup>. However, if the removal of a specific parameter is intended, other pH values can be

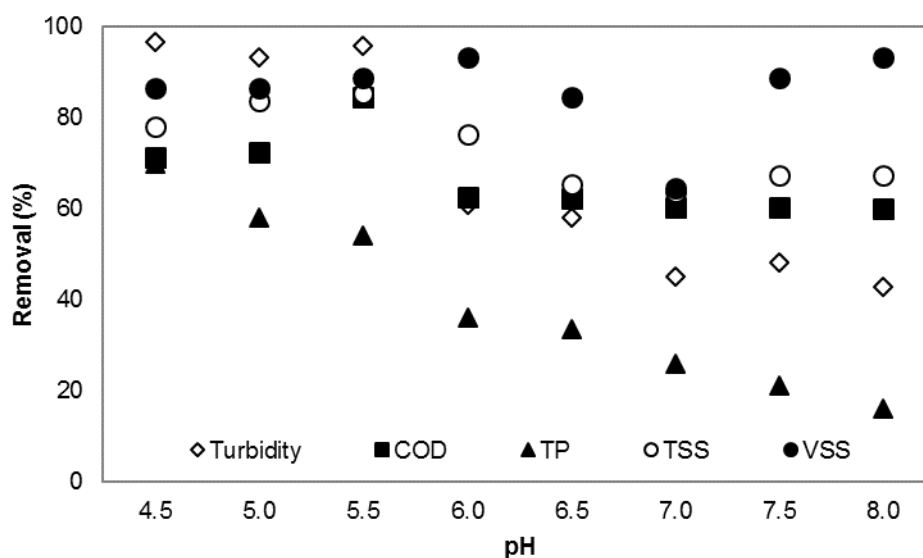


selected. For example, if the purpose was removing the solid fraction pH 8 would be the best option; but the removal of TP could be maximized at pH 5.5.



**Figure 7.3** - pH influence on the removal of turbidity, COD, TP, TSS and VSS using  $0.4 \text{ g L}^{-1}$  of aluminium sulphate as coagulant/flocculant.

Ferric chloride. The pH influence in ferric chloride coagulation/flocculation is presented in Figure 7.4. Tests were conducted using a coagulant dosage of  $0.4 \text{ g L}^{-1}$  and within the pH range of 4.5–8.0. In general, there were obtained better results with the lowest pH values. The best compromise can be reached with an initial pH of 5.5. In this case were achieved reductions of 84.5% COD, 95.8% turbidity, 54.1% total polyphenols, 85.5% TSS and 88.9% VSS. In general,  $\text{FeCl}_3$  acts by colloidal destabilization, resulting in the agglomeration of the small particles into flocs. In the experiments with iron coagulants, the iron precipitation involves the generation of  $\text{Fe}^{3+}$ ,  $\text{FeOH}^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ , and  $\text{Fe}(\text{OH})_3$ . At pH 5.5, below the isoelectric point (which in the case of ferric hydroxide is pH 8), the charge adsorption neutralization mechanism is of considerable importance<sup>[19]</sup>. Other experiments were performed with the same coagulant dosage ( $0.4 \text{ g L}^{-1}$ ). For calcium hydroxide, within the pH range 7.0–10.5, the best removal obtained was 36.3% turbidity, 68.5% COD, 85.5% TSS, 93.3% VSS and 43.3% total polyphenols. Using ferrous sulphate, within the pH range 8.0–11.5, a removal of 74.5% turbidity, 43.4% COD, 76.4% TSS, 82.2% VSS and 32.7% total polyphenols was achieved (results not shown).



