Nuno Alexandre Amaral Matos da Silva

# INTEGRATION STRATEGIES FOR WASTEWATER TREATMENT: ADVANCED OXIDATION PROCESSES AND CONVENTIONAL TECHNOLOGIES

Thesis submitted to the Chemical Engineering Department, Faculty of Sciences and Technology of the University of Coimbra, in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering, under the supervision of Professor Doctor Rosa Maria de Oliveira Quinta Ferreira, Eng. Sérgio Manuel Castro Silva and Doctor Rui Carlos Cardoso Martins

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Universidade de Coimbra

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

# Integration Strategies for Wastewater Treatment: Advanced Oxidation Processes and Conventional Technologies

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**DEPARTMENT OF CHEMICAL ENGINEERING**
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*Dissertation by*:
Nuno Alexandre Amaral Matos da Silva

A thesis presented with due permission for the
public examination in the Sala dos Capelos
at University of Coimbra, Portugal, to obtain
the degree of Doctor in Chemical Engineering.

Coimbra Portugal, 2015

FCT Fundação para a Ciência e a Tecnologia
POPH QUALIFICAR É CRESCER
QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL PORTUGAL 2007.2013
GOVERNO DA REPÚBLICA PORTUGUESA
UNIÃO EUROPEIA Fundo Social Europeu
adventech® advanced environmental technologies

*“I know it seems hard sometimes but remember one thing.*
*Through every dark night, there’s a bright day after that.*
*So no matter how hard it get, stick your chest out, keep your head up…. and handle it.”*

***Tupac Amaru Shakur***

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# Abstract

Society development is leading to an unbridled search for new and more complex products. This enables more intensive production processes, yielding effluents containing pollutants with a high environmental impact, particularly in hydric media. The problems arising from such activities require manufacturing processes adaptation due to environmental restrictions (pollution reduction at source). However, when it becomes impossible, the application of adequate treatment technologies is requested to the specificity of industrial facilities and the environment where the wastewater will be discharged.

Among the existing set of techno-economic solutions, stand out the Advanced Oxidation Processes (AOPs). They are so named because they originate hydroxyl radicals $HO^{\bullet}$, which are highly oxidative being able of degrading a wide range of contaminants. Among these systems, those that operate at ambient temperature and pressure as Fenton and ozonation processes are economically hihlighted.

In this ambit and as the motivating key objective of the present thesis, the performed work arose to give an answer to the requests made to Adventech for the development of wastewater treatment solutions from many different industries and resulted into several commercial proposals. Thus, the overall goal of this research embraced the development and optimization of Advanced Oxidation Processes in order to be integrated with biological treatment systems. Therefore, several integrated treatment schemes were analyzed, with the main target to scrutinize their viability and proceed with the implementation at industrial scale

In this context, the effluent resulting from olive oil mills characterized by high levels of Chemical Oxygen Demand (COD) and low biodegradability ($BOD_5$/COD) was subject of study. Various treatment processes were applied and among them, coagulation / flocculation followed by the homogeneous Fenton process was tested to potentiate a posterior biological treatment. A coagulation / flocculation pre-treatment shows to be essential to enhance homogeneous Fenton process for the production of a treated waste water with the requirements for disposal into the municipal collector, allowing to obtain 90% of COD reduction and 92% abatement in Total Phenolic Content.

The treated effluent revealed also a significant biodegradability increase (0.05 to 0.65) and a decrease of 95% and 96% of Total Suspended Solids (TSS) and Total Dissolved Solids (TDS), respectively. Subsequently, the obtained results were extrapolated for a real waste water treatment plant (WWTP), located in the province of Extremadura, Spain, where approximately 1,000 $m^3$ of oleic effluent were treated. In this unit up to 30% of COD reduction was achieved in the coagulation

stage and a maximum removal of 90% during the oxidation process was obtained, being possible to discharge treated water with 200 $mgO_2.L^{-1}$.

The seasonal effluent from elderberry processing, with a low biodegradability ($BOD_5/COD = 0.05$) and a low/moderate COD (680 mg $O_2$. $L^{-1}$) was purpose object of study too. The oxidation by Fenton treatment was able to achieve an abatement of 70% for the chemical oxygen demand, corresponding to an amount lower than 150 $mgO_2.L^{-1}$, as well as complete removal of the phenol content and an increased biodegradability to 0.2 ($BOD_5 < 40$ $mgO_2$. $L^{-1}$) enabling its direct disposal into drain water.

Due to seasonality, with high flow rates and organic loads during the harvesting season, the wineries WWTP are oversized in relation to their requirements over the remaining year. Thus it was intended to develop a technology with the aim of reducing the operational and investment costs, and contribute to diminish the shortcomings regarding the treatment effectiveness in the productive period. The winery effluent, that tends to be acid (pH= 4.6), with a high COD (5500 $mgO_2.L^{-1}$) and a reduced biodegradability ($BOD_5/COD= 0.23$), was subjected to depurative treatment involving coagulation/flocculation and Fenton's process. At the end an effluent with pH of 8.5, COD removal of about 60% (2240 mg $O_2.L^{-1}$) and an increase in biodegradability to 0.40 was attained, thus enabling an efficient biological treatment. This was subsequently confirmed through the resulting effluent from the biological system (retention time of 10 days) with COD values below 150 mg $O_2.L^{-1}$, allowing the effluent water discharge into the hydro resources.

Another study undertaken along the present work was the treatment of landfill leachate. Single and hydrogen peroxide aided ($O_3/H_2O_2$) ozononation were tested in order to increasing the biodegradability and lowering the wastewater toxicity. The highest organic matter removal was observed for higher pH values when using ozone assisted with hydrogen peroxide with a removal of 45% in COD and 89% of color reduction. Additionally, an increase of the $BOD_5/COD$ ratio from 0.05 to 0.29 resulted in an effluent near to the limit threshold for discharge into the municipal collector showing also high potential for further biological treatment.

Two different wastewaters coming from the washing vegetables (VW) and chemical production (CP) were submitted to ozone stage treatments $O_3$ and $O_3/H_2O_2$. This combined system revealed higher oxidation potential of those two reaction systems with superior values of COD and TOC removal. Indeed, 100% (0 $mgO_2.L^{-1}$) decrease for COD and 33% (38 $mgC.L^{-1}$) reduction for TOC after 120 min were reached for the VW effluent, whereas for the CP effluent 96% (38 $mgO_2.L^{-1}$) for COD degradation and 66% (62 $mgC.L^{-1}$) for TOC lessening were obtained after 180 minutes of reaction. With these results it was concluded that the wastewate reuse was possible and feasible, fulfilling all environmental requirements.

An industrial effluent from the automotive cable coating production, refractory to biological oxidation (biodegradability <0.11), and with high content in COD (10500 ± 1240 $mgO_2.L^{-1}$) was also a case study. Some pre-treatments such as coagulation/flocculation, Fenton and ozonation processes were tested. Afterwards, it was concluded that combining the oxidative mechanisms of ozone (direct and indirect oxidation) with sequences of defined stages, caused by the pH changes along the oxidation, allowed to reach in 24 h operation 98.2% COD removal with a final value of 220 $mgO_2.L^{-1}$.

After the treatment of different effluents and achieving so different depurative operating conditions, it was noteworthy that it is necessary to develop specific and differentiated treatment systems in accordance to the characteristics of the effluent and the final aim for the treated water.

# Resumo

A evolução da sociedade originou uma procura desenfreada por novos produtos cada vez mais complexos, tornando os processos produtivos mais intensivos, originando efluentes que contêm poluentes com um elevado impacte ambiental, em particular nos meios hídricos. Os problemas decorrentes destas atividades requerem a adaptação dos processos de fabrico às restrições ambientais (redução de poluição na fonte). No entanto, quando isto se torna impossível, recorre-se à instalação de tecnologias de tratamento adequada à especificidade das unidades industriais e do meio para onde as águas residuais serão descarregadas.

No conjunto de soluções tecno-económicas existentes, destacam-se os Processos Avançados de Oxidação (AOPs). São assim denominados porque originam radicais hidroxilo $HO^{\bullet}$, os quais são altamente oxidativos sendo capazes de degradar um vasto conjunto de contaminantes. De entre estes sistemas de tratamento, destacam-se aqueles que operam à temperatura e pressão ambiente como os processos de Fenton e de Ozonólise.

Neste âmbito, e como motivação chave da presente tese, os trabalhos efetuados decorreram com o intuito de dar resposta às solicitações realizadas à Adventech para desenvolvimento de soluções de tratamento de efluentes provenientes das mais variadas indústrias, tendo resultado em propostas comerciais. Assim, o objetivo global neste trabalho de investigação é o desenvolvimento e otimização de Processos Avançados de Oxidação de modo a serem integrados com sistemas de tratamento biológico, para além dos tratamentos primários existentes, e determinar de que modo a conjugação dos diferentes tipos de tratamento se torna uma metodologia depurativa efetiva, tendo como principal objetivo escrutinar a sua viabilidade e proceder à sua implementação à escala industrial.

Neste contexto, os efluentes provenientes de lagares de Azeite caracterizados por elevados teores de Carência Química de Oxigénio (CQO) e baixa biodegradabilidade ($CBO_5$/CQO) foram alvo de estudo. Assim, foram aplicados processos de tratamento variados, entre os quais coagulação/floculação, seguidos do processo de Fenton homogéneo, e análise da possibilidade de aplicação de um posterior tratamento biológico. A integração de um processo como coagulação/floculação mostrou ser essencial para potenciar o processo de Fenton homogéneo, conseguindo-se através desta associação a produção de uma água residual tratada com os requisitos necessários à sua descarga em coletor municipal, obtendo-se uma redução de 90% e 92% da CQO e Conteúdo Total Fenólico, respetivamente. O efluente tratado obteve um aumento significativo da sua biodegradabilidade (de 0.05 para 0.65) e uma redução dos Sólidos Suspensos Totais (SST) e Sólidos Dissolvidos Totais (SDT) de 95% e 96% respetivamente. Posteriormente extrapolaram-se os

resultados obtidos para uma ETARI real, situada na província da Estremadura, Espanha, onde foram depurados aproximadamente 1000 $m^3$ de efluente oleico. Nesta unidade obteve-se uma redução de 30% da CQO no estágio da coagulação e atingiu-se uma redução máxima de 90% de CQO durante o processo oxidativo, descarregando uma água tratada com 200 $mgO_2.L^{-1}$.

O efluente sazonal proveniente da transformação de baga de sabugueiro, apresenta uma diminuta biodegradabilidade ($CBO_5/CQO = 0.05$ e CQO moderado 680 mg $O_2$. $L^{-1}$) e foi também objeto de estudo. A oxidação pelo tratamento de Fenton permitiu uma redução de 70% da carência química de oxigénio, atingindo um valor inferior a 150 $mgO_2.L^{-1}$. Por outro lado, este sistema permitiu a remoção total do conteúdo fenólico e um aumento de biodegradabilidade para 0.2 ($CBO_5$ <40 $mgO_2.L^{-1}$), atingindo-se os valores limites de descarga em vala hídrica.

Devido à sazonalidade, com elevados caudais e carga orgânicas durante a vindima, as ETARS vinícolas são sobredimensionadas em relação às suas necessidades durante o restante ano. Pretendeu-se deste modo desenvolver uma tecnologia de modo a reduzir os custos operacionais e de investimento, e contribuir para a diminuição das deficiências ao nível da eficiência do tratamento, na época produtiva. O efluente vinícola, com pH tendencialmente ácido (4.6), um CQO elevado 5500 ($mgO_2.L^{-1}$) e uma biodegradabilidade diminuta ($CBO_5/CQO$ de 0.23), foi sujeito a tratamento depurativo. No final do tratamento conseguindo um efluente com pH de 8.5, uma remoção de CQO de aproximadamente 60% (2240 mg $O_2.L^{-1}$) e um aumento da biodegradabilidade para 0.40, possibilitando assim um tratamento biológico eficiente, comprovado posteriormente com um efluente resultante de tratamento biológico (com um tempo de retenção de 10 dias) com valores inferiores a 150 mg $O_2.L^{-1}$ permitindo que este efluente seja descarregado em vala hídrica.

Outro objeto de estudo foi o tratamento de Lixiviados de aterro sanitário. Procedeu-se ao tratamento por ozonólise simples e também auxiliada por peróxido de hidrogénio ($O_3/H_2O_2$) com intuito de aumentar a biodegradabilidade e diminuir a toxicidade da água residual. A maior remoção de matéria orgânica foi verificada a pH's elevados quando se utilizou ozono coadjuvado com peróxido de hidrogénio com uma remoção de 45% da COD, 89% de cor e um aumento da razão $CBO_5/CQO$ de 0.05 para 0.29 resultando um efluente com um valor perto do limite para descarga em coletor municipal mas igualmente com elevado potencial para posterior tratamento biológico.

Dois efluentes distintos, provenientes da lavagem de produtos hortícolas (VW) e da produção de químicos (CP) foram submetidos a ozonólise ($O_3$) e $O_3/H_2O_2$. O sistema combinado $O_3/H_2O_2$ apresentou um maior potencial de oxidação com valores superiores de remoção de COD e TOC, alcançando 100% (0 $mgO_2.L^{-1}$) e 33% (38 $mgC.L^{-1}$) após 120 min para o efluente VW e 96% (38 $mgO_2.L^{-1}$) e 66% (62 $mgC.L^{-1}$) para o efluente CP após 180 minutos de reação. Com os resultados obtidos é possível concluir que a reutilização das águas residuais é possível e viável preenchendo todos os requisitos ambientais.

Um efluente industrial proveniente da produção de revestimento de cablagem automóvel refratário à oxidação biológica (biodegradabilidade <0.11), com um elevado teor de CQO (10500±1240 $mgO_2.L^{-1}$) foi alvo de estudo. Como metodologias de tratamento, foram testados alguns sistemas como coagulação/floculação, Processo de Fenton e Ozonólise. Posteriormente concluiu-se que combinando os mecanismos oxidativos do ozono (oxidação direta e indireta) com sequências de fases definidas, promovidas pela variação de pH ao longo da oxidação, alcançou-se em 24 h de operação, 98.2 % de remoção de CQO com um valor final de 220 $mgO_2.L^{-1}$.

Após o tratamento de diferentes efluentes e com a obtenção de condições operatórias depurativas distintas, é de realçar que é necessário desenvolver sistemas de tratamento diferenciados e específicos de acordo as características do efluente e com o objetivo de tratamento. Sendo, portanto, fulcral tratar cada água residual como um caso de estudo requerendo um screening para selecionar os processos de tratamento mais promissores seguidos de uma otimização cuidada.

# NOMENCLATURE

•$HO_2$ hydroperoxyl radicals

•OH Hydroxyl Radicals

AOPs Advanced Oxidation Processes

AOS Average Oxidation State

AOX Adsordable Organic Halogens

BOD Biochemical Oxygen Demand

$BOD_5$ Biochemical Oxygen Demand for 5 days

$BOD_7$ Biochemical Oxygen Demand for 7 days

COD Chemical Oxygen Demand

CWO Catalytic Wet Oxidation

DO Dissolved Oxygen

DOC Dissolved Organic Carbon

$EC_{20}$ Effective concentration

$EC_{50}$ Median Effective concentration

IC Inorganic carbon

ISO International Standards Organization

MF Microfiltration

NDIR Non Dispersive Infrared Detector

NF Nanofiltration

NTP Normal Pressure and Temperature

OD Oxygen Demand

OMW Olive Mill Wastewater

OUR Oxygen Uptake Rate

RO Reverse Osmosis

SBI Sludge Biotic Index

SBR Sequencing Batch Reactor

T Temperature

t Time

TC Total Carbon

TOC Total Organic Carbon

TPh Total Phenolic Content

TSS Total Suspended Solids

UF Ultrafiltration

WWTP Wastewater Treatment Plant

$\lambda$ Wavelength

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## II. STATE OF ART

## IV. EXPERIMENTAL RESULTS AND DISCUSSION

# I. INTRODUCTION

A new kind of technologies has assumed a major role and takes a more prominent part in water treatment in last years, the advanced oxidation processes (AOPs). These methodologies show to be effective for numerous applications such as disinfection of drinking water and removal of a wide variety of organic contaminants and pollutants from wastewaters.

However, these processes still need to be further studied and enhanced so that their implementation and application can be widespread. The new approach of application involves their integration with biological treatments, trying to combine the capabilities of each step when compared with the efficiencies and costs of a single system.

The main objective of wastewater treatment technologies is to achieve the prerequisite quality of the treated effluents for its discharge, whether in municipal collector or hydro ditch or even reuse. Therefore, depending on each referred final destination the treatment requirements will vary.

Currently there are several depuration methods for wastewater that, independently or combined, allow to fulfill the regulation requests in the resultant treated wastewaters. For this reason, an exhaustive labor in R&D is needed for developing, testing, designing and installing efficient and economical wastewater treatments in accordance with the effluents characterization and to the desired quality of final water.

## I.1 Water and Environmental Pollution

The industrial production of new compounds in order to sustain the progress and emerging demands of human life leads to an exponential consume of raw materials, an unbalanced spending of hydrological resources and to a huge amount of contaminated effluents (Martins and Quinta-Ferreira, 2011; Poyatos *et al.,* 2009).

Water must be considered as a priceless natural reserve indispensable to ensure the adequate development of living activities. Consequently, the increased public concern has been forcing governments to improve environmental restrictions by imposing more stringent guidelines to such wastewaters production and disposal. Beyond this, environmental pollution of atmosphere and soil are also of concern. In general, pollution can be described as an adverse change in chemical, physical and biological characteristics of air, water and land that can affect society health, ecosystems behavior, industrial development, and cultural assets (Tabrizi and Mehrvar, 2004).

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Water pollutants can be organic and inorganic compounds and heavy metals, all substances with properties to make it undrinkable or inappropriate for the support of animal and plant life (Martins *et al.,* 2010). Inadequate water treatment systems capable of reducing the concentration of toxic substances leads certainly to a deterioration of water sources quality and, thus, of drinking water. Apossible result of this action is serious irreversible damage for the ecossystems, ranging from the weakening or vanishing of a determined life environment to changes in the health of those entities living there.

Industrial processes are characterized by the production of toxic and complex effluents, whose pollutants nature and composition differ as function of the industrial sector. Normally, industry may deliver environmental contaminants as solid wastes, liquid materials, and polluted gases. These are the result of process stages and systems transformation, which are meant to be dumped and whose composition contains often substances in such quantities that are effectively dangerous to the health of humans and to the quality of natural resources needing this way a treatment process or individual disposal. Indeed, industrial wastewaters presenting a miscellaneous matrix of different pollutants contain often bio refractory compounds that are very hard to treat through traditional systems such as those based on biological approaches because of their resistance, inhibitory character or toxicity (Martins *et al.,* 2011). In such cases, where the biological treatment procedures are not effective, except if there is a specific treatment, wastes finish up being discharged into the environment, leading that a small volume of wastewater is capable of contaminating a huge quantity of natural water.

Agro-industrial wastewaters are normally characterized by variable volume and wide diversity of chemical products commonly presenting suspended solids, unstable pH, high Chemical Oxygen Demand (COD), high Total Organic Carbon (TOC), low Biochemical Oxygen Demand (BOD), diminished BOD/COD ratio and elevated levels of toxicity. The impact of their discharges depends not only on biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. In consequence, if they are directly disposed of to the nature, environmental hazards will arise from it. Thus, efficient remediation technologies have to be implemented to avoid environmental pollution.

## I.2 Methodologies Approaches to Wastewater Treatment

The technologies applied in industrial effluents treatment can be categorized broadly as biological treatments, physical separation techniques, and chemical or advanced oxidation processes (AOPs). In many ocassions, combinations of processes have been proposed to improve the efficiency in the removal of contaminants or to reduce the size of equipment and consumption of chemicals (Pignatello *et al.*, 2006). Currently, a great number of the industrial wastewaters treatment plants encompass basically the same type of treatment schemes including suspended solids removal, homogenization and equalization tanks, neutralization steps, physical-chemical processes as coagulation/flocullation and membrane filtration based systems, biological systems with activated sludge, sand filters and adsorption columns. The most common scheme to treat wastewater drop into three stages: primary treatment, as grit removal, grinding and sedimentation; secondary treatment, which uses oxidation of dissolved organic matter by means of biologically active sludge; tertiary treatment involving advanced techniques as polishing methods to achieve the desirable values for the treatment purpose that can be disposal or reutilization.

Regarding coagulation-flocculation, adsorption, foam flotation or membranes filtration, pollutants are transferred between phases originating subsequent wastes thus requiring additional treatment or disposal, whereas biological and advanced oxidation chemical processes are desirable destructive methods. For real effluents employing sometimes more than one depurative technique is more beneficial. Decision about the selection of treatment methods is also influenced by the intermediates formed during oxidization. These greatly differ for each treatment process due to the multitude of chemical reactions that are possible to occur. Therefore, the selection, design, and operation of such processes and their post-treatment methods should be carefully carried out for each particular effluent. The characteristics of chemical pollutants such as toxicity and biodegradability are normally changed and, therefore, suitable techniques should be opted for further cleaning of the new products. Due to its accuracy, minimal analytical effort and short analysis time, COD, TOC and $BOD_5$/COD ratio are used as the main parameters to measure the effluent quality achieved by each process. Other parameters such as pH, total suspended solids and the toxicity level should also be evaluated.

## I.3 AOPs as an Effective Treatment Methodology

Nowadays, biological processes are the preferred choice for wastewater treatment. They are relatively inexpensive and the running costs are low. Among them, the aerobic activated sludge processes are widely used as the main treatment that significantly reduces the COD. On the other hand, anaerobic biodegradation only achieves partial COD removal, requiring a subsequent aerobic treatment to reach complete degradation. However, those applications are not possible when the wastewaters are complex and contain bio recalcitrant compounds because of their resistance, inhibitory character or significant toxicity that inibthis the microorganism's action. Thus, chemical processes are an alternative when biological treatments are unable to decrease both toxicity and COD from industrial wastewater (Bautista *et al.*, 2007; Li *et al.*, 2009).