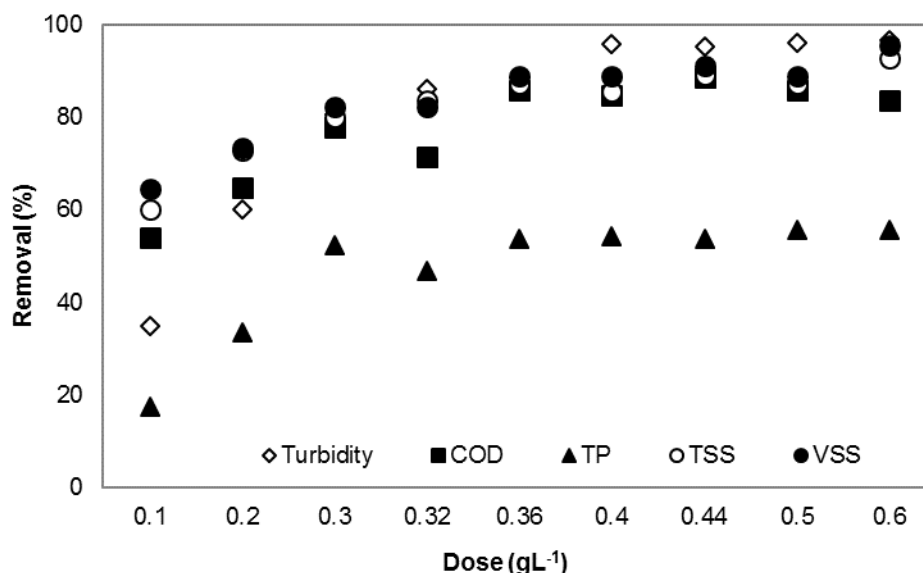
**Figure 7.4** - Effect of pH on the removal of turbidity, COD, TP, TSS and VSS using  $0.4 \text{ g L}^{-1}$  of ferric chloride as coagulant/flocculant.

From an overall analysis of the coagulation/flocculation experiments, performed within the optimal pH range of the coagulants, it is possible support that ferric chloride had the best capacity to remove the pollutant load present in concentrated fruit juice wastewater. Turbidity, COD, TSS and VSS are parameters which achieved, whitening optimal conditions, reductions over 85%. For total polyphenols there were obtained removals of only 50%. Thus, in the further step it was found the optimal dosage of ferric chloride which must be added to our wastewater.

### 7.3.5. Ferric chloride dosage optimization

A treatment setup comprising only ferric chloride at  $\text{pH} = 5.5$  was selected as a best compromise to evaluate the effect of different coagulant dosages on the removal of COD, TP and TSS. Figure 7.5 shows the removal achieved for each ferric chloride dosage. It is clear from results that the removal percentage of all the monitored parameters increased considerably through the use of superior dosages of ferric chloride. There are two mechanisms by which high coagulant dosages can improve the coagulation rate: (a) increasing the concentration of metal hydroxide precipitate and consequently the aggregation rate and (b) by the enmeshing particulates into ever larger aggregates by sweep-floc coagulation<sup>[19]</sup>. However, such behaviour occurs until a

plateau that starts around the dosage of  $0.44 \text{ g L}^{-1}$ , where the percentage of removal stabilizes. In that sense, a ferric chloride dosage of  $0.44 \text{ g L}^{-1}$  can be selected as best compromise.



**Figure 7.5** - Optimization of ferric chloride dosage on the removal of turbidity, COD, TP, TSS and VSS.

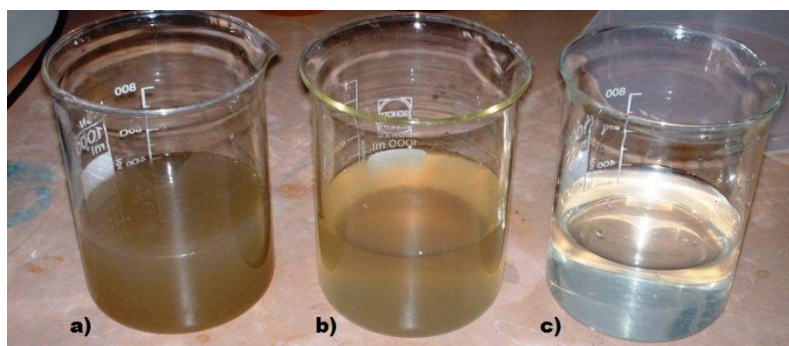
The optimal conditions of pH and coagulant dose established for fruit juice wastewater, will be due to the hydrated metal ion ( $\text{Fe}^{3+}$ ) from  $\text{FeCl}_3$  dissolution, which is hydrolysed to yield monomeric species in the form of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $\text{Fe}(\text{OH})_{3(s)}$  and  $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ . Polymeric species such as  $[\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$  and  $[\text{Fe}_2(\text{H}_2\text{O})_7(\text{OH})_3]^{3+}$  can also occur. These resulting metal hydroxide polymers have amorphous structures with large surface areas, positive charges and hydrophobic properties which favours organic particles interaction into the fruit juice wastewater<sup>[20]</sup>.

Table 7.4 presents a general view of all the treatment processes studied, as well as the legal values of discharge into surface waters. It can be seen that aerobic biological treatment followed by post-coagulation/flocculation process may achieve a global removal of 94.4% to turbidity, 99.6% COD, 99.7% BOD<sub>5</sub>, 98.1% TSS, 97.1% VSS, 96.9% total polyphenols and 99.1% TOC. These results reveal that combining an aerobic biological treatment with a ferric chloride coagulation/flocculation a synergistic effect is achieved in the fruit juice wastewater depuration.

**Table 7.4** - Evolution of different parameters along adopted process, comparison with standards and final percentage reduction.

<i>Parameters</i>	<i>Raw wastewater</i>	<i>After biological treatment</i>	<i>After chemical treatment</i>	<i>Legal value</i>	<i>Reduction (%)</i>
<b>Turbidity</b> (NTU)	716	424	40.2	---	94.4
<b>COD</b> (mg O <sub>2</sub> /L)	21 040	660	75.1	150	99.6
<b>BOD<sub>5</sub></b> (mg O <sub>2</sub> /L)	13 900	275	30.0	40	99.7
<b>TSS</b> (mg/L)	3 130	550	58.7	60	98.1
<b>VSS</b> (mg/L)	1360	450	42.1	---	97.1
<b>Total Polyphenols</b> (mg gallic acid/L)	512	30	14	---	96.9
<b>TOC</b> (mg C/ L)	6 770	255	57.9	---	99.1

Finally, Figure 7.6 shows a visual comparison of the fruit juice wastewater obtained after each treatment step. The raw fruit juice wastewater (**a**) with a dark brown colour; the biologically treated fruit juice wastewater (**b**) with a brown light colour; and the fruit juice wastewater treated with both biological and coagulation/flocculation (**c**) is completely colourless.



**Figure 7.6** - Fruit juice wastewater (FJW) samples after the different treatment steps: (**a**) raw FJW, (**b**) biologically treated FJW, and (**c**) biological and coagulation/flocculation treated FJW.

## **7.4. Conclusions**

The fruit juice wastewater (from pear and apple processing) could be efficiently treated by the combination of an aerobic biological treatment followed by a coagulation/flocculation process (using ferric chloride). This integrated scheme leads to good performances, allowing the direct discharge into watercourses.

Aerobic biological treatment reaches an efficient removal of pollutant load of this wastewater (above 94% of COD removal). The best results (98% of COD removal) were obtained in reactors with an initial biomass content of 2 and 3 g L<sup>-1</sup>, initial COD loads of 20 g COD L<sup>-1</sup> and aeration period of 18 h/day. These removal values were obtained with a HRT of 14 days. The kinetic study made with the AQUASIM<sup>®</sup> software allowed to conclude that the Haldane's model was the one that best fitted the experimental data. The kinetic constants obtained for the Haldane's model with the AQUASIM<sup>®</sup> software are:  $k_s$  from 6.0 to 20 g COD L<sup>-1</sup>,  $v_{max}$  from 2.0 to 5.1 g COD g<sup>-1</sup> VSS day<sup>-1</sup> and  $k_i$  values between 0.10 and 0.50 g COD L<sup>-1</sup>, that corresponds to  $v^*$  from 0.11 to 0.26 g COD g<sup>-1</sup> VSS day<sup>-1</sup> for substrate concentrations ( $S^*$ ) among 0.77 and 3.16 g COD L<sup>-1</sup>. The post-coagulation/flocculation affects positively the overall performance of the proposed two-step process.

From this work it is possible to say that chemical coagulation/flocculation is particularly effective in removing turbidity, COD and solids (total and volatile) from fruit juice wastewater. Ferric chloride at pH = 5.5 was selected as the most efficient coagulant to be applied after biological pre-treatment. This coagulant yields a remarkable turbidity and COD removal (respectively 94.4% and of 99.6%) using 0.44 g L<sup>-1</sup> of ferric chloride.

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## **8. MAIN CONCLUSIONS AND SUGGESTIONS OF FUTURE WORK**

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## **8. MAIN CONCLUSIONS AND SUGGESTIONS OF FUTURE WORK**

### **8.1. Main conclusions**

This section presents a synopsis of most relevant results as well as the main conclusions obtained from experimental work stated in previous chapters.

The main objective of this thesis was to study wastewater treatment strategies, such as the application of advanced oxidation processes (AOPs) or their combination with biological processes applied to different industrial and agro-industrial wastewater with environmental concern to the region of Trás-os-Montes and Alto Douro. Considering the differences of this type of effluents and its variability as a function of several factors, each of studied wastewater was treated based on their characteristics.