Progresses in wastewater treatment technologies have been leading to better efficiencies. Advanced Oxidation Processes (AOPs) ($O_3$, $O_3/H_2O_2$, $O_3$/UV, $H_2O_2$/UV, $O_3/H_2O_2$/UV, $H_2O_2/Fe^{2+}$) are more reliable than conventional chemical oxidation processes that use potassium permanganate or chlorine, since AOPs have higher oxidation potential and do not produce chlorinated by-products. Nevertheless, while these techniques revealed to have benefits regarding process yield, it is important to evaluate economical investment and treatment advantages when deciding if the application of a technology is appropriate and cost effective.

AOPs typically operate with less energy requirements than direct oxidation and have been proposed in the last years as powerful advanced technologies for the treatment of biorecalcitrant organic compounds, with a variety of applications showing high degradation efficiencies (Azbar *et al.*, 2003). However, for the development and application of these novel industrial processes it is necessary to consider numerous supplementary aspects, mainly economics (investment and operational costs), methodologies for the process efficiency assessment, implementation area, and automatic control as well. Thus, the process optimization and integration with less expensive technologies urge to be considered in order to increase their viability and acceptance, thus lowering the operational and investment costs, which restrict their dissemination and implementation. In fact, complete mineralization by AOPs treatment may result in high costs, because the by-products formed during the oxidative treatment are usually refractory to further oxidation by chemical means requiring harsher conditions (Hagman *et al.*, 2008). Moreover, it must be also considered the combination of different AOPs which commonly causes the manifestation of attractive synergic effects that can considerably reduce the reaction time and the dosages of required reactants.

## I.4 Motivation and Scope

Currently, the remediation of industrial effluents is far away to have an adequate solution. Consequently, the increased public concern and pressures from environmental non-governmental institutions as well as the adoption of common legislation with tighter international regulations endorses the demand for technical solutions and the application of environmental practices to reduce and mitigate the environmental problems associated with the wastewaters. In this regard, advanced oxidation processes (AOPs) are well known efficient depuration methodologies; nevertheless, their current industrial application is still limited.

As previously mentioned, the high cost derived from the use of AOPs can make attractive the possibility of coupling these effective technologies with less costly biological treatments. Nonetheless, from this point of view, it is necessary further advancement and understanding on the utilization of these processes. In fact, in the case of low biodegradable compounds, the oxidation of organic compounds by AOPs usually produces oxygenated organic products and low molecular weight acids that are more amenable to microorganisms. With toxic compounds, the AOPs will be extended until the point that no biological inhibition due to toxicity will be observed. A new promising application urges with the integration of these oxidation methodologies with the traditional biological treatments, taking the advantage of the potentialities of each one as a unique treatment system.

In this context, the main goal of this Doctoral thesis is to explore new methodologies for the remediation of agro-industrial wastewaters by combining and integrating chemical and biological treatments. Due to this reason, the scope is to improve the understanding of homogeneous Fenton systems and ozonation applications to determine the factors that control the decomposition of organic compounds present in wastewaters by means of advanced oxidation promoted preferentially by hydroxyl radicals. This knowledge can help to increase the efficiency of Fenton’s and ozonation-based treatment processes when applied to wastewaters. Furthermore, biodegradability evolution of the pollutant effluents will be analyzed in sequence to evaluate the viability of the integration with chemical-biological depuration processes.

## I.5 Thesis organization

This PhD thesis structure is a direct consequence from the performed work and the attained results that permitted to write different papers published and/or submitted for publication in international journals, throughout the work carried out during the first two years in the Department of Chemical Engineering, Faculty of Sciences and Technologie of the University of Coimbra (FCTUC), and further at ADVENTECH (Advanced Environmental Technologies).

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 favor these effluents remediation. To achieve 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 this kind of technologies will greatly help the selection of the effective treatments to be applied to each specific effluent.

The thesis is structured as a compilation of the research conduced in this project. The main studies comprise 7 papers that are published or submitted for publication. This work is divided in chapters including an Introduction, Stat-of-Art of the applied treatment technologies, Materials and Methods, Results and Discussion and finally the main Conclusions and Future Work.

Chapter I considers a general introduction focused in the water problematic and in the treatment technologies that will be tested in this thesis. Emphasis on the influence and preponderance of industrial wastewaters contribution to the environmental contamination burden will be given. This part also presents some parameters used to quantify the pollution levels. Moreover, a compilation with the descriptions of the AOPs that are used for the treatment of industrial wastewaters is provided too.

Chapter II presents a general introduction and review of the state-of-the-art focused in treatment technologies that will be tested in this thesis - the application of Advanced Oxidation Processes in the treatment of several wastewaters. In the first part, the current state-of-art of Ozone based and Fenton technologies in pollution abatement is provided through a survey of the technical principles and chemical mechanisms involved in the oxidative processes. An approach to AOPs, which explains their fundamental principles and objectives, with a focus on the Fenton Homogeneous process, the ozonation and Perozonation processes will be referred. Afterwards, the fundamentals of aerobic biological treatments in suspended sludge systems are described, as well as some concepts related with the coagulation / flocculation process. Finally, an assessment to chemical oxidation processes integrated with biological oxidation and physico-chemical systems allow showing the dependency and complementarity between these different processes.

The Materials and Methods are presented in Chapter III with a detailed description of methodologies and essential equipment used for their application, including chemical and biological assays. At the final part, procedures and installations used to perform experimental trials are described.

The experimental results of the AOPs technologies used for the depuration of real industrial wastewaters are discussed in Chapter IV. It comprises seven developed works. The chapter begins with an overview of the various studies carried out with the Fenton oxidation, applied to treat olive mill, winery and elderberry wastewaters. In this regard, there was always the compromise of the final resultant treated water being able to be submitted to posterior biological treatment, even if discharged into a municipal wastewater treatment plant. Thereafter the work involving ozone based processes is described. This was used to treat landfill leachate, chemical and carrot washing effluent and a wastewater from coating automotive electrics industry, emphasizing the major results and accomplished goals.

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

## I.6 References

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# II. STATE OF ART

## II.1 Advanced Oxidation Processes (AOPs)

AOPs are defined as processes that generate highly reactive oxygen radicals. The "advanced" term is used due to the fact that the oxidation reactions are accelerated when radical compounds enter the system. The result is the possible on-site total destruction of refractory organics without the generation of sludge or residues (Gogate and Pandit, 2004b; Cañizares *et al.*, 2007).

These treatment processes use the highly reactive, non-selective hydroxyl radical ($HO^\bullet$) as the primary oxidant in sufficient quantity to affect water purification, at near ambient temperature and pressure so that in many cases no more toxic compounds can be produced during the reaction and complete organic matter mineralization can be achieved. After fluorine, the hydroxyl radical is the most powerful agent to oxidize and mineralize almost every organic molecule, yielding $CO_2$ and $H_2O$ and inorganic ions; Table II.1.1 shows the oxidation potential of oxidizing agents used in water treatments.

***Table II.1.1- Standard reduction potential of some oxidants in acidic media (Pera-Titus et al., 2004)***

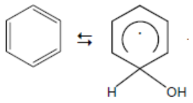
| OXIDANT | STANDARD REDUCTION POTENTIAL |
|---|---|
| **Fluorine ($F_2$)** | 3.03 |
| **Hydroxyl Radical ($HO^\bullet$)** | 2.80 |
| **Atomic Oxygen** | 2.42 |
| **Ozone ($O_3$)** | 2.07 |
| **Hydrogen Peroxide ($H_2O_2$)** | 1.77 |
| **Potassium Permanganate ($KMnO_4$)** | 1.67 |
| **Chlorine** | 1.36 |
| **Bromine** | 1.09 |

Due to their high standard reduction potential of 2.8 V in acidic media, the ($HO^\bullet$) radicals are able to oxidize almost all organic compounds except for some of the simplest organic compounds like the acetic acid, acetone or simple chloride derivatives as chloroform. These molecules are typical oxidation products of larger molecules (Poyatos *et al.*, 2009). Thus, hydroxyl radicals are able to partially remove the fraction of high molecular weight organics. This, usually improves wastewater biodegradability enhancing the possible application of a posterior bio-treatment (Bautista *et al.*, 2007; Li *et al.*, 2009; Goi *et al.*, 2009; Primo *et al.*, 2008; Ntampou *et al., 2006*).

Radicals attack to the pollutants depends in the nature of the parent organic species: abstraction of a hydrogen atom in the case of alkanes and alcohols, electron transfer to hydroxyl radicals and addition to one atom of a multiple atom compound as it often happens with aromatic structures or olefins (Equations II.1 to II.3) (Azbar *et al.*, 2004; Pignatello *et al.*, 2006).

$$\mathrm{HO\bullet + RH \rightarrow H_2O + R\bullet} \qquad \textbf{(II.1)}$$

$$\mathrm{HO\bullet + RX \rightarrow RX\bullet^{+} + OH^{-}} \qquad \textbf{(II.2)}$$

$\mathrm{HO\bullet +}$  $\rightarrow$ further reactions **(II.3)**

There are several AOPs that can be selected to degrade organic compounds. Their classification is often difficult and can be done within distinct aspects such as the mechanism followed for the production of radicals (chemical, photochemical or electrochemical), the number of phases (homogeneous or heterogeneous), their cost or their efficiency among many others (Pera-Titus *et al.*, 2004; Tabrizi and Mehrvar, 2004). Among them, the most popular utilizations incorporate treatment with ozone (in homogeneous phase with single ozonation or combined with $H_2O_2$ and/or UV radiation and in heterogeneous phase in presence of solid catalysts), Fenton type reactions (such as Fenton, photo-Fenton, electro-Fenton or heterogeneous Fenton processes), and also $H_2O_2$/UV systems and heterogeneous photo catalysis with $TiO_2$ (single or with $H_2O_2$) (Poyatos *et al.*, 2009).

Fenton oxidation is an advanced oxidation technology in which a mixture of hydrogen peroxide and iron (II) salts is added directly to the wastewater. Ozonation has been used for the non-persistent disinfection of water. Fenton oxidation and ozonation have both been widely applied in lab scale studies for the treatment of model effluents. However, there is still lacking in literature works involving these interesting systems at a real scale for the abatement of the pollutant character of actual streams. These processes are frequently able to diminish the COD down to the discharge limits set by authorities. However, in some cases these AOPs must be complemented with other techniques in order to achieve the final depuration level. This leads to a more complex process and to an increase in the global treatment cost.

Drawback factors that can affect the formation and concentration of hydroxyl radicals in water treatment include pH, natural organic matter (NOM) and alkalinity (Tuhkanen *et al.,* 2004). NOM is hydroxyl radical scavenger and alkalinity induces carbonate species ($HCO_3^-$ and $CO_3^{2-}$) that can also react with those radicals to produce carbonate ion radicals (Pera-Titus *et al.,* 2004; Tuhkanen, 2004; Ma *et al.,* 2005) (Equations II.4 and II.5):

$$\mathrm{HO}\bullet + \mathrm{HCO_3^-} \rightarrow \mathrm{CO_3^-}\bullet + \mathrm{H_2O} \qquad \textbf{(II.4)}$$

$$\mathrm{HO}\bullet + \mathrm{CO_3^{2-}}\bullet \rightarrow \mathrm{CO_3^-}\bullet + \mathrm{OH^-} \qquad \textbf{(II.5)}$$

However, even if the carbonate radicals can react with organic compounds the reaction is slower and more selective compared to the one with the hydroxyl radicals. Beyond this, the carbonate radicals can also react with $H_2O_2$ in aqueous medium (Equations II.6 e II.7) (Andreozzi *et al.,* 1999; Pera-Titus *et al.,* 2004; Ma *et al.,* 2005).

$$\mathrm{HCO_3}\bullet + H_2O_2 \rightarrow \mathrm{HO_2}\bullet + \mathrm{H_2CO_3} \qquad \textbf{(II.6)}$$

$$\mathrm{CO_3^-}\bullet + \mathrm{HO_2}^- \rightarrow \mathrm{O_2}\bullet + \mathrm{HCO_3^-} \qquad \textbf{(II.7)}$$

In addition to the problems described, the water organic charge, in general expressed as COD (Chemical Oxygen Demand), can also become a limitation to the application of these technologies. Normally the wastewater that has COD values below 10 g.L$^{-1}$ can be treated with these processes, but if the quantity of COD is high, the amount of reactant needed is very high, with negative effects on the treatment cost. Thus, generally, these processes must be envisaged as a step in the overall wastewater treatment scheme that should, whenever possible, encompass biological oxidation. These integration strategies must be optimized to reach operating conditions able to properly treat the wastewater at the lowest cost.

## II.2 Fenton and Fenton-Like Processes

Fenton reaction was discovered by H.J.H. Fenton (Fenton, 1894) who observed that the utilization of hydrogen peroxide and iron salt as catalyst could oxidize various organic molecules. In 1932, it was found that the mechanism of Fenton oxidation is based on the generation of hydroxyl radicals by the catalytic decomposition of the $H_2O_2$ in acidic media (Haber and Weiss (1932)).

This technique reveals a particular interest since it can be held in normal temperature and pressure conditions, using easily to handle reagents and involving short reaction times. Nowadays, the Fenton reaction is known to be a very efficient treatment process in the removal of many hazardous organics.

### II.2.1 Homogeneous Fenton Process

The Fenton process generally involves four stages: pH adjustment, oxidation, neutralization, and coagulation / precipitation. This type of reaction is generally studied and used as a catalytic process based on the electron transfer between $H_2O_2$ and a transition metal acting as a homogeneous catalyst, where the most common is ferrous salt (Gogate and Pandit, 2004a, Guedes *et al.,* 2003).

The mechanism of Fenton's oxidation involves principally the steps described below in Equations (II.8 - II.10). The traditional accepted Fenton reaction implies the oxidation of ferrous to ferric ions (Fe (II) to Fe (III)) to decompose hydrogen peroxide into hydroxyl radicals ($HO^\bullet$) and $OH^-$ (Neyens and Baeyesn, 2003; Wang, 2008):

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + OH^- + \mathrm{HO}\bullet \qquad \textbf{(II.8)}$$

However, the generated Fe (III) in the presence of excess hydrogen peroxide can be reduced and form more radicals and again ferrous iron. This secondary process, designated as Fenton-like, is slower than the Fenton reaction, and permits Fe(II) regeneration in a cyclic mechanism (Equations II.8 and II.9) (de Laat *et al.*,2004). For this reason iron is added in small amounts while $H_2O_2$ is continuously consumed.

$$Fe\ (III) + H_2O_2 \rightarrow Fe\ (II) + \mathrm{HO_2}\bullet + H^+ \qquad \textbf{(II.9)}$$

$$Fe\ (III) + \mathrm{HO_2}\bullet \rightarrow Fe\ (II) + \mathrm{O_2} + H^+ \qquad \textbf{(II.10)}$$

Equations II.9 and II.10 represent the rate-limiting step in the Fenton chemistry, as they are responsible for the regeneration of ferrous ions from the previously produced ferric ones. In fact, ferrous ion remains at a trace concentration, with approximately constant Fe (III) levels in solution. For this, the reaction rate is limited by the rate of ($HO^\bullet$) generation, which is directly related to the concentration of the iron catalyst (Neyens and Baeyesn, 2003; Pignatello *et al.*, 2006). The Fenton-like process is slower than the Fenton one and, apart from ferrous ion regeneration, hydroperoxyl radicals ($HO_2^{\bullet}$) produced are less powerful oxidants than hydroxyl ones.

Equations II.11- II.16 show other important reactions that can also take place during the Fenton process involving ferrous ion and radical reactions or hydrogen peroxide-radical reactions (Pera-Titus *et al.,* 2004; Neyens and Baeyens, 2003; Bautista *et al.*, 2008).

$$Fe\ (II) + \mathrm{HO_2} \bullet + \mathrm{H}^+ \rightarrow \mathrm{Fe\ (III)} + H_2O_2 \qquad \textbf{(II.11)}$$

$$Fe\ (II) + \mathrm{HO} \bullet + \rightarrow \mathrm{Fe\ (III)} + OH^- \qquad \textbf{(II.12)}$$

$$H_2O_2 + \mathrm{HO} \bullet \rightarrow \mathrm{HO_2} \bullet + H_2O \qquad \textbf{(II.13)}$$

$$2\ \mathrm{HO} \bullet \rightarrow H_2O_2 \qquad \textbf{(II.14)}$$

$$2\ \mathrm{HO_2} \bullet \rightarrow H_2O_2 + O_2 \qquad \textbf{(II.15)}$$

$$\mathrm{HO_2} \bullet + \mathrm{HO} \bullet \rightarrow H_2O + O_2 \qquad \textbf{(II.16)}$$

The production of hydroxyl radicals occurs during the chain initiation reaction though they can be scavenged by ferrous ions, hydroperoxyl radicals and/or even auto scavenged. Besides, hydrogen peroxide may act both as radical generator and as scavenger (Pignatello *et al.,* 2006).

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad \textbf{(II.17)}$$

The lack of any other molecule to be oxidized may lead to the decomposition of hydrogen peroxide to molecular oxygen and water according to Equation II.17. However, even when an organic contaminant is present in solution this reaction can take place at some extent, meaning a waste of bulk oxidant (Pignatello *et al.*, 2006) and thus an unnecessary increase on the treatment costs.

Although the degradation rate of pollutants is accelerated with increased $Fe^{2+}$ concentration (Equation II.8), excessive $Fe^{2+}$ dosage only increases the degradation rate marginally and contributes to increase total dissolved solids (Pera-Titus *et al.*,2004; Neyens and Baeyesn, 2003; Bautista *et al.*, 2008). This can be referred as a disadvantage of this process since dissolved iron must be removed from solution prior to the effluent discharge.

### II.2.2 Operating Conditions

The main factors that influence the performance of such complex reactive systems are the medium pH, the concentration of the initial iron species and the hydrogen peroxide dosage required for oxidation, as well as initial concentration of pollutants (Zhang *et al.,* 2009; Wu *et al.,* 2011).

In what concerns the solution pH, Fenton's is strongly dependent mainly due to iron and hydrogen peroxide speciation factors (Neyens and Baeyens, 2003). The optimum pH of the reaction medium has been found to be from 2 to 4, described as an optimum range for free radicals generation.

The effect of pH on the Fenton process is complex. At pH values above 5, lower activity is detected due to the presence of inactive iron oxo-hydroxides or even the formation of iron (III) hydroxide complexes precipitates. Accordingly, less free iron ions are accessible to hydrogen peroxide leading to a reduction of $HO^{\bullet}$ radicals, decreasing also the oxidation process efficiency. In addition, the rapid $H_2O_2$ decomposition and respective production of molecular oxygen is carried out and less hydroxyl radicals are generated (De Laat *et al.,* 2004; Wu *et al.,* 2010).

Lower pH's can lead to a decrease on efficiency, frequently related with the effect over Fe III and hydrogen peroxide reactions. This is due to the formation of iron (III) peroxocomplexes. Thus, at very low pH, Fenton reaction efficiency is decreased again due to iron speciation. At a pH below 2, the decomposition of hydrogen peroxide by $Fe^{2+}$ is inhibited; furthermore, the reaction chain of regeneration of $Fe^{2+}$ is affected due to the formation of some complexes such as $[Fe(H_2O)_6]^{2+}$, which react slowly with peroxide, inhibithing the formation of $HO^{\bullet}$ radicals. It may also occur the formation of stable oxonium ion $[H_3O_2]^+$ in the presence of high concentration of $H^+$ that enhances the peroxide electrophilic stability reducing substantially its reactivity with the $Fe^{2+}$ ions (Gogate and Pandit, 2004a; Schrank *et al.,* 2005).

During the oxidation process, pH decreases, when the iron sulfate is added and after the introduction of hydrogen peroxide. This occurs partly due to the transformation of the initial organic material into organic acids. This pH change indicates that the reaction is going on in the preferred direction. An adequate control of pH could increase the oxidation efficiency. Nevertheless, the reaction buffering will always increase the operating costs in real applications. Consequently, final decision of whether or not using buffers will vary depending on each situation.

Another important factor that influences the efficiency of the Fenton oxidation process is the initial Fe (II) and hydrogen peroxide concentrations as well as the $[H_2O_2]$: $[Fe^{2+}]$ ratio. The production of the desired hydroxyl radicals occurs through the above described initiation chain reaction. However, there is no agreement on the $[H_2O_2]$: $[Fe^{2+}]$ ratio, since diverse authors have reported different ratios that lead to the best mineralization results. The ratio of hydrogen peroxide to ferrous iron $[H_2O_2]$: $[Fe^{2+}]$ and the ratio of hydrogen peroxide to organic matter $[H_2O_2]$: [COD] are key issues in the Fenton process that can greatly vary according to the type of pollutants and to the complexity of the wastewater matrix (Zhang *et al.,* 2005; Gulkaya *et al.,* 2006).

Large excesses of either iron or hydrogen peroxide could be disadvantageous, as hydroxyl radicals can be scavenged by ferrous ions (Equation II.12), hydrogen peroxide (Equation II.13), hydroperoxyl radical (Equation II.16), and also auto-scavenged (Equation II.14). It is also known that hydrogen peroxide may be active as radical generator and as scavenger or both in simultaneous (Gogate and Pandit, 2004b; Namkung *et al.*, 2008). On the other hand, a major catalyst dosage corresponds to more active Fe, accelerating the decomposition of $H_2O_2$, and in this case also more Fe ion are expected in the solution, leading to an increase in the number of hydroxyl radicals (Xu *et al.*, 2009). Regarding the $[H_2O_2]$: $[Fe^{2+}]$ ratio, when the value is low, ferrous iron can act as a coagulant in the presence of organic compounds, due to the generation of ferric hydroxo complexes, as well as the formation of ferric oxy-hydroxides after the neutralization stage promoting a higher removal efficiency through the coagulation step, showing that there are significant synergistic effects between oxidation and coagulation in the Fenton process (Martins *et al.*, 2005; Wu *et al.*, 2011).