In this way, for studies carried out to aiming an effective treatment based on main physico-chemical parameters reduction from treated effluents, are presented the respective conclusions.

### **Chapter 2 - Tertiary treatment of pulp mill wastewater by solar photo-Fenton**

In this work was reported a pulp mill wastewater (PMW) tertiary treatment by Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and solar photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ ) processes in a pilot plant based on compound parabolic collectors (CPCs). The first set of experiments, performed with 1.3, 20 and 50  $\text{mg L}^{-1}$  of iron at pH 2.8, to ascertain the influence of the iron dosage on DOC removal shown greater efficiencies if higher concentrations of iron were used. However, Fenton reaction cannot be considered an attractive option, because of the relatively long treatment time and high amount of iron needed to achieve complete mineralization. The DOC removal achieved was 4%, 18% and 36% working with 1.3, 20 and 50  $\text{mg L}^{-1}$  of iron respectively

On the other hand, solar photo-Fenton assays proved to be more efficient. Experiments with 5  $\text{mg Fe L}^{-1}$  obtained DOC removal rates higher than 90% requiring

31 kJ L<sup>-1</sup> of energy and 50 mM of H<sub>2</sub>O<sub>2</sub>; using 10 mg Fe L<sup>-1</sup> the energy necessary slightly decreases to 26 kJ L<sup>-1</sup> but the H<sub>2</sub>O<sub>2</sub> consumed was 59 mM.

Toxicity and biodegradability assays, carried out at different stages of solar photo-Fenton reaction suggests that more oxidized organic intermediates are formed and rise the wastewater biodegradability up to the low-biodegradability level in the final period of the treatment. Thus, a combination of a solar photo-Fenton and a biological process can be applied to reduce the solar photo-Fenton treatment costs and improve the quality of the final effluent from cellulose production.

### **Chapter 3 - Mature landfill leachate treatment by coagulation/flocculation and solar photo-Fenton**

This work reported the treatment of a mature landfill leachate through the application of chemical-based treatment strategy such as coagulation-flocculation and solar photo-Fenton process. From different chemicals used in coagulation-flocculation trials, in order to evaluate the role of different initial pH and chemicals concentration, ferric chloride showed the best capacity to remove solids and colour, and reduced substantially COD from leachate. The selected conditions were pH 5 and coagulant dose of 2 g L<sup>-1</sup> of such reagent. Fenton process was not efficient enough to allow the direct release of treated leachate into natural water streams, even when coagulation/flocculation was combined with Fenton's reagent.

In order to overcome previous drawbacks, photo-Fenton process was tested as a feasibly alternative. In direct solar photo-Fenton global DOC reduction was about 54% after 110 kJ L<sup>-1</sup> of consumed energy and 15.8 hours however was observed that pH adjustment step of raw leachate represented the main DOC reduction (around 42%). Solar photo-Fenton process combined with coagulation pre-treatment revealed a DOC reduction of 75% (final DOC of 420 mg L<sup>-1</sup> and COD of 980 mg L<sup>-1</sup>) with 110 kJ L<sup>-1</sup> of accumulated UV energy (around 11.5 hours) and a H<sub>2</sub>O<sub>2</sub> consumption of 115 mM.

Although COD values obtained from this strategy cannot led to discharge treated water in natural water bodies, it improved enough to be released into public sewage.

#### **Chapter 4 - Combined treatment of olive mill wastewater by Fenton's reagent and anaerobic biological process**

This work presented the application of a Fenton's reagent pre-treatment combined with an anaerobic biological process to remove the olive mill wastewater (OMW) pollutant load. Preliminary experiments performed were able to define optimal conditions to treat the OMW studied. Thus, the established conditions, a fixed  $\text{H}_2\text{O}_2/\text{COD}$  ratio of 0.20,  $\text{pH} = 3.5$  and a  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio of 15 allowed a COD conversion of only 17.6% and total polyphenol removal of 82.5% after 8 hours of reaction.

The comparison between the results obtained in the combined process (Fenton oxidation + anaerobic digestion) with those obtained in simple anaerobic degradation revealed an increase in the organic matter conversion. For example, in experiments starting COD of about  $3.5 \text{ g L}^{-1}$  gave a value of COD conversion of 55.4% and 73.7% respectively, for original olive mill wastewater and for chemical pre-treated with Fenton's reagent olive mill wastewater. Methane yield also increased for combined process experiments. An average of 306 mL of  $\text{CH}_4/\text{g COD}$  was degraded, exceeding the value of 288 mL of  $\text{CH}_4/\text{g COD}$  obtained in the tests of simple anaerobic degradation of olive mill wastewater.