Fenton reaction rate tends to increase when rising hydrogen peroxide concentration. Usually, the hydrogen peroxide dosage used is superior to the stoichiometric one, since the consumption of $H_2O_2$ is not equivalent to the generation rate of hydroxyl radicals, once a part is decomposed into water and oxygen by non-radical pathways. There is a range where the increase in the $H_2O_2$ concentration improves COD removal; however there is a limit in hydrogen peroxide dose, above which the process performance does not improve and may even worsen (Pignatello *et al.*, 2006). The reason for this is caused by hydroxyl radicals scavenging effect (Equation II.13). For similar reasons it is believed that the use of high ferrous ion concentrations are appropriate for enhancing the production of $HO^{\bullet}$. Since hydrogen peroxide decomposes to yield ($HO^{\bullet}$) radicals, they generally react with ferrous ion and not with hydrogen peroxide in absence of organic matter (Schrank *et al.,* 2005), due to the fact that the reaction between hydroxyl radicals and ferrous ions is faster than between $HO^{\bullet}$ and $H_2O_2$. The increase in the iron (catalyst) concentration favors the oxidation rate and COD reduction. Consequently, the presence of organics affects the behavior of ferrous ions, because both compete for hydroxyl radicals (Pignatello *et al.,* 2006).

Some studies were performed to attempt to reduce hydrogen peroxide radical scavenger effect keeping its concentration at a low level. This has been carried out by periodically adding hydrogen peroxide to the Fenton reactor, decreasing the oxidant waste during the treatment. To avoid this competitive reactions, different dosing times of the reactants (continuous or by aliquots) could favor the process avoiding these scavenger effects, and also achieve higher removal efficiency and promote easiness of operation. (Wang *et al.*, 2008; Martins *et al.*, 2010)

The Fenton's process has been used at room temperature and is rarely applied at higher temperatures, although the rate of Fenton reaction enhances when increasing the temperature. As the temperature increases above 40- 50°C the efficiency of $H_2O_2$ decreases due to the accelerated thermal decomposition of hydrogen peroxide into oxygen and water affecting thus the process performance.

There is thus a cumbersome interaction between the parameters that affect the performance of Fenton's process. Depending on the effluent depuration goals, different operating conditions should be employed to achieve the desired degradation efficiencies.

### II.2.3 Benefits and Limitations

The Fenton process constitutes an attractive oxidative system that presents some advantages such as operation at room temperature and atmospheric pressure, use of non- expensive reagents and not requiring refined instrumentation (Bautista *et al.,* 2007). Reagents, like iron, are available, easy to store and to handle, safe, nontoxic and they do not cause environmental damages (Pignatello *et al.,* 2006). The hydrogen peroxide is not so expensive when compared with other oxidants and is also easy to handle without no environmental harmfulness. Apart from these benefits, no additional energy input is required to activate $H_2O_2$, hence this is a cost effective method to generate $HO^\bullet$ (Bautista *et al.,* 2007). At the end of the oxidation treatment by increasing the medium pH, the dissolved iron can be removed by precipitation, and consequently any residual $H_2O_2$ decomposes into $O_2$ and $H_2O$ with improved efficiency through coagulation, removing some organic matter at the same time that solid sludge is formed (Altinbas *et al.,* 2003; Cañizares *et al.,* 2007).

Nevertheless, various drawbacks can be identified. One of the most important is the operational cost associated with the reagents consumption and problems such as corrosion of equipment (due to the acidic and alkaline conditions); inability to break down refractory chemicals are also pointed out as process limitations (Gogate and Pandit, 2004a; Cañizares *et al.,* 2007). Other related shortcomings are the necessity of buffering the pH for favorable operational conditions, the waste of oxidant due to the radical scavenger effect of hydrogen peroxide and its self-decomposition, as well as the adverse effect of excessive $H_2O_2$ dosage in the overall degradation of pollutants due to the reaction between $HO^\bullet$ and excess $H_2O_2$ (Gogate and Pandit 2004a; Liao *et al.,* 2009). The continuous augmentation of iron ions dissolved in the treated effluent and the formation of solid sludge after neutralization is a strong environmental weakness as well (Feng *et al.,* 2003; Benatti *et al.,* 2006; Bautista *et al.,* 2007).

In consequence, the previously identified drawbacks can cause a significant economic and environmental impact. Besides, recovery of iron ions and their following recycle and reuse has to be performed. Iron reusability has been typically carried by solid sludge or by supporting iron ions on heterogeneous supports (Centi *et al.*, 2000). Thus, it is necessary to investigate technologies that permit an efficient use of hydrogen peroxide as an effective oxidant agent.

### II.2.4 Applications to Wastewater Treatment

Fenton's reagent can be employed to treat a variety of organic pollutants present in wastewaters. And more especially further applications are becoming a fast growing field of applied research. Table II.2.1 summarizes studies in literature regarding Fenton process for the purification of industrial waste waters by chronological order since 2003, and presents the operating conditions and the main conclusions as well.

Illustrative bench scale works that may be highlighted are the treatment of industrial wastewaters as tanning industry wastewaters (Schrank *et al.*, 2005; Lofrano *et al.*, 2007), phenolic compounds (Namkung *et al.*, 2008; Martins *et al.*, 2010a), paper pulp blenching effluents (Catalkaya and Kargi, 2007), dy-containg textile effluents (Schrank *et al.*, 2005; Gulkaya *et al.*, 2006; Altinbas *et al.*, 2003; Azbar *et al.*, 2004; Fu *et al.*, 2010; Rodríguez *et al.*, 2010; Shi-long *et al.*, 2009), pharmaceutical wastewater (Melero *et al.*, 2007), cosmetic industry effluent (Bautista *et al.*, 2007) fine chemical effluents (Cañizares *et al.*, 2009), chemical laboratory wastewaters (Benatti *et al.*,2006), detergents industries (Martins *et al.*, 2011) complex industrial wastewater (Bianco *et al.*, 2011), pharmaceuticals and personal care effluent (Li *et al.*, 2012). Trapido and collaborators (2006) have studied the application of Fenton's to degrade semicoke oil leachate. The most representative use of this process involves landfill leachates treatment (Lopez *et al.* ,2004; Zhang *et al.*, 2005; Yang Deng, 2007; Goi *et al.*, 2009; Gotvajn *et al.*, 2009a; Wang *et al.*, 2009; and Cortez *et al.*, 2011).

On the other hand, several agro-industrial effluents have been case studies, as wine-distilleries (Cañizares *et al.*, 2007; Martins *et al.*, 2009; Martins *et al.*, 2013) , black olive plants (Cañizares *et al.*, 2009), cork cooking wastewater (Guedes *et al.*, 2003), milk whey cheese production wastewaters (Martins *et al.*, 2009), palm oil mill effluent (Aris *et al.*, 2008) and one of the most studied wastewater, olive mill effluent (Nieto *et al.*, 2007; Cañizares *et al.*, 2009 ; Martins and Quinta Ferreira, 2011).

In this context, the application of Homogeneous Fenton has been studied with promising results in the purification of effluents from dyeing (Schrank *et al.*, 2005), featuring significant removals of chemical oxygen demand exceeding 90% (Gulkaya *et al.*, 2006) and up to 75% of total organic carbon decrease. This process has actually been effective in the oxidation of landfill leachate with COD removal always above 50% (Wang *et al.*, 2009; Goi *et al.*, 2009) with the enhancement of wastewater biodegradability. Studies were conducted using this process for the treatment of the effluents with broad chemical composition as the cosmetic industry and pharmaceutical wastewater featuring COD and TOC removals of 70% and 75%, respectively (Melero *et al.*, 2007), as well as in wastewater from industrial production of olive oil and fine chemicals (Cañizares *et al.*, 2007 and 2009) demonstrating COD reductions above 70% for olive oil effluents. In the case of the effluents of cork cooking, 80% of COD abatement was possible (Guedes *et al.*, 2003). Besides, interesting organic matter removals were obtained for wastewaters from water-based paint (Kurt *et al.*, 2006), olive mill effluent (Nieto *et al.*, 2007), leather tanning industry (Lofrano *et al.*, 2007), landfill leachate (Gotvajn *et al.*, 2009), milk whey cheese production (Martins *et al.*, 2010c) complex industrial wastewater (Bianco *et al.*, 2011), usually also complemented with an increase in biodegradability.

Importantly, is the fact that high efficiencies for a variety of effluents with distinct characteristics can be attained. This demonstrates how Fenton process can be an effective solution for the purification of agro-industrial effluents.

***Table II.2.1- Literature overview of the Homogeneous Fenton Process***

| POLLUTANT | OPERATIONAL CONDITIONS | PRINCIPAL CONCLUSIONS | AUTORS |
|---|---|---|---|
| **Cork Cooking Wastewater** | pH = 3.2,<br>$[H_2O_2]$ =10.6 g.L$^{-1}$<br>$[H_2O_2]$: $[Fe^{2+}]$ =5 (w/w)<br>$BOD_5$/COD = 0.27 | TOC $_{removal}$ = 67 %<br>COD $_{removal}$ = 81 %<br>$BOD_5$/COD = 0.63 | Guedes *et al.*, (2003) |
| **Blue 2b (B54)<br>Red 12b (R31)** | pH = 3<br>$[H_2O_2]$ = 14.03.10$^{-2}$ mM<br>$[Fe^{2+}]$ = 8.93.10$^{-2}$ Mm<br>T= 30 °C | COD $_{removal}$= 70%<br>Color $_{removal}$ = 97% | Malik and Saha, (2003) |
| **Polyester and Acetate Fiber Dyeing Effluent** | pH = 5,<br>$[H_2O_2]$ = 300 mg.L$^{-1}$<br>$[Fe^{2+}]$ = 500 mg.L$^{-1}$ | COD $_{removal}$ = 96%<br>Color $_{removal}$ = 94 % | Azbar *et al.*, (2004) |
| **Landfill Leachate** | pH = 3<br>$[Fe^{2+}]$ = 275 mg.L$^{-1}$<br>$[H_2O_2]$ =3300 mg. L$^{-1}$<br>$BOD_5$/COD Initial = 0.2 | $BOD_5$/COD final ≥ 0.5<br>COD $_{removal}$ = 60 % | Lopez *et al.*, (2004) |
| **Dyeing Industry Effluent** | pH = 3.5<br>$[H_2O_2]$ = 500 mg.L$^{-1}$<br>$[Fe^{2+}]$ = 100 mg.L$^{-1}$ | TOC $_{removal}$ = 80%<br>COD $_{removal}$ = 45 %<br>$BOD_5$/COD = 0.8 | Schrank *et al.*, (2005) |
| **Tannery Wastewater** | pH = 3.5,<br>$[H_2O_2]$ = 100 g.L$^{-1}$<br>$[Fe^{2+}]$ = 100 mg.L$^{-1}$ | TOC $_{removal}$ = 50%<br>COD $_{removal}$ = 50% | Schrank *et al.*, (2005) |
| **Landfill Leachate** | pH = 2.5<br>$[H_2O_2]$: $[Fe^{2+}]$= 0.075 M/0.05 M<br>COD = 1000 mg.L$^{-1}$ | COD $_{removal}$= 61%, | Zhang *et al.*, (2005) |
| **Dyeing Industry Effluent** | pH = 3<br>$[FeSO_4]$ = 5.5 g.L$^{-1}$<br>$[H_2O_2]$ = 385 g.L$^{-1}$<br>T=50 ºc | TOC $_{removal}$ = 75%<br>COD $_{removal}$= 95% | Gulkaya *et al.*, (2006) |
| **Water-Based Paint Wastewater** | pH: 3.0.<br>$[Fe^{2+}]$ = 100 mg.L$^{-1}$<br>$[H_2O_2]$ = 3320 mg.L$^{-1}$ | COD $_{removal}$ = 80% | Kurt *et al.*, (2006) |
| **Four Types Of Industrial Wastewater:** | $[H_2O_2]$ = 5,5,4,5 g.dm$^{-3}$<br>$[Fe^{2+}:H_2O_2]$ =0.33,0.5, 0.33,0.33<br>CODo = 13 400, 2005, 1494 and 234 mg.L$^{-1}$ | COD $_{removal}$ = 87.8, 86.3, 88.6, 71.7 % | Barbusiński., (2006) |
| **Textile Effluent** | $Fe_2O_3$<br>pH = 3.0<br>$[H_2O_2]$ = 300 g.L$^{-1}$ | COD $_{removal}$ = 72% | Dantas *et al.*, (2006) |

*Table II.2.1- Literature overview of the Homogeneous Fenton Process (cont.)*

| | | | |
|---|---|---|---|
| **Chemical Laboratory Wastewaters** | pH= 3.5<br>[COD]: $[H_2O_2]$ = 1 : 9<br>$[H_2O_2]$: $[Fe^{2+}]$ = 4.5 : 1 | $COD_{removal} = 96\%$<br>$Color_{removal} = 55.5\%$ | Benatti *et al.*, (2006) |
| **Semicoke Oil Leachate** | $[H_2O_2]$: [COD] = 3:1 (mg/mg)<br>$[H_2O_2]$: $[Fe^{2+}]$ =10:1 (M/M) | $COD_{removal} = 79\%$<br>BOD/COD = 0.64 | Trapido *et al.*, (2006) |
| **Olive Mill Effluent** | pH = 3<br>$[Fe^{2+}]$ = 667 $mg.L^{-1}$<br>$[H_2O_2]$= 25 $g.dm^{-3}$ | $TOC_{removal} = 70\%$ | Cañizares *et al.*, (2007) |
| **Cosmetic Industry Effluent** | pH = 3<br>$[H_2O_2]$ = Estq.<br>$[Fe^{2+}]$ = 200 $mg.L^{-1}$ | TOC conversion = 45%<br>COD = under discharge limit | Bautista *et al.*, (2007) |
| **Landfill Leachate** | pH =3<br>$[H_2O_{22}]$:$[Fe\ ^{2+}]$ = 3<br>$[H_2O_2]$ = 240 mM | $COD_{removal} = 61\%$ | Yang Deng, (2007) |
| **Olive Mill Effluent** | pH 3.0,<br>$[H_2O_2]$ = 100 $g.dm^{-3}$,<br>$[FeCl_3]$: $[H_2O_2]$ = 0.04 | $COD_{removal} = 92.6\ \%$<br>$TP_{removal} = 99.8\ \%$ | Nieto *et al.*, (2007) |
| **Pulp Mill Effluent** | pH = 5,<br>$[H_2O_2]$ = 50 mM<br>$[Fe\ ^{2+}]$ = 2.5 mM | $TOC_{removal} = 88\ \%$<br>$Color_{removal} = 84\%$<br>$AOX_{removal} = 89\%$ | Catalkaya and Kargi, (2007) |
| **Leather Tanning Industry Wastewaster** | pH = 3<br>$[H_2O_2]$ : $[FeSO_4]$ = 600:500 (mg/mg).$L^{-1}$<br>t = 15 min | $COD_{removal}$ = 80-90% | Lofrano *et al.*, (2007) |
| **Pharmaceutical Wastewater** | pH = 3<br>$[H_2O_2]$ = 12,000 $mg.L^{-1}$<br>$[Fe\ ^{2+}$,Cu, Mn] = 110 $mg.L^{-1}$<br>T = 70 - 80 ◦C | $TOC_{removal} = 75\%$<br>$COD_{removal} = 70\%$<br>$BOD_{5\ removal}= 65\%$ | Melero *et al.*, (2007) |
| **Phenolic Solution** | pH = 2<br>$H_2O_2$ (3%) = 60 $ml.h^{-1}$<br>Retention time of solution = 2 min (100 $mL.min.^{-1}$) | $TOC_{conversion}$ = $TOC_{elimination}$ | Namkung *et al.*, (2008) |
| **Landfill Leachate** | pH = 4.5<br>$[H_2O_2]$: $[Fe^{2+}]$ = 5 : 1 (M/M),<br>$[H_2O_2]$: [COD] = 2 : 1 (w/w) | $COD_{removal} = 71\%$<br>$(BOD_7)$/COD = 0.70 | Goi *et al.*, (2009) |
| **Landfill Leachate** | pH = 4.0 ± 0.2<br>$[H_2O_2]$: $[Fe^{2+}]$ = 3 M : 0.3M<br>T = 40-50°C | $COD_{removal} = 86\%$<br>$(BOD_7)$/COD = 0.29 | Gotvajn *et al.*, (2009) |
| **Landfill Leachate** | pH = 5,<br>$[H_2O_2]$: $[Fe^{2+}]$ = 1.2 (m : m)<br>$[H_2O_2]$ = 5.4 $mMol.L^{-1}$ | $COD_{removal} = 56\%$<br>$Color_{removal}$ =10 degrees | Wang *et al.*, (2009) |
| **Fine Chemical** | pH=3 | $TOC_{removal} = 50.6\%$<br>$COD_{removal}$ = 45.% | Cañizares *et al.*, (2009) |
| **Olive Mill Effluent** | pH=3 | $TOC_{removal} = 70\%$<br>$COD_{removal} = 77\%$ | Cañizares *et al.*, (2009) |
| **Winery Wastewater** | pH= 3<br>$[H_2O_2]$ = 14 $g.L^{-1}$<br>$[Fe^{2+}]$ = 4000 mg $L^{-1}$ | $TOC_{removal}= 31\%$<br>$TP_{removal}=100\%$ | Martins *et al.*, (2009) |
| **Palm Oil Mill Effluent** | pH=3<br>$[H_2O_2]$ = 902.5 mg $L^{-1}$<br>$[Fe^{2+}]$ = 348.7 mg $L^{-1}$ | $COD_{removal} = 75.2\%$<br>$Color_{removal}= 92.4\%$ | Ari *et al.*, (2008) |
| **Dimethyl Disulfide (Dmds)** | pH =3<br>$[H_2O_2]$ = 5 $mg.L^{-1}$<br>$[Fe^{2+}]$ = 1 $mg.L^{-1}$ | 95% degradation of DMDS | Krüger *et al.*, (2009) |
| **Niedta Wastewater** | pH=3<br>$[H_2O_2]$ = 141 mM,<br>$[Fe^{2+}]$ = 1.0 mM, | Ni (II) $_{removal}$ =92.8% | Fu *et al.*, (2009) |
| **Dye Producing Wastewater** | pH=3,<br>$[H_2O_2]$ =500 mg $l^{-1}$,<br>$[H_2O_2]$ : $[Fe^{2+}]$ =6 (w/w)<br>$BOD_5$/COD = 0.03 | $COD_{removal} = 55\ \%$<br>$BOD_5$/COD = 0.47 | Shi-long *et al.*, (2009) |
| **Acid Red 73 (AR 73)** | pH = 3.0<br>$[H_2O_2]_0$ = 2 mM<br>[Zero Valent Iron]$_0$ = 0.3 $g.L^{-1}$ | 96.8 degradation of AR 73 | Fu *et al.*, (2010) |
| **Simulated Phenolic Wastewater** | pH = 3<br>$[H_2O_2]$ = 488 mM<br>$[Fe^{2+}]$ = 271 mg<br>$BOD_5$/COD = 0.3 | $TOC_{removal} = 67\ \%$<br>$COD_{removal} = 81\ \%$<br>$BOD_5$/COD = 0.8 | Martins *et al.*, (2010a) |

***Table II.2.1- Literature overview of the Homogeneous Fenton Process (cont.)***

| | | | |
|---|---|---|---|
| **Acid Orange II (AOII)** | T =30◦C<br>pH = 3.0<br>$H_2O_2/AO_{II}$ = 5 (w/w)<br>$[H_2O_2]:[Fe^{2+}]$ = 3.5(w/w) | TOC $_{removal}$= 55%<br>Color $_{removal}$= 85% | Rodríguez *et al.*, (2010) |
| **Milk Whey Cheese Production Wastewaters** | pH= 3-3.5<br>$[H_2O_2]$ =0.5 M<br>$[H_2O_2]: [Fe^{2+}]$ = 2 (w/w) | COD $_{removal}$ = 96% | Martins *et al.*, (2010) |
| **Detergents Industries** | pH = 3<br>$[H_2O_2]$ = 125 mM<br>$[Fe^{2+}]$ = 25 mM | COD $_{removal}$ = 21%<br>$BOD_5$/COD = 0.80 | Martins *et al.*, (2011) |
| **Complex Industrial Wastewater** | pH=3<br>$[H_2O_2]$: [COD] = 0.58<br>$[H_2O_2]: [Fe^{2+}]$ =15<br>COD = 32 g.L$^{-1}$ | COD $_{removal}$ = 80 % | Bianco *et al.*, (2011) |
| **Landfill Leachate** | pH= 3,<br>$[H_2O_2]: [Fe^{2+}]$ = 3:1<br>$[Fe^{2+}]$ = 4 mmol L$^{-1}$<br>$BOD_5$/COD=0.1<br>COD=340 mg L$^{-1}$ | TOC $_{removal}$ = 42%<br>COD $_{removal}$ = 46%<br>UV$_{254\ removal}$ =61%<br>$BOD_5$/COD = 0.15 | Cortez *et al.*, (2011) |
| **Olive Mill Wastewaters** | pH = 3<br>$[H_2O_2]$ = 220 mM<br>$[Fe^{2+}]$ = 60 mM | COD $_{removal}$ = 71%<br>$BOD_5$/COD = 0.47 | Martins and Quinta Ferreira, (2011) |
| **Pharmaceuticals and Personal Care Effluent** | $[Fe^{2+}]$ = 20 mg.L$^{-1}$<br>$[H_2O_2]: [Fe^{2+}]$ = 2.5 | COD $_{removal}$ = 30% | Li *et al.*, (2012) |
| **Distillery** | pH=3<br>$[H_2O_2]$ = 1.5 M<br>$[H_2O_2]: [Fe^{2+}]$ = 15 | COD $_{removal}$ = 50% | Martins *et al.*, (2013) |

## II.3 Ozonation

Ozone ($O_3$) is an allotropic form of oxygen and it is a powerful oxidizing agent. Among the most common oxidizers, only hydroxyl and fluorine have higher oxidation potential. Its principle disinfectant action is known from a century ago as able to contribute to the mineralization of various organic and inorganic compounds. Thus, ozonation is an AOP, talented to produce hydroxyl radicals from the decomposition of ozone which is catalyzed by hydroxide ions or initiated by the presence of traces of other substances, like transition metal cations (Lin *et al.,* 2002). However, it was only during the last 30 years that its importance in water treatment has grown.

### II.3.1 Single Ozonation ($O_3$)

Ozone is generally produced in situ by a high-voltage electric discharge in the presence of air or oxygen. It is a gas at normal temperature and pressure and its solubility in water depends on temperature, partial pressure in the gas phase and pH (Eckenfelder, 2000). Moreover, ozone is unstable and its rate of decomposition increases with temperature and pH. The chemistry implicated in the ozone formation is represented as follows (Equations II.18 and II.20):

$$O_2 + \ energy \ \rightarrow \mathrm{O} \bullet + \mathrm{O} \bullet \qquad \textbf{(II.18)}$$

$$O_2 + \mathrm{O} \bullet \ \rightarrow O_3 \qquad \textbf{(II.19)}$$

The reaction mechanism between ozone and dissolved organic substances has been described by innumerous authors. Ozone can react with the organic load present in the wastewater by two possible pathways of oxidation in water depending on the pH (Gunten, 2003; Moussavi *et al.,* 2009). The combination of both pathways for degradation of compounds depends on their nature (Gogate and Pandit, 2004a; Pera-Titus *et al.,* 2004).

The direct pathway takes place at low pH, it is slow and highly selective on the electrophilc attack of the high electronic density positions through the reaction between ozone and the dissolved compounds, and usually occurs by means of the ozonation of multiple bonds or in nucleophilic centers (Kasprzyk-Hordern *et al.,* 2003), Equation II.20.

$$O_3 + \mathrm{Organic\ Compounds} \quad \rightarrow \mathrm{Organic\ Compounds_{ox}} + \ \mathrm{Byproducts} \qquad \textbf{(II.20)}$$

The radical pathway, indirect type, occurs through the reaction of hydroxyl radicals, a more effective oxidant compared to ozone, generated from ozone decomposition. This mechanism can be favored in a basic environment (pH >8), where hydroxide ions ($OH^-$) start ozone decomposition. (Gunten, 2003; Chandrasekara *et al.,* 2009). The ozone molecules are decomposed into free radicals

($O_2^{-\bullet}$ and $H_2O^\bullet$), and subsequently produce hydroxyl radicals, which will attack organic compounds. Radicals are nonselective and promote very powerful chain reactions, which can lead to organic compounds mineralization. Therefore, ozonation is more efficient when the conditions favor $HO^\bullet$ production (Kasprzyk-Hordern *et al.,* 2003; Pera-Titus *et al.,* 2004; Ikehata and El-Din, 2004).

The reactions of ozone with hydroxide (II.21) and hydroperoxide ions (II.22) initiate the ozone decomposition chain mechanism:

$$O_3 + \mathrm{OH}^- \rightarrow HO_2^- + O_2 \qquad \textbf{(II.21)}$$

$$O_3 + HO_2^- \rightarrow \mathrm{HO}_2 \bullet + O_2^- \bullet \qquad \textbf{(II.22)}$$

The next stage is the reaction between ozone and the superoxide radical ($O_2^{-\bullet}$) a major agent of the propagation of ozone decomposition, producing the desirable hydroxyl radical (Equations II.23 at II.27):

$$\mathrm{HO}_2 \bullet \leftrightarrow O_2^- \bullet + \mathrm{H}^+ \qquad \textbf{(II.23)}$$

$$O_2^- \bullet + O_3 \rightarrow O_3^- \bullet + O_2 \qquad \textbf{(II.24)}$$

$$O_3^- \bullet + \mathrm{H}^+ \leftrightarrow \mathrm{HO}_3 \bullet \qquad \textbf{(II.25)}$$

$$\mathrm{HO}_3 \bullet \rightarrow \mathrm{HO} \bullet + O_2 \qquad \textbf{(II.25)}$$

$$\mathrm{HO} \bullet + O_3 \rightarrow \mathrm{HO}_2 \bullet + O_2 \qquad \textbf{(II.27)}$$

The complex reaction system is maintained by the promoters which are all molecules capable of transforming hydroxyl radicals into superoxide radicals. At the end, ozone decomposition reactions can be finished when hydroxyl radicals react with compounds capable of consuming $HO^\bullet$ radicals (inhibitors), without regeneration of the superoxide radical. Moreover, the above mentioned hydroxyl radical scavengers may also limit or inhibit the oxidation of the target compounds by these radicals (Kasprzyk-Hordern *et al.,* 2003; Pera-Titus *et al.*, 2004; Chandrasekara *et al.*, 2009).

To summarize, in the ozonation process there are two possible pathways to be considered: the reactions with molecular ozone (direct pathway), and the reactions with hydroxyl radicals produced by ozone decomposition (radical pathway) (Liotta *et al.,* 2009; Pirgalıoglu and Özbelge, 2009). Basic pH causes an increase of ozone decomposition. Both pathways are able to oxidize the organic compounds prevailing one or the other depending mainly on the medium pH, but also on the wastewater composition and ozone dosage (Alvares *et al.,* 2001) as presented in Figure II.3.1.

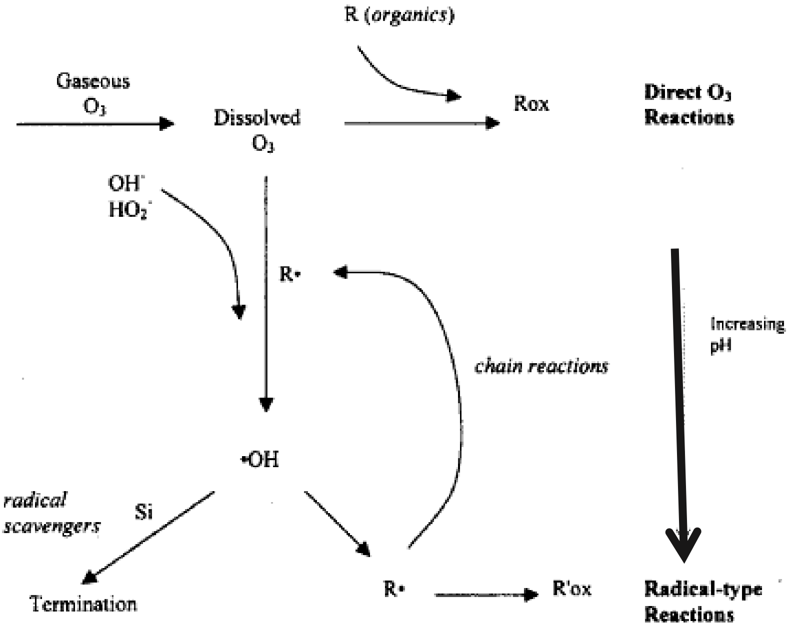


*Figure II.3.1- Primary ozone reaction with various organics in wastewaters where R = organic solutes, Rox= oxidized organic products, Si= radical scavenger species (Alvares et al., 2001)*

### II.3.2 Ozone + Hydrogen Peroxide ($O_3/H_2O_2$)

Unless pH is increased, ozonation does not produce enough ($HO^{\bullet}$) radical concentration in order to completely mineralize dissolved pollutants; specially organic compounds having a high molecular weight usually lead to small compounds which are refractory to further reaction with ozone. Another way to increase the production of hydroxyl radicals is through the addition of hydrogen peroxide into the ozonation reactor (Gunten, 2003; Azbar *et al.,* 2004; Poyatos *et al.,* 2009).

This combined system can initiate the decomposition cycle of ozone, resulting in the formation of the desired hydroxyl radicals. In aqueous medium, hydrogen peroxide is partially dissociated in ionic species ($HO_2^-$), which react with ozone, that is decomposed and origins a chain reactions scheme (Gunten, 2003; Gogate and Pandit, 2004b; Qiang *et al.,* 2010). By that, both radicals are formed and will degrade more effectively the pollutants. The initiation stage is shown by Equation (II.28):

$$O_3 + \mathrm{HO}_2^- \rightarrow \mathrm{HO}_2 \bullet + O_3 \bullet \qquad \textbf{(II.28)}$$

And, the global reaction that takes place is present in Equation II.29:

$$2\ O_3 + H_2O_2 \rightarrow 3\ O_2 + 2\mathrm{HO} \bullet \qquad \textbf{(II.29)}$$

This combined system benefits from synergistic effects, leading to superior conversion yields than those of single ozonation. It is reported that the process can be used to treat pollutants in very low concentrations, at pH values between 7 and 8, and the optimum $H_2O_2/O_3$ mass ratio is from 0.35 to 0.5 (Gogate and Pandit, 2004b; Gunten, 2003; Hagman *et al.*, 2008). Nevertheless, the best performance was achieved when $H_2O_2$ was added after the oxidation of highly reactive substances by single ozonation (Qiang *et al.,* 2010); this entails lower operational costs since hydrogen peroxide will be only added in a second stage aiming the degradation of the saturated by-products which are no further reactive with molecular ozone. In this line, Matilainen and Sillanpää (2010) concluded that ozonation followed by perozonation is the best sequence for DOC (Dissolved Organic Carbon) abatement when compared with the reverse methodology.

However, the increased concentration of hydrogen peroxide, enhances the degradation rate until a load limit that inhibits the reaction, related with a scavenger effect, because there is a consumption of hydroxyl radicals by $H_2O_2$ in excess, Equation II.30:

$$H_2O_2 + \mathrm{HO}\,\bullet \rightarrow \mathrm{HO_2}\bullet + H_2O \qquad \textbf{(II.30)}$$

The implementation of this radical system makes degradation of refractory molecules possible, combining the advantages of selective molecular ozone reactions and posterior non-selective free radical attack reactions (Gogate and Pandit, 2004b; Azbar *et al.,* 2004).

### II.3.3 Operating Conditions

In ozonation, what affects more the process efficiency is the dependence of each mechanism pathway on several factors principally the pH but also the temperature and chemical composition of the aqueous solution.

Therefore, ozone decomposition rate is highly dependent upon the pH of the wastewater and on the nature of the pollutants. In general, under acidic conditions (pH < 4) the direct pathway rules, whereas for pH > 10 is mainly the radical (Kasprzyk-Hordern *et al.,* 2003). Under neutral conditions, both mechanisms can be important and should always be considered when designing a treatment system. However, excessive high pH values may favor the hydroxyl radicals scavenging by carbonate and hydrogen carbonate ions, which compete with the substrate by the $HO^{\bullet}$ radicals, as described above for Fenton type reactions.

Normally, like as other AOPs, ozonation operates at room temperature. However, the temperature variation may origin distinct effects. If, on one hand it increases the reactions rate constants, on the other hand, ozone solubility drops off reducing the ozone available for the oxidation process (Alvares *et al.*, 2001).

Ozone processes can be more efficient at high pH ($O_3/OH^-$) and by the addition of hydrogen peroxide ($O_3/H_2O_2$). These systems favor the production of hydroxyl radicals ($HO^•$), which are highly reactive species. $OH^-$and $H_2O_2$ initiate a series of radical reactions that enhance ozone decomposition to yield $HO^•$. In the system $O_3/OH^-$, the hydroxide ion reacts with ozone to yield superoxide anion radicals ($O_2^{-}•$), which in their turn are involved in a series of reactions that yield $HO^•$. In the system $O_3/H_2O_2$, when hydrogen peroxide is dissolved in water, it partially dissociates into hydroperoxide ion ($HO_2^-$, the conjugated base of hydrogen peroxide), which reacts rapidly with ozone to initiate a radical chain mechanism that leads to hydroxyl radicals. In this case, overall 1 mol of $O_3$ yields 1 mol of $HO^•$. Ozonation has been used for the most diverse applications such as disinfection, odor, color and taste abstraction, oxidation of inorganic and organic compounds which enables particle removal (Sangave *et al.*, 2007).

For the perozone (ozone + hydrogen peroxide) the ozonation efficiency is enhanced by this combination; nevertheless the $H_2O_2$ excess may have a scavenging comportment on the generated radical hydroxyls, and a less reactive radical is also formed, the hydroperoxyl radical (Chandrasekara *et al.*, 2009).

### II.3.4 Benefits and Limitations

Ozone has the main advantage of leading to an efficient and quick removal of several pollutants. The demonstrated strong oxidant power permits to reach the mineralization of wastewaters when other classical treatments are inefficient. Residual ozone quickly decomposes not adding new species in the resultant treated wastewater. However, the oxidation can form by-products, which cannot be easily oxidized by ozone molecules, such as organic acids and ketones.

Ozone is also produced in situ, not being possible to store or transport. Besides, ozone generation requires a large quantity of chemical reagents ($O_2$ or air) and electrical power. The energy cost associated to the oxidant production requires then a careful analysis of the influence of ozone concentration at the reactor entrance (Rosal *et al.*, 2009; Klavarioti *et al.*, 2009). The maximum reached concentrations of ozone are approximately 4 and 8% (w/w) when produced from air or pure oxygen respectively. Other limitation is the instability of ozone in aqueous medium and depending on the water quality and turbidity ozone half-time can be within a large range of values between seconds and hours (Gunten, 2003; Kasprzyk-Hordern *et al.*, 2003).

Another important restriction is the low solubility of ozone in aqueous medium being the gas-liquid mass transfer the major constraint of the ozonation process (Pirgalıoglu and Özbelge, 2009). This limiting factor can be reduced by maximizing the interfacial contact area, through the utilization of small pore size ozone diffusers that reduce the bubble size, or by increasing the contact time between the gas and the liquid medium in large bubble columns (Andreozzi *et al.*, 1999).

The utilization of ozone based technics is very limited when applied in wastewaters with TSS (total suspended solids) content, due to the existent limitation of ozone transfer caused by the solid content achieving this way a very low percentage of solids removal; additionaly, COD content may increase due to the solubilization of the solid fraction (Campos *et al.*, 2009; Rivas *et al.*, 2009). However, this aspect can be encouraging for smaller solids which before the ozone oxidation could not be assimilated / oxidized biologically, and that subsequently to the ozone based process are solubilized / reduced to a scale that can be oxidized biologically (Wang *et al.*, 2008) increasing the effluent biodegradability.

Finally, the global analysis towards decision if industrial application will be advantageous has to involve the initial investment integrating the high capitals costs related to the process equipment, as the ozone generator, construction materials that must be resistant to oxidation and abatement system for residual ozone; special attention must be given to the gas-liquid transfer limitations (Andreozzi *et al.*, 1999).

## II.3.5 Applications to Wastewater Treatment

Throughout the last years, literature is full with successful applications of ozonation on a wide range of contaminant compounds in wastewaters.

### *II.3.5.1 Single Ozonation*

The study of ozonation for real wastewater treatment has been neglected over the years, now beginning to be of global interest the application of this methodology for the purification of several watercourses with diverse characterizations. Ozone is assumed as an oxidizing agent with a high potential for cleansing of both drinking water and effluents from chemical production showing efficiencies above 80%. Table II.3.1 summarizes studies in the literature involving the analysis of the process of ozonation in the treatment of industrial wastewater and report the main conclusions.

In this context, the use of ozone has been addressed for the oxidation of various effluents, with promising results in the degradation of landfill leachate (Chaturapruek *et al.*, 2005; Ntampou *et al.*, 2006; Goi *et al.*, 2009 and Tizaoui *et al.*, 2007) with considerable depletion of COD and Color, with the advantage of achieving a biodegradability enhancement. The application of ozonation for the treatment of a semi-coke leachate from petrochemical industry is reported (Trapido *et al.,* 2006) with a COD removal of 56% and the improvement of wastewater biodegradability to 0.59.

Phenol is one of the most studied compounds as model for phenolic wastewaters, and our previous research in this ambit revealed 88% removal of total phenol content and 24% of TOC depletion (Martins and Quinta-Ferreira, 2011) as also referred by Wu and collaborators (2004). Other type of pollutants usually studied are the dyes (Azbar *et al.,* 2004; Tapalad *et al.,* 2008; Dong *et al.,* 2007; Faria *et al.,* 2008 and Altinbas *et al.,* 2003). Single ozonation proved to be an interesting technology in the remediation of these pollutants with a global color removal around 80% and COD diminution above 80% except on the treatment of red X3-B.

In what regards chemical effluents, a wide range of applications are referred such as production of terephthalic acid (PTA) (Chandrasekar *et al.,* 2009), sulfosalicylic acid (SSal) (Ping *et al.,* 2002), alachlor (Qiang *et al.,* 2010) and fine chemical production (Cañizares *et al.,* 2009) where TOC removals around 80% and considerable COD depletion were achieved.

Ozonation was also studied in agriculture production wastewaters as winery wastewater with COD removals upper than 50% (Martins *et al.,* 2009 and Lucas *et al.,* 2010), olive oil production (Cañizares *et al.,* 2007 and 2009), elderberry wastewater where complete Total Phenol content removal was achieved (Martins *et al.,* 2012), milk whey with a remarkable $BOD_5$/COD improvement to 0.8 (Martins *et al.,* 2010) and cork-processing water (Lan *et al.,* 2008).

Other production industry studies focusing the implementation of ozonation in the treatment of wastewaters derived from paper mills (Alvárez *et al.,* 2009; Catalkaya and Kargi, 2007 and Tünay *et al.,* 2008). Tannery industry (Preethi *et al.,* 2009) and baker’s yeast industry (Altinbas *et al.,* 2003) wastewaters are also reported in the literature.

Great part of the referred works concluded that ozone based processes could be beneficial to remove the organic content but above all, diminish the latent toxicity from the wastewater, when applied prior to biological treatment (Lucas *et al.,* 2010; Martins *et al.,* 2011).

*Table II.3.1- Literature overview of the single ozonation process*

| Pollutant | OPERATIONAL CONDITIONS | PRINCIPAL CONCLUSIONS | AUTORS |
|---|---|---|---|
| **Sulfosalicylic Acid (Ssal)** | $[O_3] = 25$ mg.min$^{-1}$<br>pH =3.2<br>t = 30 min | $\text{TOC}_{\text{removal}} = 20\%$ | Ping *et al.*,<br>(2002) |
| **Pretreated Baker's Yeast Industry (By2) Effluents** | $[O_3] = 320$ mg L$^{-1}$<br>pH = 4<br>t = 20 min | $\text{COD}_{\text{removal}} = 80\%$<br>$\text{Color}_{\text{removal}} = 85\%$ | Altinbas *et al.*,<br>(2003) |
| **Polyester And Acetate Fiber Dyeing Effluent** | $[O_3] = 2$ g$O_3$.h$^{-1}$<br>pH = 9 | $\text{COD}_{\text{removal}} = 92\%$<br>$\text{Color}_{\text{removal}} = 90\ \%$ | Azbar *et al.*,<br>(2004) |
| **Landfill Leachate** | $[O_3] = 2.6$ g.L$^{-1}$<br>pH=8.70<br>$BOD_5/COD = 0.02$ | $\text{COD}_{\text{removal}}= 47\%$<br>$BOD_5/COD = 0.16$ | Wang *et al.*,<br>(2004) |
| **Landfill Leachate** | $[O_3] = 75$ mg.L$^{-1}$<br>pH = 7.0-7.5 | $\text{TOC}_{\text{removal}} = 71\%$<br>$\text{COD}_{\text{removal}} = 73\%$ | Chaturapruek *et al.*,<br>(2005) |
| **Acid Blue 113,<br>Reactive Red 241<br>Basic Red 14** | $[O_3] = 2.15$ mg.min$^{-1}$<br>pH =7<br>t = 60 min | $\text{TOC}_{\text{removal}} = 8.9\%$<br>$\text{Color}_{\text{removal}} = 100\%$ | Faria *et al.*,<br>(2005) |
| **Leachate Of Semicoke Oil** | $[O_3]= 0.089$ g.L$^{-1}$<br>pH = 10.01 | $\text{COD}_{\text{removal}} = 56\%$<br>COD/BOD = 0.59 | Trapido *et al.*,<br>(2006) |
| **Landfill Leachate** | $[O_3] = 8.3$ mg.L$^{-1}$<br>Dilution = 1:5 | $\text{COD}_{\text{removal}} = 81\%$<br>$\text{Color}_{\text{removal}} = 95\%$ | Ntampou *et al.*,<br>(2006) |
| **Olive Mill Wastewater** | pH = 12<br>$[O_3]= 33.33$ mg.L$^{-1}$ | $\text{TOC}_{\text{removal}} = 75\%$ | Cañizares *et al.*,<br>(2007) |
| **Landfill Leachate** | pH = 8.7<br>$[O_3] = 80$ g.m$^{-3}$ | $\text{COD}_{\text{removal}} = 27\%$<br>$\text{Color}_{\text{removal}} = 87\%$<br>$BOD_5/COD = 0.2$ | Tizaoui *et al.*<br>(2007) |
| **Simulated PHenolic Wastewater** | $[O_3] = 20$ g $O_3$.Nm$^{-3}$<br>t = 120 min | $\text{TOC}_{\text{removal}} = 24\%$<br>$\text{TpH}_{\text{removal}} = 88\%$ | Martins and Quinta-Ferreira,<br>(2008) |
| **Pulp Mill Effluent** | pH = 7<br>$[O_3] = 20$ g$O_3$.h$^{-1}$ | $\text{TOC}_{\text{removal}} = 29\ \%$<br>$\text{Color}_{\text{removal}} = 91\%$<br>$\text{AOX}_{\text{removal}} = 62.4\%$ | Catalkaya and Kargi,<br>(2007) |
| **Pulp And Paper Wastewater From A Biological Treatment** | $[O_3] = 40$ mg.h$^{-1}$<br>pH = 8.5<br>time = 2h | $\text{COD}_{\text{removal}} = 80\%$ | Tünay *et al.*,<br>(2008) |
| **Cork-Processing Water** | $[O_3]=$ 15 to 120mg.min$^{-1}$<br>pH=6.45<br>V=9L<br>t=120min | $\text{TOC}_{\text{removal}} = 79\%$<br>$\text{COD}_{\text{removal}} = 91\%$<br>$\text{UV}_{254\ \text{removal}} = 88\%$ | Lan *et al.*,<br>(2008) |
| **Secondary Effluent From Sewage Treatment Plant** | $[O_3] = 10$ mg.L$^{-1}$<br>pH = 6.7-7.8<br>t = 4 min | $\text{TOC}_{\text{removal}} = 25\%$<br>$\text{COD}_{\text{removal}} = 58\%$<br>$NH_3\text{-N}_{\text{removal}} = 89\%$ | Wang *et al.*,<br>(2008) |
| **Landfill Leachate** | $[O_3] = 1$ g $O_3$.L$^{-1}$<br>pH = 9 | $\text{COD}_{\text{removal}} = 48\%$ | Hagman *et al.*,<br>(2008) |
| **Tannery Effluent** | pH = 11<br>$BOD_5/COD = 0.18$ | $\text{COD}_{\text{removal}}= 92\%$<br>$\text{Color}_{\text{removal}}=90\%$<br>$BOD_5/COD = 0.49$ | Preethi *et al.*,<br>(2009) |
| **Tannery Wastewater** | pH = 11 | $\text{COD}_{\text{removal}} = 25\%$<br>$\text{Color}_{\text{removal}} = 40\%$ | Preethi *et al.*,<br>(2009) |
| **Landfill Leachate** | $[O_3] = 42$ mg.L$^{-1}$<br>pH = 11 | $\text{COD}_{\text{removal}} = 41\%$<br>$BOD_7/COD= 0.50$ | Goi *et al.*,<br>(2009) |
| **Paper Mill Wastewater** | $[O_3] = 40$ g.m$^{-3}$<br>pH = 6 | $\text{TOC}_{\text{removal}} = 25\%$<br>$\text{COD}_{\text{removal}} = 25\%$ | Alvárez *et al.*,<br>(2009) |
| **Production Of Tereflatic Acid** | $[O_3] = 0.089$ g.L$^{-1}$<br>pH = 4 | $\text{COD}_{\text{removal}} = 70\%$ | Chandrasekara *et al.*,<br>(2009) |
| **Fine Chemical** | $[O_3] = 1$ g$O_3$.h$^{-1}$<br>pH = 12 | $\text{TOC}_{\text{removal}} = 91\%$<br>$\text{COD}_{\text{removal}} = 76\%$ | Cañizares *et al.*,<br>(2009) |
| **Olive Oil** | $[O_3] = 1$ g$O_3$.h$^{-1}$<br>pH = 12 | $\text{TOC}_{\text{removal}} = 67\%$<br>$\text{COD}_{\text{removal}} = 77\%$ | Cañizares *et al.*,<br>(2009) |
| **Municipal Wastewater** | $[O_3] = 35$ ppm at 40 L.h$^{-1}$<br>t = 120 min | $\text{TOC}_{\text{removal}} = 40\%$ | Rivas *et al. 2009*,<br>(2009) |