Olive mill wastewater treatment using a combined treatment Fenton reagent-anaerobic digestion performed an oxidative treatment to remove some inhibiting compounds, thus representing an effective solution with small energy consumption, reduced sludge generation, lower nutrients requirement and potential energy recovery from wastewater.

#### **Chapter 5 - Treatment of crystallized fruit wastewater by UV-A LED photo-Fenton and coagulation-flocculation**

This work reported the treatment of crystallized fruit effluents, with a very low biodegradability ( $\text{BOD}_5/\text{COD} < 0.19$ ), through the application of a UV-A LED photo-Fenton process. Firstly, a Box-Behnken design of Response Surface Methodology was successfully employed since it was effective in estimating the influence of three independent variables:  $[\text{Fe}^{3+}]$ ,  $[\text{H}_2\text{O}_2]$  and reaction time, critically involved in the

removal of COD. These optimal conditions were applied into the two UV-A LED photo-systems at pH 3 during 360 minutes. In the first UV-A LED photo-system, an irradiance of 23 W/m<sup>2</sup> treatment reached a COD removal around 45%. Using a more powerful UV-A LED photo-system, characterized by a higher irradiance under the same current intensity, increase the yield of COD removal in the effluents from crystallized fruit industry. Thus, under same conditions, with 70 W/m<sup>2</sup> and 85 W/m<sup>2</sup> were achieved COD reductions of 65% and 74%, respectively.

After photo-Fenton experiments a coupled coagulation-flocculation step was carried out in order to increase the COD removal and to reduce the amount of total suspended solids and the turbidity in the treated sample. From the results obtained with the different coagulants, a coagulation-flocculation stage at pH 7 using the remaining iron ([Fe<sub>total</sub>]  $\approx$  325 mg/L) from photo-Fenton treatment allowed a slight increase in the removal of COD up to 80 %, removal of suspended solids (95 %) and turbidity (99 %).

This adopted strategy increased the biodegradability index of the treated effluents, allowing it conventional biological treatment such as activated sludge aiming at the complete degradation of the effluent's organic matter.

## **Chapter 6 - Treatment of winery wastewater by sulfate radicals: HSO<sub>5</sub><sup>-</sup>/metal oxidation**

This work reported the effectiveness of the HSO<sub>5</sub><sup>-</sup>/M<sup>n+</sup>/UV oxidation process on the treatment of winery wastewater in terms of chemical oxygen demand (COD) and total organic carbon (TOC) removal.

After getting the optimal conditions and following optimization for the main involved parameters such as pH, temperature, PMS concentration, transition metal and kind of radiation source, was possible to assess that:

- From the different transition metals studied, the most efficient combination on organic matter removal was PMS/Fe<sup>2+</sup>/UV;
- From the different UV sources evaluated, the most efficient was UV-A LED radiation;

- The best operational conditions were: pH = 6.5; temperature = 323 K; [PMS] = 2.5 mM; [M<sup>n+</sup>] = 1 mM (where M<sup>n+</sup> = Fe(II) or Co(II)) and UV-A LED radiation (365 nm; 70 W/m<sup>2</sup>;

- The application of previous conditions achieved a COD and TOC removal of 75% and 56%, after 90 minutes in effluents with 5000 mgO<sub>2</sub>/L of COD.

This work showed that UV-A LED radiation is a serious alternative to conventional UV lamps, since they are eco-friendly, have a low operational cost and high energy efficiency. Comparing with photo-Fenton treatments, sulfate radicals oxidation is advantageous in so far as it presented good efficiencies at neutral pH avoiding the pre- and post-adjustment of pH and no generation of ferric hydroxide sludge was observed.

## **Chapter 7** – Treatment of concentrated fruit juice wastewater by the combination of biological and chemical processes

This study evaluated the efficiency of an aerobic biological process, combined with coagulation-flocculation, in organic matter reduction from an agro-industrial wastewater generated in fruit juice concentrate company. As the resulting wastewater basically comes from fruit washing and processing, it presents a good biodegradability (BOD<sub>5</sub>/COD=0.66).

In first stage, it was found that biological experiments in reactors with an initial biomass content of 2 and 3 g.L<sup>-1</sup>, initial COD loads of 20 g COD L<sup>-1</sup> and 18 h/day aeration results on 98% of COD removal. Nevertheless, the biological treated wastewater does not comply with Portuguese restrictions to its discharge in superficial watercourse. Thus, in second stage a coagulation/flocculation process improved the efficiency of the biological treatment. From the chemicals used as coagulants and/or flocculants, ferric chloride was selected the most efficient, particularly in organic matter reduction. At pH=5.5 and using 0.44 g.L<sup>-1</sup> of ferric chloride was achieved 94.4% and of 99.6% of turbidity and COD reduction.

This integrated scheme leads to good performances, allowing the direct discharge into watercourses.



## **8.2. Recommendations for future work**

According to the obtained results, future research developments can be followed in a near opportunity in order to overcome the restrictions of this working. In this way some recommendations are proposed.

- Use emergent natural coagulants or polyelectrolytes in coagulation/flocculation treatments to observe its efficiency on treatment, thus reducing the environmental impact into water resources;
- Use different oxidants in sulphate radical's oxidation process and explore its effects when applied to a real winery wastewater;
- Test other combinations of treatments, such as the ozonation, ozone/UV, ozone/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub> systems in order to compare the obtained results with Fenton and photo-Fenton studies. As ozonation reveals to be efficient in studies presented in literature this could be an alternative;
- Application of biological treatment in studies in which it was proposed as further treatment, such as in pulp mill, mature landfill leachate and crystallized fruit wastewaters treatment;
- Perform laboratory tests with a time scale for identifying the process behaviour when the wastewater characteristics change and reproduce the optimal conditions on pilot scale in order to be applied in respective industries;
- An economic analysis and a life cycle assessment of treatment processes studied could be made. These analyses will evaluate the economic and environmental impacts of each process and allow select the most feasible process.

## **PUBLICATIONS RELATED WITH THIS WORK**

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## PUBLICATIONS RELATED WITH THIS WORK

### I. Papers published in SCI journals

1. Amor, C.; Lucas, M.S.; Pirra, A.; Peres, J.A.; “Treatment of concentrated fruit juice wastewater by the combination of biological and chemical processes”, *Journal of Environmental Science and Health - Part A*, **47** (12), 1809-1817 (2012).
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## **III. Oral communications**

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2. De Torres-Sociás, E.; Amor, C.; Lucas, M.S.; Peres, J.A.; Oller, I.; Malato, S.; "Detailed treatment line for specific landfill leachate remediation and reuse based on photo-Fenton and ozone (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>): toxicity and biodegradability assessment". International Congress on Water, Waste and Energy Management, Porto, Portugal, 16-18 July 2014.
3. Amor, C.; Rodríguez-Chueca, J.; Fernandes, J.R.; Lucas, M.S.; Tavares, P.B.; Peres, J.A.; “Application of UV-LEDs photo-Fenton to candied fruit wastewater treatment”. 22<sup>nd</sup> World Congress Ozone and Advanced Oxidation: Leading-edge science and technologies, Barcelona, Spain, 27 June - 3 July 2015.
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1. Lucas M.S.; Peres J.A.; Amor C.; Prieto-Rodríguez L.; Maldonado M.I.; Malato S.; "Pulp mill wastewater tertiary treatment by Fenton and solar photo-Fenton processes". Book of Proceedings of 7<sup>th</sup> European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications - SPEA7, ISBN: 978-989-97667-4-7. Porto, 17-20 June 2012, p.378-380.

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7. Rodríguez-Chueca, J.; Amor, C.; Barbosa, D.; Fernandes, J.R.; Lucas, M.S.; Tavares, P.B.; Peres, J.A.; “Treatment of candied fruit wastewater effluents by coupling UV-LED photo-Fenton and coagulation/flocculation”. Livro de Resumos do XX Encontro Luso-Galego de Química, Porto, Portugal, 26-28 Novembro 2014, p.249.
8. Lucas, M.S.; Rodriguez-Chueca, J.; Silva, T.; Amor, C.; Li Puma, G.; Peres J.A.; “ $\text{HSO}_5^-/\text{M}^{n+}/\text{UV-A}$  LED and photo-Fenton processes for winery wastewater treatment”. 4<sup>th</sup> European Conference on Environmental Applications of Advanced Oxidation Processes – EAAOP4 – Athens, Greece, 21-24 October, 2015. Book of abstracts p.180.