*Table II.3.1- Literature overview of the single ozonation process (cont.)*

| | | | |
|---|---|---|---|
| **Winery Wastewater** | [O$_3$] = 7. 5g .L$^{-1}$<br>pH = 4.7-5.3<br>t = 60min | COD $_{\text{removal}}$ = 54%<br>TSS $_{\text{removal}}$ = 85% | Martins *et al.*, (2009) |
| **Landfill Leachate** | [O$_3$] = 96 g O$_3$Nm$^{-3}$<br>pH = 8.2<br>t = 120 min | TOC $_{\text{removal}}$ = 37%<br>COD $_{\text{removal}}$ = 42%<br>BOD$_{5\ \text{removal}}$ = 49% | Gotvajn *et al.*, (2009b) |
| **Seafood Industry** | 0.02 g O.3 g TSS<br>pH = 5 | TSS $_{\text{removal}}$ = 6.8% | Campos *et al.*, (2009) |
| **Wastewater Treatment Plant** | [O$_3$] = 40 g O$_3$.m$^{-3}$.<br>pH = 6;<br>t = 120 min<br>TOC=170 g.m$^{-3}$<br>T = 20ºC | TOC $_{\text{removal}}$ = 23% | Alvárez *et al.*, (2009) |
| **Milk Whey** | [O$_3$] = 1.0x10$^{-2}$ gO$_3$.L$^{-1}$<br>t = 240 min<br>pH = 7.5<br>BOD$_5$/COD = 0.29 | COD $_{\text{removal}}$ = 52%<br>BOD$_5$/COD = 0.8 | Martins *et al.*, (2010) |
| **Winery Wasteawter** | [O$_3$] =100 mg.min$^{-1}$<br>pH = 4<br>t = 180 min<br>V = 9 L | COD $_{\text{removal}}$ = 52% | Lucas *et al.*, (2010) |
| **Landfill Leachate** | [O$_3$] = 5.6 g O$_3$ h$^{-1}$<br>pH = 11<br>COD=340 mg L$^{-1}$<br>BOD$_5$/COD = 0.1 | COD $_{\text{removal}}$ = 41%<br>TOC $_{\text{removal}}$ = 49%<br>UV$_{254\ \text{removal}}$ = 57%<br>BOD$_5$/COD = 0.15 | Cortez *et al.* (2011) |
| **Detergentes Wasteter** | [O$_3$] = 4.0x10$^{-2}$ gO$_3$.L$^{-1}$<br>pH= 10<br>BOD$_5$/COD = 0.32<br>t = 60 min | COD $_{\text{removal}}$ = 6%<br>BOD$_5$/COD = 0.41 | Martins *et al.*, (2011) |
| **Elderberry Wastewater** | [O$_3$] = 40 gO$_3$.m$^{-3}$<br>pH = 10<br>t = 120 min<br>BOD$_5$/COD= 0.32 | COD $_{\text{removal}}$ = 59%<br>TP $_{\text{removal}}$ = 100%<br>BOD$_5$/COD = 0.40 | Martins *et al.*, (2012) |
| **Distillery** | [O$_3$] = 4.0x10-2 g O$_3$.L$^{-1}$<br>pH = 3 | COD $_{\text{removal}}$ = 52% | Martins *et al.*, (2013) |

### *II.3.5.2 Ozone + Hydrogen Peroxide ($O_3/H_2O_2$ - Perozone)*

Perozone was recently applied for the depuration of several types of wastewater as it is shown in Table II..3.2 such as landfill leachate (Tizaoui *et al.,* 2007; Hagman *et al.,* 2008; Gotvajn *et al.,* 2009b and Cortez *et al.* 2011), pulp and paper wastewater (Catalkaya and Kargi, 2007; Tünay *et al.,* 2008). Two Agro Industrial wastewaters were also object of study as Milk Whey (Martins *et al.,* 2010) and Elderberry (Martins *et al.,* 2012). Also the depuration of secondary effluent from municipal wastewater (Rivas *et al.,* 2009) was analysed. With this proper treatment, COD reductions between 50 and 80% and color removal of 98% were achieved as well as improved biodegradability of a landfill leachate. Total COD was depleted on the treatment of Milk Whey. Besides TP (Total Phenol) and COD achieved a removal of 100 and 61% for Elderberry wastewater. This type of enhanced ozone based oxidation was often compared with the simple ozonation, showing in turn that achieves better removals, but not always cost/effective.

***Table II.3.2- Literature overview of the perozone***

| *POLLUTANT* | *OPERATIONAL CONDITIONS* | *PRINCIPAL CONCLUSIONS* | *AUTORS* |
|---|---|---|---|
| **Landfill Leachate** | $[O_3]$ = 80 g.m$^{-3}$<br>pH = 8.7<br>$[H_2O_2]$ = 2 g.L$^{-1}$<br>Time = 1h | COD $_{removal}$ = 48%<br>Color $_{removal}$ = 94%<br>$BOD_5$/COD = 0.7 | Tizaoui *et al.,*<br>(2007) |
| **Pulp And Paper Mill Effluent** | $[O_3]$ = 20 g$O_3$.h$^{-1}$<br>pH = 11<br>$[H_2O_2]$ = 5 mM | TOC $_{removal}$ = 30.9 %<br>Color $_{removal}$ = 81.2%<br>AOX $_{removal}$= 95% | Catalkaya and Kargi,<br>(2007) |
| **Pulp And Paper Wastewater From A Biological Treatment** | $[O_3]$ = 40 mg.min$^{-1}$<br>pH = 7<br>$[Fe^{3+}]$ = 50 mg.L$^{-1}$<br>$H_2O_2/O_3$ = 0.5 mol/mol<br>t = 4 h | COD $_{removal}$ = 83% | Tünay *et al.,*<br>(2008) |
| **Landfill Leachate** | $[O_3]$ = 1 g.L$^{-1}$<br>pH = 8-8.5<br>$[H_2O_2]$ = 1 g.L$^{-1}$ | COD $_{removal}$ = 55% | Hagman *et al.,*<br>(2008) |
| **Landfill Leachate** | $[O_3]$ = 96 g $O_3$Nm$^{-3}$<br>pH = 8.2<br>t = 120 min | TOC $_{removal}$ = 37%<br>COD $_{removal}$ = 42%<br>$BOD_5$ $_{removal}$ = 49% | Gotvajn *et al.,*<br>(2009b) |
| **Secondary Effluente From Municipal Wastewater** | $[O_3]$ =35 ppm at 40 L h$^{-1}$<br>$[H_2O_2]$ = 0.01M<br>t =120 min | TOC $_{removal}$= 80% | Rivas *et al.,*<br>(2009) |
| **Milk Whey** | $[O_3]$= 1.0x10-2 g $O_3$.L$^{-1}$<br>pH = 7.5<br>$[H_2O_2]$ = 334 mM<br>t = 240 min | COD removal =100% | Martins *et al.,*<br>(2010) |
| **Landfill Leachate** | $[O_3]$ =5.6 g $O_3$.h$^{-1}$<br>pH =7<br>COD=340 mg L$^{-1}$<br>$BOD_5$/COD=0.1 | COD $_{removal}$ = 66%<br>$UV_{254}$ $_{removal}$ = 57%<br>$BOD_5$/COD = 0.24 | Cortez *et al.,*<br>(2011) |
| **Elderberry Wastewater** | $[O_3]$ =40 g $O_3$.m$^{-3}$<br>pH = 6.6<br>$[H_2O_2]$ = 16.5 mM<br>t = 120 min<br>$BOD_5$/COD = 0.32 | COD $_{removal}$ = 61%<br>TP $_{removal}$ = 100%<br>$BOD_5$/COD = 0.41 | Martins *et al.,*<br>(2012) |

## II.4 Coagulation / Flocculation

In wastewater treatments, the coagulation process is used to improve solids removal, thus enhancing COD and inorganic content removal. Simultaneously, the effectiveness of all the processes upstream will be enhanced, by increasing the homogeneity of the medium and promoting organic charge stabilization. Besides, this process usually leads to higher biodegradability (Mert *et al.*, 2010), along with toxicity and color removal (Kumar *et al.*, 2011), thereby favoring the biological oxidative processes (Sarika *et al.*, 2005), as well as chemical degradation processes as AOPs. Thus this is an essential and cost effective process for water and industrial wastewaters treatment (Barbusinski and Pieczykolan, 2010; Sahu and Chaudhari, 2013; Upadhyay and Mistry, 2012; Chauhan and Dikshit, 2012).

Often the terms coagulation and flocculation are used synonymously in spite of existing a subtle difference between them. Coagulation consists in the process where charge neutralization results in the particles destabilization, while the term flocculation is used to designate the process that promotes the formation of particles in suspension into larger agglomerates from small agglomerates. These are formed as a result of coagulation using high molecular weight polymeric materials, through the collision of the destabilized particles by coagulant interaction (Sarika *et al.*, 2005; Farajnezhad and Gharbani, 2012).

In this section the issues related to the implementation of the coagulation process employed as pre-treatment in the experimental studies will be addressed.

### II.4.1 Coagulation

Coagulation is an essential component in water and wastewater treatment operations (Liang *et al.*, 2009). Colloidal particles existing in wastewater usually carry negative charges on their surface, which leads to the stabilization of the suspension. The process involves reactions between the organic molecules of the effluent and the coagulants, which impose changes in the surface properties of those colloidal particles inducing their destabilization through charge neutralization, due to the fact that they possess positive charges (cationic). This way, they interact with an electrical double layer of ions and the resulting negative zeta potential (is related to the surface charge, a property that all materials possess, or acquire, when suspended in a fluid.) promotes the absence of repulsive forces between the colloidal particles, which become destabilized and begin to clump together, inducing the precipitation of the dissolved material. The numerous successful colloid collisions origin micro flocs and their growth into visible flocs facilitating the separation of solids by gravity (Sher *et al.*, 2013). If high dosages of coagulants are added, the concentration of the colloids ions in the diffuse layer may increase to a level that the zeta potential shifts to a positive charge. The particles will be then positively charged and will become again colloidal stable in suspension (Jiang and Wang, 2009; Aygun and Yilmaz, 2010), promoting a reverse effect that was expected.

### *II.4.1.1 Coagulation (fundamentals)*

Among the various applications and performed studies, several fundamental theories have been presented that allowed the identification of certain mechanisms for providing the destabilization of particles that depend on the nature of the interactions between the chemical coagulants and pollutants. There are four referred mechanisms for coagulation, namely adsorption charge neutralization, sweep coagulation, layer compression, and inter particle bridging (Eckenfelder, 2000; Hendricks, 2013). The predominant observed mechanisms during conventional coagulation with metal coagulants are adsorption charge neutralization and sweep coagulation (Liang *et al.,* 2009; Tzoupanos and Zouboulis, 2008; Jiang and Wang, 2009).

#### *II.4.1.1.1 Adsorption charge neutralization*

Adsorption charge neutralization coagulation is the most important process when metal salts are applied. An increase in the electrolyte concentration, when adding the metal salts, endorse counter ions present in the diffuse part of the electrical double layer in the stable colloidal suspension, which origins the particles destabilization. In this way, the exterior of the colloidal particle is destabilized and collide with other particles creating removable flocs.

#### *II.4.1.1.2 Precipitation coagulation (or sweep coagulation)*

Depending on the amount of coagulant added, the mixture pH, and the concentration of some types of colloids in water, metallic hydroxides precipitates may be formed. When the coagulant is added at higher dosages and at relative high pH, the primary coagulation mechanism tends first to the formation of metal hydroxide precipitates, followed by the adsorption of the remaining colloid particles in solution or co-precipitation favoring the entrapment (Amir *et al.,* 2009; Liu *et al.,* 2012). In this case, precipitates form “sweep flocs” that tend to drag particles by coagulant metal-hydroxides as it settles out of suspension (Tzoupanos and Zouboulis, 2008). Precipitation coagulation is the most widely used where there is flocculation and sedimentation, due to the higher pH range coverage, also leading to easiness of operation. This mechanism favors the turbidity removal when metal salts are added (Liu *et al.,* 2012), through the formation of stable hydroxides and the entrapment of a considerate amount of colloids inside the “net structure” of the hydroxides

#### *II.4.1.1.3 Adsorptive coagulation*

The process of adsorptive coagulation is defined as the destabilization of the colloids in solution by adsorption of long hydroxide chains promoted by the pH variations at alkaline conditions, on the oxidized particle surface. In the adsorption mechanism and charge neutralization after the addition of coagulant, the hydrolysis of metal ions occurs with subsequent adsorption of hydrolyzed species, usually positive charged, on the surface of the colloids leading to a destabilization. The adsorption is caused by mutual attraction of opposite charge and/or Van der Waals‘mass force.

#### *II.4.1.1.4 Inter particle bridging*

A special type of adsorptive coagulation is entitled as bridging flocculation. In bridging flocculation, adsorption mechanism and bridge formation is due to the addition of natural or synthetic polymers as coagulants. When the coagulating agent comes into contact with a colloidal particle it adsorbs some of its reactive groups causing their destabilization in both particles. In turn, the free segments of the polymers of the previously disrupted particles are adsorbed on the surface of another particle, promoting their aggregation.

### ***II.4.1.2 Types of coagulants***

The most common chemicals applied as coagulants are aluminum and iron salts, as aluminum sulphate (referred to as alum), ferrous sulphate, ferric sulfate, ferric chloride (Tatsi et al. 2003), although alkalis lime (CaO), as well as hydrated lime are also used as coagulants (Chauhan *et al.,* 2012; Santo *et al.,* 2012) that additionally are employed to promote and maintain the alkalinity, thus improving the process (Ismail *et al.,* 2012).

When metal coagulants are added to water, the metal ions hydrolyze quickly, developing a series of metal hydrolysis species (Labanowski *et al.,* 2010). These species are dependent mainly on pH, coagulant dosage (Aygun and Yilmaz, 2010) and mixing level. However, aluminum and ferric coagulants can be used to generate inorganic polymeric coagulants. These coagulants are typically generated by partially neutralizing concentrated solutions of aluminum or ferric with a base such as sodium hydroxide prior to their use in the coagulation process. The principal advantages of pre-polymerized inorganic coagulants are that they are able to function efficiently over wide ranges of pH and raw water temperatures (Lofrano *et al.,* 2006). They are less sensitive to low water temperatures, and since lower dosages are required (Liu *et al.,* 2012) consequently less chemical residues are produced. This way, lower chloride, sulfate and metals loads will lead to lower final TDS concentration (Tzoupanos and Zouboulis, 2008).

#### *II.4.1.3 Types of flocculants*

Polymers are synthetic or natural organic compounds that tend to be large molecules composed of chains of smaller "monomer" groups and are often used in combination with other coagulants such as aluminum or ferric chloride to optimize solids removal. Because of their large size and charge characteristics, polymers can promote destabilization through bridging, charge neutralization, or both (Brostow *et al.,* 2009).

The organic polymers frequently used in wastewater treatment are cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged) and are categorized into two major types: very high molecular weight polyacrylamides (PAMs) flocculants with different active groups, which may be anionic, cationic or nonionic or low to mid molecular weight cationic floculants based on (non-) quaternised dimethylamine (polyamines) and diallyldimethyl ammonium chlorides (DADMACs) (Tripathy and Ranjan, 2006).

Due to their length, the polymer chains are able to attach to different particles. An important characteristic of flocculation, is that lower electrolyte additions are need to promote destabilization by bridging/patching mechanisms, acting as a coagulant, achieving the proposased suspended particles removal (Metcalf and Eddy, 2004).

### II.4.2 Operating Conditions

The foremost issues that influence the performance of coagulation systems are the raw water characteristics, temperature, pH and alkalinity, the type and concentration of the coagulant, as well as the mixture velocity gradient and mixing time (Ismail *et al.,* 2012; Sun *et al.,* 2009; Santo *et al.,* 2012). Coagulant selection and optimal dosages are critical to process efficiency (Ginos *et al.,* 2006). Maintaining or not proper control of these chemicals can mean the difference between an optimized or inefficient treatment, being need the adjustment of coagulant dosages at intervals to achieve optimal coagulation during the process due to the water characteristics changing. In this way the required concentration of coagulant is related with the concentration of organic matter and ionic species, pH, temperature, among others factors.  (Ntampou *et al.,* 2006; Dihang *et al.,* 2008; Sher *et al.,* 2013; Santo *et al.,* 2012). When a lower coagulant dosage is needed and the preferable mechanism is the destabilization through charge neutralization and not sweep floc development, the mixing should occur faster because chemical reactions could happen very quickly at low dosages (Aygun and Yilmaz, 2010; Papaphilippou *et al.,* 2013). At higher dosages, the primary coagulation mechanism tends to be entrapment, the inorganic coagulant precipitates forming a "sweep floc" that tends to capture suspended solids as it settles out of suspension (Liang *et al.,* 2009; Amir *et al.,* 2009).

It is extremely important that the coagulant is dispersed quickly and efficiently because the destabilizing agents are the intermediate products of the coagulant reaction. These intermediates are short-lived and they must contact the solids particles (Jiang and Wang, 2009). In some cases, excessive mixing may serve to break up coagulant molecules or floc particles, thus reducing the efficacy of the solids removal processes (Ismail *et al.,* 2012). With increase in pH, these species become charged and the mechanism of action changes. By this, the hydroxide precipitation, induced by the pH change, leads to the possibility of potentiate the sweep flocculation mechanism (Aygun and Yilmaz, 2010). Water pH plays an important role because the solubility of the aluminum and iron species is pH dependent (Moghaddam *et al.,* 2010).

Alkalinity refers to the acid-neutralizing ability of the wastewater, being a general indicator of buffering capacity. There is a direct relationship between this parameter and pH, as high alkalinity wastewaters have a higher pH. As the metallic coagulants are acidic, the coagulant addition will consume the alkalinity which may lead to pH decrease into values that will diminish the process efficiency (Ntampou *et al.,* 2006; Liang *et al.,* 2009). In contrast, water with high alkalinity might require higher coagulants doses to depress the pH to values favorable for coagulation (Barbusinski and Pieczykolan, 2010; Kumar *et al.,* 2011). Other factor that is important is the temperature, due to the fact that it affects the viscosity of the water changing thus the coagulant solubility. Lower temperature waters can decrease the hydrolysis and precipitation kinetics promoting more irregular and less compact flocs (Xiao *et al.,* 2009).

Conventionally, the arrangement of chemical addition for coagulation processes demands first the pH correction, then the metal coagulant addition, and finally the flocculant introduction (Zemmouri *et al.,* 2012). However, there are instances where other sequences are more effective, including inverting the sequence of metal coagulant and polymer addition, and the sequence of metal coagulant addition and pH adjustment.

### II.4.3 Benefits and Limitations

As one of the most applied treatment processes to wastewater depuration, coagulation/ flocculation treatment has some advantages and limitations. Advantages are based on the fact that it is a simple treatment, involving a well-known procedure, has a multiplicity of different systems to be employed in a variety of treatments, including both potable water and wastewater, with well-developed equipment and control systems. All this makes its implementation to be greatly easy in the most diverse sectors (Moghaddam *et al.,* 2010). In addition, this process not only produces coagulation of colloids but also typically results in the precipitation of soluble compounds, such as phosphates (Tassoula *et al.,* 2007; Tatsi *et al.,* 2003). Furthermore, coagulation can also lead to the removal of particles larger than colloids due to the entrapment of such particles in the flocs formed during coagulation, enhancing primary treatment to reduce suspended solids, organic loads (Aygun and Yilmaz, 2010), and also some hazardous metals as chromium (Lofrano *et al.,* 2006).

The advantage of organic polymers is that they are more effective at small dosages, and the combination of flocculants with coagulants enhances the floc-settling rate (Tatsi *et al.,* 2003; Ginos *et al.,* 2006) and improve process economics as well (Sarika *et al.,* 2005). Natural polymers are also biodegradableand are stable for different operational conditions (Brostow *et al.,* 2009). Even though they may be more expensive, a smaller amount may be needed, thereby saving money in the coagulation/flocculation process.

However, the inherent disadvantage to this process is the generation of large quantities of chemical sludge that depend on the type of coagulant as well as of the operation conditions (Tatsi *et al.,* 2003; Ginos *et al.,* 2006; Kestioglu, 2005). If its classification is hazardous waste, there is the need for secured land filling adequate to hazardous solid wastes (Moghaddam *et al.,* 2010). The process also increases the total dissolved salt (total dissolved solids) (Barbusinski and Pieczykolan, 2010; Liang *et al.,* 2009; Liu *et al.,* 2012; Zemmouri *et al.,* 2012).

As stated, if there is a surplus of coagulant dosage it can favor a decrease in the removal efficiency possibly due to partial re-stabilization of colloids (Mavros *et al.,* 2008). Other limitation is the susceptibility of the process efficiency due to changes in wastewater matrix variance (type and concentration of pollutants, pH, TDS) (Sun *et al.,* 2009). Different conditions may lead to the need of readjusting the coagulation conditions (Moghaddam *et al.,* 2010; Aboulhassan *et al.,* 2006).

### II.4.4 Applications to Wastewater Treatment

The coagulation process has been employed for many years for a wide diversity of wastewaters. Table II.4.1 presents studies for treatment of industrials wastewaters, showing the operational conditions and the attained efficiencies.

Petroleum wastewater treatment was evaluated by this chemical/physical process (Farajnezhad, and Gharbani, 2012, Santo *et al.*, 2012), as well as tannery leather wastewater (Lofrano *et al.*, 2006), Pulp and paper (Kumar *et al.*, 2011), microelectronic factory wastewater (Aboulhassan, *et al.*, 2006), municipal wastewater (Ismail *et al.*, 2012), detergents wastewater (Aygun and Yilmaz, 2010) and industrial polymer effluent (Sher *et al.*, 2013).

Part of the presented works are the result of developed studies where coagulation was applied as pre or post treatment of wastewaters, being a complementary process of integrated schemes of multiple depurative stages. This is the case of the treatment of olive oil mill effluents which has been integrated with Fenton, (Gino al., 2006; Rizzo *et al.*, 2008; Mert *et al.*, 2010), Photo-Fenton (Rizzo *et al.*, 2008; Papaphilippou *et al.*, 2013) with Ozonolysis (Ntampou *et al.*, 2006 and Lafi *et al.*, 2010), anaerobic digestion (Pekin *et al.*, 2010), $H_2O_2$ / UV and UV / $O_3$ (Kestioglu *et al.*, 2005). In the case of treating landfill leachates flocculation was integrated with Ozonolysis (Ntampou *et al.*, 2006) and for the wastewater treatment of mollases coagulation was applied after an aerobic biological treatment (Liang *et al.*, 2009). Coagulation used as pretreatment can effectively remove organic and inorganic matter enhancing the subsequent treatment based on advanced oxidation processes (Wu *et al.*, 2004).

From this perspective, the utilization of coagulation/flocculation processes, reveals promising results when integrated with AOPs treatments of olive mills effluents, leading to substantial removals of chemical oxygen demand as 90%, 95% and 94%, for $O_3$, $O_3$/UV and $H_2O_2$/UV processes (Lafi *et al.*, 2010; Mert *et al.*, 2010). In another work, COD removal range was about 10-40% after coagulation and the degradation increased to about 60% by Fenton reaction (Ginos *et al.*, 2006).

A landfill leachate was able to be discharged after being treated through a coagulation-ozonation process. Coagulation permitted to achieve COD removals up to 72%, and ozonation as post-treatment attained a COD of 150 $mgO_2.L^{-1}$ leading to a global COD reduction of 85% of COD (Ntampou *et al.*, 2006).

*Table II.4.1- Literature overview of the Coagulation/Flocculation Process*

| POLLUTANT | OPERATIONAL CONDITIONS | PRINCIPAL CONCLUSIONS | AUTORS |
|---|---|---|---|
| **Landfill Leachates** | $[Al_2(SO_4)_3.18H_2O]$=2 g.L$^{-1}$,<br>pH =10. | COD $_{removal}$ = 80% | Tatsi *et al.,*<br>(2003) |
| **Landfill leachate** | $[FeCl_3]$= 900 mgl$^{-1}$ | COD $_{removal}$= 60 % | Wu *et al.,*<br>(2004) |
| **Olive mill wastewater** | Acid cracking + $FeCl_3$ coagulation 3000 mg.L$^{-1}$<br>pH= 8 | COD $_{removal}$= 95%<br>TP=40 ± 1.3% | Kestioglu *et al.,*<br>(2005) |
| **Landfill Leachate** | $[FeCl_3]$ = 700-950 mg.L$^{-1}$<br>[Nalco 4684] = 3.0 mg.L$^{-1}$<br>pH=4.0-5.0 | COD $_{removal}$= 38%<br>DOC $_{removal}$= 42% | Bila *et al.,*<br>(2005) |
| **Microelectronic Factory Wstewater** | $[FeCl_3]$=900 mg.L$^{-1}$<br>pH = 8<br>COD=5846.76 ±508 mg$O_2$.L$^{-1}$<br>$BOD_5$/COD= 0.17 | Surfactant $_{removal}$= 22%<br>COD $_{removal}$= 88%<br>$BOD_5$/COD = 0.41 | Aboulhassan, *et al.,*<br>(2006) |
| **Landfill Leachate** | 7 and 11 mM for Fe and Al<br>pH=8 | Color $_{removal}$ = 98%<br>$UV_{254nm}$ =82 and 75%<br>COD $_{removal}$ = 72% and 62% | Ntampou *et al.,*<br>(2006) |
| **Olive Mill** | [Lime]=50 g.L$^{-1}$<br>[Cationic Floculant]=167 mg.L$^{-1}$ | COD $_{removal}$ = 30.4%<br>TP= 47.9% | Ginos *et al.,*<br>(2006) |
| **Tannery Leather Wastewater** | [poly aluminium ferric chloride]= 900mg.l$^{-1}$<br>pH=8.5 | TSS $_{removal}$=98%<br>COD $_{removal}$= 76% | Lofrano *et al.,*<br>(2006) |
| **Landfill Leachate** | [Ferric sulfate]=2400 mg.L$^{-1}$<br>pH=4.5 | COD $_{removal}$ =67%<br>Color $_{removal}$ =96% | De Velasquez *et al.,*<br>(2006) |
| **Municipal Waste Water** | [Ferric chloride]=7.5mg.L$^{-1}$<br>pH=7.2 | COD $_{removal}$= 50 %<br>Phosphorous $_{removal}$= 95%<br>Turbidity $_{removal}$= 80% | Tassoula *et al.,*<br>(2007) |
| **coffee processing wastewater** | flocculant [Ecofloc 6260]=6 ml (1%)<br>coagulant, [T-1]= 1.5 ml.L-1<br>pH=4.6 | COD $_{removal}$= 58 % | Zayas *et al.,*<br>(2007) |
| **Olive Pomace Leachate** | $[Al^{3+}]$=7.5mM<br>COD=3500 mg.L$^{-1}$<br>pH=7.6 | Solids $_{removal}$= 80%<br>Color $_{removal}$=93% | Mavros *et al.,*<br>(2008) |
| **Olive Mill Wastewater** | chitosan = 400mg L$^{-1}$<br>pH=4.3 | TSS $_{removal}$= 81% | Rizzo *et al.,*<br>(2008) |
| **Molasses Effluent** | [ferric chloride] =3.5 g.L$^{-1}$<br>pH=8 | COD $_{removal}$ =86%<br>Color $_{removal}$ =96% | Liang *et al.,*<br>(2009) |
| **Landfill Leachate** | [ferrous sulfate]=10 g.L$^{-1}$<br>pH=11.7 | COD $_{removal}$= 22%<br>Color $_{removal}$= 42%<br>Turbidity $_{removal}$=31% | Amir,<br>(2009) |
| **Detergents Wastewater** | [ferric chloride] =2 g.L$^{-1}$<br>[clay minerals] =500 mg.L$^{-1}$<br>[anionic polyelectrolyte] =50 mg.L$^{-1}$ pH=11 | COD $_{removal}$= 87% | Aygun and Yilmaz,<br>(2010) |
| **Landfill Leachate** | $[FeClSO_4]$= 500 mg.L$^{-1}$<br>pH=5 | COD $_{removal}$= 39% | Barbusinski and Pieczykolan,<br>(2010) |
| **Landfill Leachate** | $[Al_2(SO_4)_3.14H_2O]$=0.75 g.L$^{-1}$<br>PH=6.2 | COD $_{removal}$=38 %<br>DOC $_{removal}$= 45%,<br>$UV_{254\ removal}$= 60%% | Labanowski, *et al.,*<br>(2010) |
| **Olive Oil Mill Wastewater** | $Al^{3+}$ and $Fe^{3+}$<br>pH=9 | COD $_{removal}$ = 54% and 58% | Lafi *et al.,*<br>(2010) |
| **Olive Mill Effluents** | [Poly aluminium chloride]=1.25 g.L$^{-1}$<br>pH= 8.5 | TP= 26%<br>TSS=26% | Pekin *et al.,*<br>(2010) |
| **Pulp And Paper** | [Poly aluminium chloride]=8 ml.L$^{-1}$<br>pH=5 | COD $_{removal}$= 84%<br>Color $_{removal}$=92% | Kumar *et al.,*<br>(2011) |
| **Municipal Wastewater** | [Alum]=60 mg.L$^{-1}$<br>pH = 6-6.5 | TSS=83%<br>COD=65%<br>BOD =55%<br>TP=76% | Ismail *et al.,*<br>(2012) |

*Table II.4.1- Literature overview of the Coagulation/Flocculation Process (cont.)*

| | | | |
|---|---|---|---|
| **Petroleum Refinery Effluent** | [PAX18]= 28.6 mg $L^{-1}$<br>[NALCO 71408]=.5 mg $L^{-1}$<br>pH=6-7 | COD $_{removal}$=85.3 %<br>TOC $_{removal}$= 82.4%,<br>Turbidity $_{removal}$=81.4% | Santo *et al.,*<br>(2012) |
| **Landfill Leachate** | [$FeCl_3.6H_2O$]=10 $g.L^{-1}$<br>pH =8.0 | COD $_{removal}$=68.7%<br>Color $_{removal}$= 93.3%,<br>Turbidity $_{removal}$= 98.9%<br>HA $_{removal}$ = 80.2% | Liu *et al.,*<br>(2012) |
| **Molasses Spentwash** | [Ferrous Sulfate]=40 $g.L^{-1}$<br>pH= 11 | COD $^{removal}$= 46.4%<br>Color $^{removal}$= 82.5% | Chauhan *et al.,*<br>(2012) |
| **Petroleum Waste Water** | [PACl]= 10mg.$L^{-1}$<br>pH=7.5 | COD $^{removal}$= 72%<br>Color $^{removal}$=88.5% | Farajnezhad and Gharbani<br>(2012) |
| **Olive Mill** | [$FeSO_4.7H_2O$]= 6.67 $g.L^{-1}$<br>anionic polyelectrolyte 0.287 $g.L^{-1}$<br>pH=5.3 | TSS $^{removal}$=97±1.3%<br>COD $^{removal}$= 72±1.5%<br>TP= 40±1.3% | Papaphilippou *et al.,*<br>(2013) |
| **Pesticide Wastewater (Fenton)** | [Aluminium sulphate] = 12 $g.l^{-1}$<br>pH= 8-9<br>COD= 8700±200 $mgO_2.L^{-1}$ | COD $_{removal}$= 55%<br>BOD $_{removal}$= 66% | Amita and Mistry,<br>(2013) |
| **Textile Effluent** | [$FeSO_4$]=2 $kg.m^{-3}$<br>[CaO]= 2.5 $kg.m^{-3}$<br>pH=10.9 | COD $_{removal}$= 61.3% | Mukhlish *et al.,*<br>(2013) |
| **Industrial Polymer Effluent** | [$Al_2(SO_4)_3$] =7.5 $mL.L^{-1}$<br>[anionic polyacrylamide]=7.5mL.$L^{-1}$<br>pH 6-8 | COD $_{removal}$=98%<br>SS $_{removal}$= 91%,<br>Turbidity $_{removal}$= 99% | Sher *et al.,*<br>(2013) |
| **Distillery** | pH=3<br>flocullant<br>4698 SH | TSS $_{removal}$= 91%<br>COD $_{removal}$= 2% | Martins *et al.,*<br>(2013) |

## II.5 Biological Treatment

Biological treatment is the most frequent, economically and ecologically attractive technique for wastewater management compared with chemical and physical remediation (Tabrizi and Mehrvar, 2004). With appropriate analysis and environmental control, most of the wastewaters can be treated biologically. Consequently, it is essential to comprehend the characteristics of each biological process to guarantee that the suitable environment is produced and controlled effectively.

Generally by means of activated sludge in adequate conditions (Droste, 1990), has conclusive advantages for the oxidation of organic pollutants. However, many compounds cannot be successfully eliminated by biological oxidation because of their inherent high toxicity. The need to pH adjustment to an adequate value and comply with the nutrients and oxygen in sufficient quantities for the transforming microorganisms are standard requirements for the viability of the process that depends fundamentally on the health and activity of those microorganisms.

### II.5.1 Fundamentals

The principal goals of the biological treatment of wastewater are coagulation of colloidal organic matter, removal of carbonaceous BOD and elimination of the non-settled colloidal solids in order to stabilize organic matter. Besides all of that, for an industrial wastewater, the main objective is to eliminate and decrease the concentration of organic and inorganic compounds such as nitrogen and phosphorous (Metcalf and Eddy, 1991).

The process consists in a group of microbial cells that use energy and carbon for cells growth and preservation, by means of biochemical reactions. There are two kinds of processes in the biological treatment, aerobic and anaerobic. The former is done in the presence of oxygen while the anaerobic is executed in the oxygen absence (Metcalf and Eddy, 1991). Microorganisms can be classified as aerobic, anaerobic or facultative depending on their oxygen requirements. The facultative are those capable to operate in either presence or absence of molecular oxygen. Biological processes can be also classified according to the microorganisms location, if they are fixed on solid supports or kept in suspension in the aqueous medium (Tabrizi and Mehrvar, 2004). In both cases, in order to make the treatment more complete, it is normally necessary to guarantee the removal of the microbial cells from the wastewater after the treatment.

The biotreatment units are constituted by a large heterogeneity of organized complexes of biological populations. The most important microorganisms implicated are bacteriabut other metabolic activities are important in bioremediation. Those microorganisms are used to convert the colloidal and dissolved organic matter into less complex compounds, gases and into cell tissue. Since cell tissue has specific gravity a little higher than water, the resultant cells can be easily removed by gravity settling (Carucci *et al.,* 1995).

The necessities of treatment and the environmental conditions influence the microorganisms selection and the biological process operation. Consequently, it is essential to control some parameters, as for instance, the hydraulic regime and mixing. These permit to determine the substrate accessibility to microorganisms and the oxygen and inorganic nutrients availability, as well as vital elements for cells synthesis such as nitrogen and phosphorous and trace elements such as potassium, calcium and magnesium. Otherwise, the cellular growth can slow down. These elements need to be present at a specified ratio to allow an appropriate growth. Many industrial effluents are nutrient deficient; therefore, principally nitrogen and/or phosphorous must be added (Carucci *et al.,* 1995). The ratios at which nutrients should be supplied are expressed in COD: N: P ratios and various optimal ratios are reported in literature as 100:10:1 (Metcalf and Eddy, 1991).

The design of the processes is based on an assessment of microbial growth and substrate conversion kinetics. This mostly involves the use of Monod-type equations together with cell yield and decay expressions which are then combined with the hydraulic properties of the reactor to yield efficiency expressions.

This work is based on an aerobic treatment since it is easier to carry out, more rapid and leads to an effective process for the biodegradation of the majority of pollutants.

### II.5.2 Aerobic Treatment

Aerobic effluent treatments are essentially based on the bacteria capacity of assimilating biodegradable organic matter present in a wastewater. Normally, this is the chosen method for biological treatment of a polluted wastewater with many organic compounds aerobically oxidable. This process aims the decomposition of organic matter yielding carbon and water as final mineralization products, mainly by action of heterotrophic bacteria's (with consequent energy production through fermentation or organic matter oxidation).

Biodegradation of organic matter under aerobic conditions involves the oxidation of organic compounds to carbon dioxide, water, nitrate, phosphate and sulphate. The process of decomposition during biological treatment can be determined by these changes in the effluent.

The biochemical reactions involved in the microbial metabolism in the aerobic degradation can be described by the following simplified biochemical reactions (Equations II.31 to II.33), where

CHON represents the organic matter and new cells are represented by $C_8H_{15}O_4N$ (Metcalf and Eddy, 1991):

***Oxidation:***

$$CHON + O_2 \xrightarrow{Bacteria} CO_2 + H_2O + NH_4^+ + other\ products + Energy \qquad \textbf{(II.31)}$$

***Cells production:***

$$CHON + Energy \xrightarrow{Bacteria} \mathrm{C_8H_{15}O_4N}\ (new\ cells) \qquad \textbf{(II.32)}$$

***Endogenous respiration (auto-oxidation)***

$$\mathrm{C_8H_{15}O_4N}\ (\,cells) + 9O_2 \ \rightarrow\xrightarrow{Bacteria} 8\,CO_2 + 6\,H_2O + NH_3 + Energy \qquad \textbf{(II.33)}$$

The above described biochemical reactions involve the degradation of the substrate and energy supply for the synthesis of new cells and other biochemical processes that provide the material necessary for cell growth. In the absence of external food sources the organisms will use previously stored endogenous food supplies for their respiration which can lead to the previous products referred in Equation II.33, but also to some organic substances (Eckenfelder, 2000).

In addition to the carbon, autotrophic bacteria are able to metabolize some inorganic compounds in the aqueous medium such as nitrogen based compounds. In wastewater, nitrogen is present in the form of organic nitrogen and ammonia nitrogen, essential nutrients in the biological treatment systems. The oxidation of nitrogen compounds takes place in two stages. In the first stage, in the presence of oxygen, living organisms will convert organic nitrogen to ammonia nitrogen and in the second stage ammonia is converted to nitrite and nitrate nitrogen. Nitrification is accomplished by the presence of nitrifying autotrophic bacteria, the nitrosomonas that can catalyse the oxidation of ammonia to nitrite using molecular oxygen, while further oxidize nitrite to nitrate using oxygen derived from the water molecule. They use carbon dioxide as their source of carbon while the oxidation of ammonia gives them the required energy (Eckenfelder, 2000). This will lead to the generation of cell material as previously described in Equations II.32 and II.33 (Equations II.34 and II.35):

$$2\,NH_4^+ + 3\,O_2 \xrightarrow{Nitrosomas} 2\,NO_2^- + 4\,H^+ + 2\,H_2O + Energy \qquad \textbf{(II.34)}$$

$$2\,NO_2^- + O_2 \xrightarrow{Nitrobacter} 2\,NO_3^- + Energy \qquad \textbf{(II.35)}$$

At proper environment and operation conditions, the carbonaceous organic matter degradation and the nitrification process can simultaneous occur. However, nitrification is the limiting step in the biological treatment because the growth rates of nitrifying bacteria are slower than the heterotrophic ones.

Apart from nutrient requirements, other factors can affect the efficiency of biological treatment, as is the case of environmental conditions and nature of organics. The information of toxicity and non-biodegradable compounds from wastewater is essential because these constituents cannot be assimilated by the biomass cells. Physical characteristics such as pH and temperature of aqueous medium must be between 6-8 and 25-33ºC, respectively, because these ranges favor metabolic reactions to occur faster and permit maximum growth rates (Tabrizi and Mehrvar, 2004).

As mentioned before, in this type of process, organic matter is removed from the medium by biological metabolism, oxygen is consumed by the organisms, new cells are being created and an excess of sludge is produced. This associated sludge production is the main disadvantage, since a posterior management is required prior to its disposal. The principal objective of sludge treatment is to stabilize, to reduce odors and some of the water, to decompose some of the organic matter and eliminate disease causing organisms. Normally, a typical sludge treatment is constituted by the following steps: thickening, dewatering and stabilization process followed by a main treatment (Aloui *et al.*, 2009). The sludge volume is reduced by thickening and dewatering processes. Subsequently, is stabilized by oxidation with chlorine, thermal treatment or anaerobic digestion. To conclude, the solid residues are normally incinerated, destined to land applications or deposited at a landfill.

### II.5.3 Basic Types of Aerobic Biological Systems for Wastewaters Treatment

An elementar classification of biological systems can be done in view of the aggregation state of biomass. Therefore, there are essentially two types of biological wastewater treatment processes, thesuspended growth and immobilized growth biological system.

Suspended growth biological systems depend on mixing to keep microorganisms in suspension, and guarantee that they are in continuous contact which most substrate as possible. In the immobilized growth systems, microorganisms are linked to a solid medium and the effluent passes through the medium as a film.

The immobilized growth configurations are advantageous compared to the suspend growth systems when the wastewater has high concentrations of pollutants, because this type of configuration permits a higher cellular density. Beyond this, it has been demonstrated that this system is more tolerable to shock loadings and produces less biological sludge. However, it is very difficult to do the quantification of biomass (Eckenfelder, 2000).

Therefore, since the concentration and the quantity of treated effluents to be used in this future work are not expected to be too high, suspended growth system will be used to assess biodegradation.

Suspended growth systems maintain the biomass in suspension in the wastewater during the treatment time. The biomass grows as suspended flocs of microorganisms. Normally, some type of mixing is employed to guarantee a constant contact with the substrate. Once biodegradation is over, biomass flocks are removed for clarification.

The common types of suspended growth configurations principally consist on batch or continuous flow reactors. Aerobic active sludge process operating in continuous flow mode includes a biological reactor coupled to a solids capture device, such as a clarifier or a solid separator. There is the introduction of wastewater in an aerated and mixed tank containing the suspended microorganisms. Once the biological degradation is carried out, biomass is settled out in a separated clarifier tank. At the end, a part of the biomass is recycled back to the process and the rest is periodically wasted (Tabrizi and Mehrvar, 2004).

The batch operation is the oldest type and the most commonly used version is called Sequencing Batch Reactor (SBR). Contrary to continuous flow mode, the SBR holds the complete biological treatment in a single tank, following a timed controlled sequence composed in five stages: filling, reaction, settling, draw and idle. The raw wastewater is added to the reactor and mixed with the biomass held in the tank. The metabolic biological reactions, involving the consumption of organic matter in presence of oxygen initiated during filling, are completed in the reaction phase by starting the proper mixing and/or aeration. Aeration and mixing are then stopped promoting the settling stage where the sludge is separated from the supernatant formed during the sedimentation. The reactor then is emptied and prepared for a new cycle of treatment (idle). During the idle, the sludge in excess is wasted (Eckenfelder, 2000).

The most remarkable advantage of the SBR technology is the simplicity, the suitability for simple automatization, the easy managing of unexpected effects, flexibility of operation, and the lower economic costs. However, major drawbacks are the requirement of a fairly large bioreactor with a long treatment time and the great quantity of excess sludge production.

## II.6 Combination of AOPs with Chemical and Biological Treatments

For the treatment of wastewaters that are non-toxic in general, the biological process is the most appropriate from an economical point of view (Alvares *et al.,* 2001). However, when the effluent is characterized by bio-toxic or recalcitrant organics, biological processes alone are not always capable to make an effluent suitable for discharge into hydrological resources. Thus, the combination between chemical andbiological treatments arise as appropriate solutions (Mantzavinos and Psillakis, 2004; Gogate and Pandit, 2004b).

### II.6.1 Fundamentals

In general, chemical processes using oxidizing agents, such as ozone and hydrogen peroxide, are relatively expensive due to the associated elevated investment and operational costs with high energy and chemicals demand. Thus they can often be prohibitive for wastewater treatment (Gogate and Pandit, 2004a; Sangave *et al.,* 2007; Primo *et al.,* 2008).

Thus, process optimization and, when possible, process integration with less expensive technologies need to be considered (Bautista *et al.,* 2008; Primo *et al.,* 2008; Mandal *et al.,* 2010b). In this process plan, AOPs can be envisaged as pretreatments to enhance biodegradability and diminish toxicity (Parra *et al.,* 2000; Sarria *et al.,* 2001 and 2002) since such chemical oxidation systems generally produce oxygenated organic by-products and low molecular weight acids that are more biodegradable (Mantzavinos and Psillakis, 2004; Sangave *et al.,* 2007). With the AOPs, toxic compounds would be removed until no inhibition due to its toxicity is present and/or non-biodegradable compounds turned into more biodegradable (Cañizares *et al.,* 2000; Klavarioti *et al.,* 2009; Alvares *et al.,* 2001; Sangave *et al.,* 2007). After that, pre-treated effluents can be safely sent to the biological treatment that will reduce contamination levels down to the legislation limits (Comninellis *et al.,* 2008; Primo *et al.,* 2008).

In particular, the oxidant agent should be used mainly towards recalcitrant compounds oxidation hence avoiding removing biodegradable pollutants that can be biologically degraded, with the aim of transforming refractory compounds into more biodegradable ones, avoiding their mineralization (Di Iaconi, 2012). This aspect is economically attractive, as investment and the operating costs are much lower for a biological process than for an AOP. In fact, the investment costs for biological processes are from 5 to 20 times lower than for chemical systems, while treatment costs are lower within a range from 3 to 10 times (Scott and Ollis, 1996; Cañizares *et al.,* 2000). Thus, the synergistic effect of coupling chemical-biological oxidation, could increase COD removal, and simultaneously reduce the chemicals requirements, achieving an interesting economic advantage (Mandal *et al.*, 2010a).

Focusing on this strategy, a scheme used to plan a combined chemical oxidation process with a biological treatment is presented in Figure II.6.1. The wastewater can be classified as biodegradable or non-biodegradable. Biodegradable wastewaters can be directly bio treated (Tabrizi and Mehrvar, 2004). When the wastewater contains small concentrations of recalcitrant pollutants, partly biodegradable, there are two possible alternatives. An adaption of the activated sludge to remove the small biodegradable fraction of wastewater and then carry out an AOP stage to abate the remaining refractory COD can be chosen. On the other hand, for non-biodegradable wastewaters chemical oxidation is the first stage avoiding complete mineralization and aiming to enhance biodegradability in order to produce an effluent able to be submitted to a posterior biotreatment (Mantzavinos and Psillakis, 2004). Thereby, a wastewater highly or completely resistant to conventional biological oxidation can be totally mineralized using a combined chemical-biological system (Aparício *et al.*, 2007).

In a combined biological-chemical-biological treatment, the first biological step has the function of removing biodegradable organic compounds. The chemical process allows reducing pollutants concentration and yield more oxidized compounds, which are in most cases more easily biodegradable and the second biological step concludes the oxidation treatment (Bertanza *et al.*, 2001).

When working with integrated biological and chemical processes, a few aspects must be avoided. The chemical oxidants cannot be mixed with the bio culture, because they could damage the microorganisms. When a biological process is receiving the oxidized effluent, excessive chemical oxidation may result in highly oxidized products with little metabolic value for the microorganisms (Aparicio *et al.*, 2007). Large doses of oxidant or contact times could be wasted on easily biodegradable intermediates resulting in decreased efficiency. pH also can have a harmful effect, normally for acidic values. Chemical wastewaters treatment could require acid pH conditions, and, generally, this type of systems produce acid species in the oxidation process (Tabrizi and Mehrvar, 2004). For that reason, pH readjustment to a value near to 7 is necessary before feeding the biological reactor.

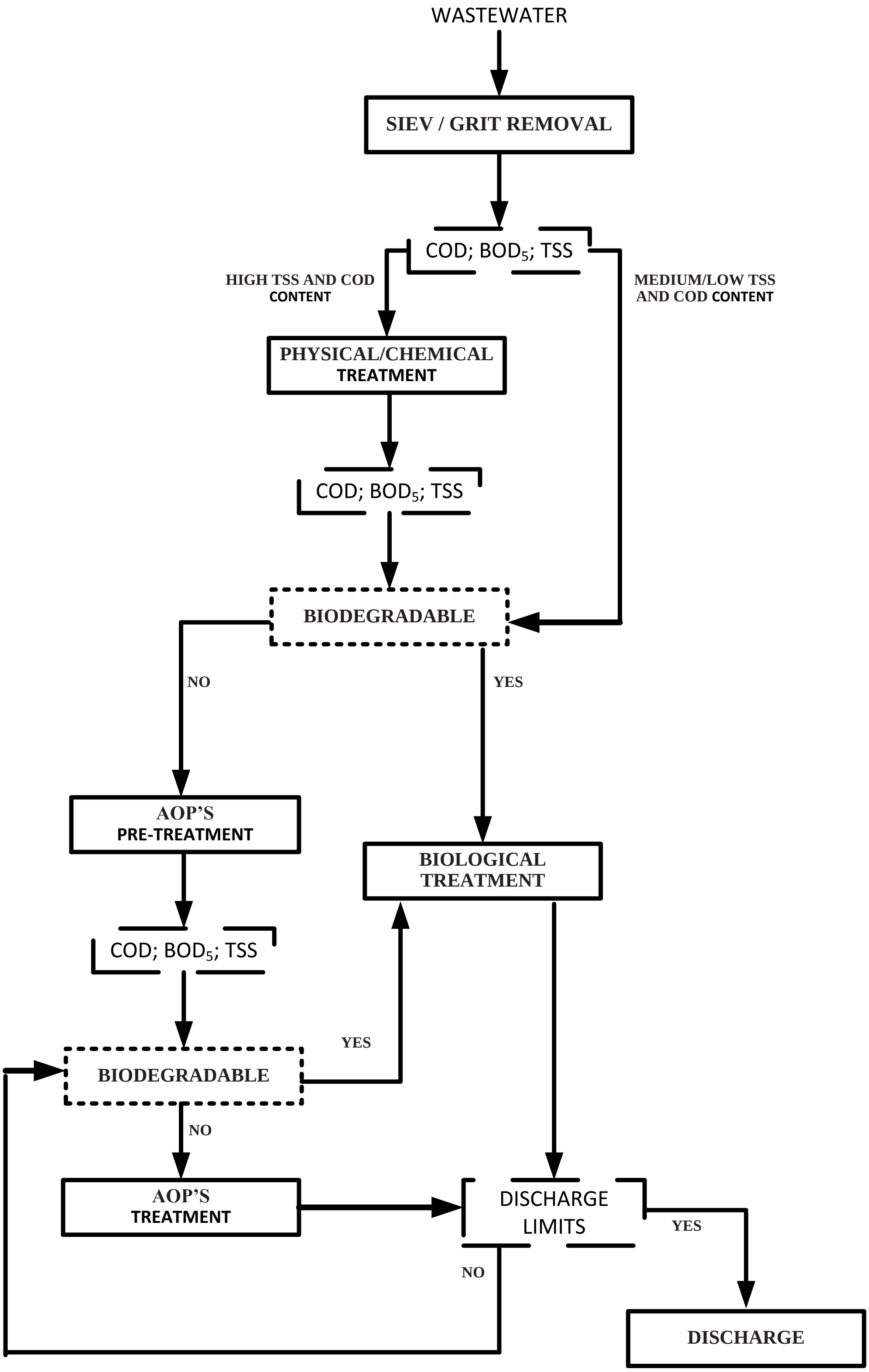


*Figure II.6.1- General strategies to wastewater treatment*

As observed from Figure II.6.1, a fundamental aspect is the assessment of the biodegradability and toxicity along the chemical process. This is to determine an optimal pretreatment time that is able to guarantee the application of the coupled system (Andreozzi *et al.,* 1999). There are various tests used to provide the biodegradability and toxicity of the generated by products, either by ecotoxicological analyses or by chemical characterization (Schrank *et al.,* 2005). The biodegradation tests such as $BOD_5$ are usually used to predict the biodegradation behavior of a material in the medium through standardized methods leading to the $BOD_5$/COD ratio (Mantzavinos and Psillakis, 2004; Gotvajn *et al.,* 2009) that constitutes an index of screening aerobic biodegradability. It is recognized that an effluent presenting a ratio $BOD_5/COD > 0.4$ may be considered biodegradable (Tabrizi and Mehrvar, 2004; Esplugas *et al.,* 2004). On the other hand, ready biodegradability assessment by means of respirometric techniques is well considered because it measures the instantaneous response of a microorganisms community when in contact with a pollutant. Besides, it permits to establish the toxic character of the sample (Gutiérrez *et al.,* 2002; Mantzavinos and Psillakis, 2004; Gotvajn *et al.,* 2009b).

Regarding the toxicity, besides the respirometric method, the measurement of the activity inhibition of different microorganisms such as luminescent bacteria (*Vibrio fischeri*) is generally employed (Gutiérrez *et al.,* 2002; Gotvajn *et al.,* 2009a; Perdigón-Melón *et al.,* 2010). Acute bioassays are considered of simple execution and manipulation, as well as low cost and reliability and repeatability characteristics. In our research group all these methodologies have been used in our latest research in this field. In this ambit, respirometry, $BOD_5$, $BOD_5$/COD ratio and *Vibrio fischeri* light inhibition were used to assess the biodegradability and toxicity of the treated wastewaters (Martins *et al.,* 2010a and 2010b).

## II.6.2 Applications to Wastewater Treatment

In line with what was previously described, the coagulation appears as one of the easiest techniques to implement, with results in several studies. Table II.6.1 depicts the treatment methods associated with integrated processes in which Advanced Oxidation Processes are applied, presenting also the main conclusions.

A wide range of studies has already stated the potential of these coupled systems to treat different model compounds and real wastewaters from various origins. Examples are olive mill wastewaters, paper pulp bleaching effluents, textile waters, wastewaters containing pesticides, wine-distillery effluents and landfill leachates, among others.

The choice of the appropriate chemical and biological units depends on the characteristics of the wastewater and the treatment purpos. The biological process may involve isolated or mixed organisms cultures acting under different oxygen environments and located on fixed solids supports or suspended in the media. Among the proposed coupled technologies, special attention has been given to combining AOPs and aerobic biological processes.

Typical sequences are composed by ozonation ($O_3$) - aerobic treatment (Chaturaprek *et al.*, 2005; Wang *et al.*, 2008; Lafi *et al.*, 2009; Li *et al.*, 2010; Sangave *et al.*, 2007; Aparicio *et al.*, 2007; Moraes *et al.*, 2006, Di Iaconi, 2012), and Fenton type reactions - aerobic treatment (Bressan *et al.*, 2004; Chen *et al.*, 2007; Wang *et al.*, 2008; Wang *et al.*, 2009; Lodha and Chaudhari, 2007; Tünay *et al.*, 2008; You *et al.*, 2011, Mandal *et al.*, 2010a). Also dealing with aerobic biological treatments, the inverse strategies such the aerobic process followed by ozonation (Lafi *et al.*, 2009) or by Fenton (Blanco *et al.*, 2011) have been reported.

Finally, more complex chemical-biological processes have also been proposed. As the example of the treatment cycle that implies a two stage aerobic - $O_3$ sequence (Sangave *et al.*, 2007; García-Montaño *et al.*, 2008; Hagman *et al.*, 2008), ozonation and Fenton in the same process (Goi *et al.*, 2009, Martins *et al.*, 2013) or the applications of two or more treatment stages, as the case of flocculation-Fenton-ozonation to attain a biological oxidizable wastewater. Usually, this kind of integrated processes have a previous coagulation/flocculation stage for solids elimination and attempt of some COD removal (Chen *et al.*, 2007; Wang *et al.*, 2008; Wang *et al.*, 2009), having the effect of equalizing the effluent to the variation in solids content.

The use of a physical/chemical treatment before an oxidation stage is commonly employed to treat landfill leachates (Bila, 2005; de Velasquez and Monje-Ramirez, 2006; Ntampou *et al.*, 2006; Deng, 2007), cosmetics and chemicals wastewater (Perdigón-Melón *et al.*, 2008, Xing and Sun, 2009), wash jeans wastewater (Wang *et al.*, 2008) and herbicide and pesticide production wastewaters (Martins *et al.*, 2005 and Chen *et al.*, 2007, respectively). Coagulation followed by ozonation has been a process widely used for an initial removal of the suspensions and some solids as reported in the treatment of landfill leachate (Velasquez, and Monje-Ramirez, 2006; Ntampou *et al.*, 2006; Poznyak *et al.*, 2008). The reverse, ozonation followed by coagulation / flocculation was the subject of study of Ntampou *et al.*, (2006) with better removal of chemical oxygen demand than the reaction system described above. The coagulation process coupled with the Fenton process was studied in the treatment of an effluent from the cosmetics industry (Perdigon-Melon *et al.*, 2008) and for combined industrial and domestic wastewater, achieving 90% and 100% of COD and color removal, respectivley (Badawy and Ali, 2006).

The combination of Fenton process followed by ozonation and the reverse scheme was analyzed for landfill leachate (Goi *et al.,* 2009) and distillery effluent (Martins *et al.,* 2013) with the first option showing better results, increasing the $BOD_5/COD$ to 0.98 on the last one. Regarding ozonation followed by biological systems, proposals were made for the treatment of domestic sewage by biofiltration (Wang *et al.,* 2008), effluent of landfill leachate (Chaturaprek et al.,2005, Di Iaconi *et al.,* 2012), production of oil (Lafi *et al.,* 2009) tannery and textile factory wastewater (Di Iaconi *et al.,* 2012). Similar to the latter, the scheme biological + ozonation + biological was referred by Sangave and collaborators (2008) for the purification of distilleries effluents and for the treatment of oil mill effluents (Lafi *et al.*, 2009). Ramos (2009) proposed the system of chemical precipitation followed by ozonation for purifying cleansing effluents from paper industry. The Fenton process followed by an aerobic biological process was proposed for the depuration of detergents wastewaters (Wang *et al.,* 2008), while Chen and assistants (2007) used a clotting pre stage for the purification of pesticides residual waters and for olive oil mill effluents treatment with a remarkable 90% of COD depletion (Bressan *et al.,* 2004). Primo *et al.* (2008) suggested the Fenton process with subsequent neutralization and ultrafiltration as a feasible treatment for landfill leachate, reaching 80% removal of COD and total depletion of color, solids and iron. Processes with 4 steps, coagulation, hydrolysis, Fenton and filtration, were applied to effluent from jeans washing with removals above 90% for COD, color and suspended solids (Wang *et al.,* 2008).

The major highlight of the presented works is undoubtedly the increase of the ratio $BOD_5/COD$ by the action of chemical oxidative treatments before the biological processes, and the polishing effects of AOPs by oxidizing the remaining organic matter refractory to biological treatment.

***Table II.6.1- Literature overview of the integrated AOP´s processes***

| ***POLLUTANT*** | ***INTEGRATED PROCESSES*** | ***OPERATING CONDITIONS/EFFICIENCY*** | ***PRINCIPAL CONCLUSIONS*** | ***AUTORS*** |
|---|---|---|---|---|
| **Olive Oil Mill Wastewaters** | Fenton- aerobic biological treatment | Fenton:<br>$COD_{removal}$ = 80-90%<br>SBR:<br>$COD_{remova\ l}$= around 40% | Combined treatment:<br>$COD_{removal}$ = 90%<br>3/5 $[H_2O_2]$ | Bressan *et al.,* (2004) |
| **Landfill Leachate** | Ozonation - membrane bioreactor | TOC = 740 $mg.L^{-1}$<br>COD = 8000-9000 $mg.L^{-1}$ | $COD_{removal}$ = 78% | Chaturaprek *et al.,* (2005) |
| **Landfill Leachate** | Coagulation/flocculation(1) - ozonation (2) - biological treatment | pH=8<br>$BOD_5/COD = 0.05$<br>(1)$Al_2(SO_4)_3$<br>(2) $[O_3] = 3$ $g.L^{-1}$ | (1) COD and $DOC_{removal}$ = 40 and 25%<br>(2) $BOD_5/COD = 0.05$<br>$COD_{removal}$ = 73%<br>$DOC_{removal}$ = 63% | Bila *et al.,* (2005) |
| **Herbicide Trifluraline Production Wastewater** | coagulation-Fenton-sedimentation | Coagulation: pH=9<br>Fenton sludge : 500 mg. $.L^{-1}$<br>$Fe^{3+}$=500 $mg.L^{-1}$<br>Fenton: pH=3<br>$[H_2O_2]$ = 550 $mg..L^{-1}$<br>$[Fe^{2+}]$ = 400 $mg..L^{-1}$ | $COD_{removal}$ = 63.4%<br>$Color_{removal}$ = 91.6% | Martins (b) *et al.,* 2005 |

*Table II.6.1- Literature overview of the integrated AOP´s processes (cont.)*

| | | | | |
|---|---|---|---|---|
| **Landfill Leachate** | Coagulation - ozonation | COD=1720 mg.L$^{-1}$ | COD $_{removal}$ = 67%<br>Color $_{removal}$= 100% | de Velasquez, and Monje-Ramirez, (2006) |
| **Combined Industrial And Domestic Wastewater** | Coagulation-Fenton | [$FeCl_3$]= 400 mg.L$^{-1}$<br>cationic polymer = 2 mg. L$^{-1}$<br>pH 3<br>[$H_2O_2$] = 550 mg.L$^{-1}$<br>[$Fe^{2+}$ ] = 400 mg.L$^{-1}$ | COD $_{removal}$ = 90%<br>Color $_{removal}$ = 100%<br>BOD/COD = 0.31 to 0.63 | Badawy and Ali, (2006) |
| **Pulp And Paper Effluent (Kraft E1 And Black Liquor Effluent)** | Ozonation - biological process | Ozonation<br>pH = 11<br>[$O_3$] = 14 mg.L$^{-1}$<br>t = 15 min | TOC $_{removal}$ E1=37%<br>E1 and black liquor<br>Color $_{removal}$ =27% and 14% | Moraes *et al.*, (2006) |
| **Landfill Leachate** | Ozonation - Coagulation /flocculation | COD = 5050 mg $O_2$.L$^{-1}$<br>$BOD_5$/COD = 0.17 | COD $_{removal}$ = 96.8% | Ntampou *et al.*, (2006) |
| **Landfill Leachate** | Coagulation/ flocculation - Ozonation | COD = 5050 mg $O_2$.L$^{-1}$<br>$BOD_5$/COD=0.17 | COD $_{removal}$ = 95.6% | Ntampou *et al.*, (2006) |
| **Distillery Wastewater** | Ozonation - aerobic process - ozonation | pH = 9<br>TOC = 27000 mg.L$^{-1}$<br>COD = 62000 mg.L$^{-1}$ | COD $_{removal}$ = 67%<br>Color $_{removal}$ = 100% | Sangave *et al.*, (2007) |
| **Pesticide Production Wastewater** | Coagulation - Fenton- biofilm reactor | pH = 1.5 - 2<br>$BOD_5$/COD = 0.18 | COD $_{removal}$ = 85%<br>$BOD_5$/COD = 0.47 (Fenton) | Chen *et al.*, (2007) |
| **Wastewater From A Resin-Producing Factory** | Ozonation - biological treatment | pH = 8.75<br>[$O_3$]=13 ± 1.2 mg.L$^{-1}$<br>time = 180 min | COD $_{removal}$ = 100%<br>Organic N $_{removal}$ = 77% | Aparicio *et al.*, (2007) |
| **Distillery Wastewater** | aerobic treatment - Ozonation - aerobic treatment | pH = 9<br>[$O_3$] = 19 mg.L$^{-1}$<br>t = 4h | COD $_{removal}$ = 79%<br>Color $_{removal}$ = 100% | Sangave *et al.*, (2007) |
| **Pesticide Wastewater** | Fenton Oxidation-MBBR | $BOD_5$/COD= 0.18<br>COD =33700±2100 mg.L$^{-1}$ | Fenton oxidation:<br>COD $_{removal}$ = 64%<br>$BOD_5$/COD=0.47<br>MBBR:<br>COD $_{removal}$ =85% | Chen *et al.*, (2007) |
| **Landfill Leachate** | Coagulation-Fenton | pH = 3<br>[$H_2O_2$] = 240 mM<br>[$H_2O_2$]: [$Fe^{2+}$]= 3 | COD $_{removal}$ = 75% | Deng, (2007) |
| **Linear Alkylbenzene Sulfonate (Las)** | Fenton - aerobic process (20h) | COD = 1652 mg.L$^{-1}$<br>LAS = 528 mg.L$^{-1}$ | COD $_{removal}$ = 95%<br>LAS $_{removal}$ = 99% | Wang *et al.*, (2008) |
| **Cosmetic Production Wastewater** | Coagulation - Fenton | COD = 4150 mg $O_2$.L$^{-1}$<br>$BOD_5$/COD = 0.003<br>TOC = 1220 mg.L$^{-1}$<br>Phenol = 21 mg.L$^{-1}$ | COD $_{removal}$ = 96%<br>Phenol $_{removal}$ = 99%<br>$BOD_5$/COD=0.37 | Pérdigon-Mélon *et al.;* (2008) |
| **Landfill Leachate** | Coagulation/flocculation - Ozonation | COD = 4580 mg $O_2$.L$^{-1}$ | COD $_{removal}$ = 68% (coagulation)<br>Color $_{removal}$ = 100% | Poznyak *et al.*, (2008) |
| **Landfill Leachate** | Fenton - neutralization - Ultrafiltration | COD = 2100 mg $O_2$.L$^{-1}$<br>$BOD_5$/COD = 0.08 | COD $_{removal}$ = 80%<br>Color $_{removal}$ = 100%<br>TSS $_{removal}$ = 100% | Primo *et al.*, (2008) |
| **Secundary Savage Wastewater** | Ozonation - biofiltration | COD=52 mg.L$^{-1}$<br>$NH_3$-N=19 mg.L$^{-1}$<br>TOC=13 mg.L$^{-1}$ | TOC $_{removal}$ = 34 %<br>COD $_{removal}$ = 55%<br>$NH_3$-N $_{removal}$ = 92% | Wang *et al.*, (2008) |
| **Wash Jeans Wastewater** | Coagulation-hydrolyses/ acidification-Fenton - sand filters | COD = 1200 mg.L$^{-1}$<br>$BOD_5$ = 330 mg.L$^{-1}$<br>SS = 287 mg.L$^{-1}$ | COD $_{removal}$ = 95%,<br>$BOD_5$ $_{removal}$ = 94%<br>SS $_{removal}$ = 97%<br>Color $_{removal}$ = 95% | Wang *et al.*, (2008) |
| **Pulp And Paper Wastewater** | Fenton - immobilized biomass treatment | (Fenton) :pH = 2,<br>[$H_2O_2$]: [$Fe^{2+}$] = 1:2 (mol/mol)<br>[$H_2O_2$]: [COD] = 2:1 (mol/mol)<br>time = 2hours | COD $_{removal}$ = 88% | Tünay *et al.*, (2008) |

*Table II.6.1-Literature overview of the integrated AOP´s processes (cont.)*

| | | | | |
|---|---|---|---|---|
| **Cibacron Red** | two stage aerobic-anaerobic method - ozonation | (Ozonation)<br>pH =10.5<br>$[O_3]$= 1.75 g.h$^{-1}$<br>t=150 min | TOC$_{removal}$ = 83%<br>Aerobic treatment = 9% | García-Montaño *et al.*, (2008) |
| **Landfill Leachate** | SBR - $O_3/H_2O_2$ - aerobic biological step | 2 h biological treatment as pre- and post-treatment<br>pH= 8 - 8.5<br>$[H_2O_2]$ = 1 g.L$^{-1}$ | COD$_{removal}$ = 58% | Hagman *et al.*, (2008) |
| **Cosmetics Industry Effluents** | coagulation $Fe(SO_4)$ - Fenton (dissolved $Fe^{2+}$ after coagulation as catalyst) | pH > 8 | TOC$_{removal}$ = 96%<br>TPh$_{removal}$ = 99%<br>Reduced toxicity increased biodegradability | Perdigón-Melón *et al.*, (2008) |
| **Olive Mill Effluent** | aerobic process - Ozonation | pH= 5.6<br>COD = 117.1 g.L$^{-1}$<br>$BOD_5$/COD = 0.32 | COD$_{removal}$ = 80% | Lafi *et al.*, (2009) |
| **Landfill Leachate** | Fenton - ozonation | COD = 14000 mg $O_2$.L$^{-1}$<br>$BOD_7$/COD = 0.44 | COD$_{removal}$ = 70%<br>$BOD_7$/COD = 0.70 | Goi *et al.*, (2009) |
| **Landfill Leachate** | Ozonation - fenton | COD = 14000 mg $O_2$.L$^{-1}$<br>$BOD_7$/COD=0.44 | COD$_{removal}$ = 60% $BOD_7$/COD = 0.40 | Goi *et al.*, (2009) |
| **Olive Mill Effluent** | Ozonation - aerobic process | pH= 5.6<br>COD = 117.1 g.L$^{-1}$<br>$BOD_5$/COD = 0.32 | COD$_{removal}$ =80% | Lafi *et al.*, (2009) |
| **Landfill Leachate** | Coagulation - Fenton -aerated biological discs | pH = 5-8<br>COD = 700 mg.L$^{-1}$<br>$BOD_5$/COD < 0.01 | COD$_{removal}$ ≥ 90%<br>Color$_{removal}$ ≥ 90% | Wang *et al.*, (2009) |
| **Paper Mill Effluent** | Chemical precipitation (pH=3) - ozonation pH=8 | Diluition = 1:10<br>pH = 9.0<br>COD = 7000 mg.L$^{-1}$<br>$BOD_5$ = 50.3 mg.L$^{-1}$<br>SST= 9.15 g.L$^{-1}$ | COD$_{removal}$ = 90% $BOD_5$/COD = 0.38 | Ramos *et al.*, (2009) |
| **Pharmaceutical Industrial Wastewater** | Fenton- aerobic biological treatment | Fenton / SBR$_{removal}$s (%)<br>TOC = 93 / 94<br>COD = 87 / 93<br>Fenton:<br>BOD/COD=0.25 to 0.5 | Combined treatment:<br>TOC$_{removal}$ = 99%<br>COD$_{removal}$ = 99%<br>TDS$_{removal}$ = 90.7%<br>TSS$_{removal}$ = 96.6% | Badawy *et al.*, 2009 |
| **Antibiotic Fermentation Wastewater** | polyferric sulfate (PFS) coagulation, Fenton and sedimentation | Coagulation: pH 4.0<br>[PFS]= 200 mg. L$^{-1}$<br>Fenton:<br>$[FeSO_4]$ =120 mg.L$^{-1}$<br>$[H_2O_2]$ =150 mg.L$^{-1}$<br>t= 1h | PFS/ Fenton/Overall $_{Removal}$ (%)<br>Color = 66.6/ 80.0 /97.3<br>COD = 72.4/ 80.4 / 96.9<br>TSS= 74.9/ 58.4 / 86.7 | Xing and Sun, (2009) |
| **Landfill Leachate** | sequencing batch reactor (SBR) - polyferric sulfate (PFS) coagulation/Fenton - biological aerated filters (UBAFs) | COD$_{removal}$<br>SBR = 76%<br>PFS and Fenton = 63% and 41%,<br>UBAFs = 37% | Combined treatment<br>COD$_{removal}$ = 97.3%<br>$(N\text{-}NH3)_{removal}$ = 99.9%<br>TP$_{removal}$ = 93.3%<br>TSS$_{removal}$ = 97% | Li *et al.*, (2009) |
| **Industrial Wastewater** | Fenton-biochemical treatment | Fenton:<br>COD$_{removal}$ = 95%<br>biochemical treatment<br>COD$_{removal}$ = 17% | Combined treatment<br>COD$_{removal}$ = 97%<br>1/5 $[H_2O_2]$ | Mandal *et al.*, (2010) |
| **Dyeing Wastewater** | Fenton oxidation - membrane bioreactor (MBR) | initial pH 5,<br>$[H_2O_2]$ = 17 mmol.L$^{-1}$<br>$[Fe^{2+}]$ = 1.7 mmol.L$^{-1}$<br>$BOD_5$/COD=0.1 to 0.44 | Combined treatment<br>TOC$_{removal}$ = 88.2%<br>Color$_{removal}$ = 91.3% | Feng *et al.*, (2010) |
| **Cosmetic Industry Effluents** | Coagulation-Fenton | Coagulation/Fenton<br>$[FeSO_4]$ = 2.29 g.L$^{-1}$<br>$[Ca(OH)_2]$ = 1.23 g.L$^{-1}$<br>$[H_2O_2]$ = 2 g.L$^{-1}$ | TOC$_{removal}$ = 97%<br>$IC_{20}$ = 0.5% to 75.3%<br>TP$_{removal}$ = 99.5% | Perdigón-Melón *et al.*, (2010) |

*Table II.6.1- Literature overview of the integrated AOP´s processes (cont.)*

| | | | | |
|---|---|---|---|---|
| **Leather Industry Wastewater** | Fenton-biochemical treatment | Fenton / aerobic treatment removal (%)<br>COD = 69 / 77<br>$BOD_5$ = 72 /80<br>Sulfide = 88/85<br>Total chromium = 5 /52 | Combined treatment removal (%)<br>COD = 93<br>$BOD_5$ = 98<br>Sulfide = 72<br>Total chromium = 62 | Mandal *et al.*, (2010b) |
| **Olive Oil Mill Effluent** | acid cracking and coagulation/flocculation- Fenton and Fenton-like | Acid Craking (AC)<br>$[FeCl_3.6H_2O]$ = 4g.L$^{-1}$<br>Fenton<br>pH = 2<br>$[H_2O_2]$ = 3g.L-1<br>$[FeCl_3.6H_2O]$ = 2.5g.L$^{-1}$ | AC+ Coagulation<br>TSS $_{removal}$=99%<br>Sludge =45 0mL.L-1<br>Combined treatment<br>COD $_{removal}$= 93%<br>Color $_{removal}$= 95% | Mert *et al.*, (2010) |
| **Textile Wastewater** | Sequencing Batch Reactor (SBR)+Fenton oxidation | Fenton:<br>COD $_{removal}$ = 70%<br>TOC $_{removal}$ = 64%<br>TSS $_{removal}$ = 99.9% | (SBR)+Fenton<br>COD $_{removal}$ =86%<br>TP $_{removal}$ =92%<br>TSS $_{removal}$=99.9% | Blanco *et al.*, (2011) |
| **Chemical Industry Wastewater** | Fenton- aerobic biological treatment | Fenton:<br>$BOD_5$/COD = 0.143 to 0.35<br>COD $_{removal}$ = 60.2% | COD $_{removal}$=95% | You *et al.*, (2011) |
| **Antibiotic Wastewater** | Fenton-SBR | $[H_2O_2]$: [COD] = 2.5 (M/M)<br>$[H_2O_2]$: $[Fe^{2+}]$ = 150 (M/M)<br>t=120 min<br>HRT of 12 h. | COD $_{removal}$= 89% | Elmolla and Chaudhuri, (2012) |
| **Landfill Leachate** | Fenton-biological anaerobic (BANF) filter-biological aerated filter (BAF) | pH 4,<br>$[H_2O_2]$: [COD] = 1.5 (n:n)<br>$[H_2O_2]$: $[Fe^{2+}]$ = 1 (n:n)<br>BAF: [C]:[N] = 4<br>BAF: [Air]: [water] = 5 | COD $_{removal}$= 96.1 %<br>TN $_{removal}$= 95.9 % | Wang *et al.*, (2012) |
| **Landfill Leachate** | Sequencing Batch Biofilter Granular Reactor (SBBGR)-Ozonation | pH = 7.9<br>$[O_3]$ = 420 ± 20 mg.L$^{-1}$<br>SBBGR treatment cycles = 8 h | SBBGR / Ozonation (final) Removals (%)<br>COD = 54.2 / 64.7<br>DOC = 58.3 / 64.5<br>TSS = 79.0 / 86.4 | Di Iaconi, (2012) |
| **Tannery Wastevater** | Sequencing Batch Biofilter Granular Reactor (SBBGR)-Ozonation | pH = 6.6<br>$[O_3]$ = 180 ± 30 mg.L$^{-1}$<br>SBBGR treatment cycles = 8 h | SBBGR / Ozonation (final) Removals (%)<br>COD = 90.7 / 92.4<br>DOC = 87.4 / 88.5<br>TSS = 75.7 / 84.8 | Di Iaconi, (2012) |
| **Textile Processing Wastewater** | Sequencing Batch Biofilter Granular Reactor (SBBGR)-Ozonation | pH = 8.1<br>$[O_3]$ = 60 ± 10 mg.L$^{-1}$<br>SBBGR treatment cycles = 8 h | SBBGR / Ozonation (final) Removals (%)<br>COD = 66.3 / 73.2<br>DOC = 68.1 / 72.2<br>TSS = 72.6 / 79.8 | Di Iaconi, (2012) |
| **Distillery Wastewater** | Fenton-Ozonation | Fenton: pH =3<br>$[H_2O_2]$ = 0.5 M,<br>$[H_2O_2]$ : [Fe2+] = 10<br>Ozonation: pH=3<br>$[O_3]$ = 40g.m$^{-3}$ | COD $_{removal}$ = 45%<br>$BOD_5$/COD=0.98 | Martins *et al.*, (2013) |

## II.7 References

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# III. ANALYTICAL METHODS AND EXPERIMENTAL PROCEDURE

This chapter describes the materials and experimental methods used in the bench and full scale studies including descriptions of the analytical methods.

## III.1 Chemical Assays

### III.1.1 pH

The pH measurements were carried out with a *Crison micropH 2000*, and a *HANNA HI 4522 pH-meter* calibrated with two buffer solutions of pH 4 and 7. The analyses were not performed on line, but after each sample withdrawal.

### III.1.2 Dissolved Organic Carbon (DOC)

DOC is the amount of carbon in the form of $CO_2$ produced when a dissolved organic substance is completely oxidized. It corresponds to the fraction of Total Organic Carbon (TOC) that passes through a 0.45 µm pore filter.

The TOC measurement is mainly required in order to evaluate the degree of mineralization of the pollutants during the oxidation process. TOC determination is based on the total oxidation of all carbon present in solution to $CO_2$ to measure the Total Carbon (TC) and the Inorganic Carbon (IC). Subsequently, TOC (mg $L^{-1}$) is calculated by subtracting IC from TC. The TOC-analyzer model that was used was a *Shimadzu 5000 TOC Analyser* with an *auto-sampler Shimadzu ASI-5000A.*

TC measurement is based on the combustion of the aqueous sample over a palladium-platin catalyst at 680°C. Thus, all carbon is converted into carbon dioxide and transported by a carrier gas to a Non Dispersive Infrared Detector (NDIR) which will determine the amount of carbon dioxide produced. For IC measurement, the sample is acidified with a 25% (w/v) phosphoric acid. At those conditions, inorganic sources of carbon such as carbonate and hydrogen carbonate are liberated as $CO_2$ and stripped from solution by the carrier gas to the NDIR.

Finally TOC is calculated as the difference between TC and IC. To determine the amount of TC, IC and TOC present in solution, standard solutions are required. A linear relationship between the detector signal and the carbon concentration leads to calibration curves allowing TC and IC quantification. Potassium phthalate is used to calibrate TOC whereas sodium carbonate and hydrogencarbonate standards are applied for IC calibration curves (Silva, 2004). All the standard solutions are prepared with water purified in a Millipore-Q system.

### III.1.3 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) measures the amount of oxygen needed to totally oxidize the organic matter contained in solution. COD estimates, thus, the amount of organic compounds present in an aqueous solution. It should be had into account the possible interferences of inorganic species ($Fe^{2+}$ and $Fe^{3+}$, $Cl^-$, $NO_2^-$, $H_2O_2$, etc).

The Chemical Oxygen Demand is determined by the method stipulated in *Standard Methods 5220 D: closed reflux*, colorimetric method (Greenberg *et al.*, 1985). The test procedure involves the heating to an elevated temperature (150°C) of a known sample volume with excess of potassium dichromate, in presence of acid ($H_2SO_4$) and Silver sulphate, as catalyst for the oxidation of organic matter, during a period of two hours in a sealed glass tube. Mercury shulphate is also included to avoid the interference of oxidized chloride.

During the oxidation time it can be noticed the change in color due to the transformation dichromate (yellow) to chromic ion (green). After this process, the vials are cooled down to room temperature. Equation III.1 shows the reduction of dichromate ion to oxidize organic matter.

$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O \qquad \textbf{(III.1)}$$

WTW CR3000 and HANNA HI 839800 thermoreactors were used for the digestion while two spectrophotometers were used, *WTM MPM3000 and HANNA HI 83224,* to detect colour changes directly providing COD data in terms of mg $O_2$ $L^{-1}$. Analyses were done at least in duplicate to check the repeatability and a potassium hydrogenophthalate solution with known concentration is used as control sample.

### III.1.4 Average Oxidation State (AOS)

The Average Oxidation State (AOS) gives the information about the carbon oxidation state in the effluent: superior COD/TOC ratios imply a higher degree of mineralization (+4) while smaller ratios means partial oxidation (-4) (Al Momani *et al.*, 2004).

These values were estimated according to the following Equation III.2:

$$AOS = \frac{4.(TOC - COD)}{TOC} \qquad \textbf{(III.2)}$$

where TOC and COD are respectively expressed in moles of C.L$^{-1}$ and moles of $O_2$.L$^{-1}$. Average oxidation state takes values between +4 for $CO_2$, the most oxidised state of C and -4 for $CH_4$, the most reduced state of C.

### III.1.5 Color and Aromatic Content Analysis by Uv/Vis SpectropHotometry

The UV/Vis-absorption spectra of pollutant solutions were recorded in the 200-900 nm range by using a *T60 PG Instruments spectrophotometer* and 10 mm light path quartz cells.

Color data are reported as the absorbance at the maximum absorption in the visible region which is considered as a quantitative estimation of the color of the solution. On the other hand, the absorbance at 254.0 nm wavelength ($UV_{254}$) is taken as the reference parameter to monitor the aromatic compounds content in solution.

### III.1.6 Total and Volatile Suspended Solids (TSS, VSS)

Suspended solids or non-filterable solids refer to matter suspended in water and wastewater. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory thresholds.

A well-mixed sample is filtered through a weighed standard glass fiber filter with a porosity of 45 µm. The residue retained on the filter is dried until constant weight at 103 to 105 °C. The increase in weight of the filter represents the total suspended solids, TSS, which include all particles suspended in water that did not pass through the filter (Equation III.3):

$$TSS = \frac{(A-B)\times 1000}{V_{sample}} \qquad \textbf{(III.3)}$$

Where A is the weight of the filter plus dried residue and B is the weight of the filter, both in g units. The sample volume is given in ml and TSS is thus calculated in g.l$^{-1}$.

The filter and dried solids attained in the previous point are ignited at 550°C to constant weight for 1 hour in a furnace. The weight lost on combustion is representative of the volatile suspended solids, VSS (Equation III.4), and included the non-dissolved organic content of the sample:

$$VSS = \frac{(A-C)\times 1000}{V_{sample}} \tag{III.4}$$

Where C is the weight of the residue plus the filter after ignition, both in g units and the sample volume is given in ml, leading to VSS in g.l$^{-1}$. The remaining solid ash, of inorganic nature, corresponds to the Fixed Total Solids (FTS g.l$^{-1}$).

### III.1.7 Total Phenol Content (TPh)

Total phenol content was determined by using the Folin-Ciocalteau method (Folin e Ciocalteau, 1927).

According to the methodology, 20 µL of sample are introduced in a cuvette, posterity diluted with 1.58 mL of distillated water. Then 100 µL of Foulin Ciocalteau reagent are added and after 3 to 6 minutes, 300 µL of a saturated solution of sodium carbonate ($Na_2CO_3$) is introduced to alkalinize the solution. After reacting during 2 h at room temperature in a dark place the absorbance is measured at 765 nm by *a T60 PG Instruments spectrophotometer* against a blank sample containing distilled water instead of sample. Results are expressed as milligrams of gallic acid equivalents (GAE) since the calibration curve was previously performed with different concentrations of this compound (Martins and Quinta-Ferreira, 2009).

### III.1.8 Total Nitrogen

Total content content was determined using Chromotropic Method in accordance with the protocol given by HANNA INSTRUMENTS.

This method allows quantifying all forms of nitrogen and nitrates through a persulfate digestion. It should be taken into account possible interferences with residual chlorine and oxidants.

Two moles of nitrate / nitrogen react with one mole of chromotropic acid to form a yellow reaction product presenting a maximum absorbance at 410 nm.

The method involves the heating to 105°C of a known sample volume with excess of potassium persulfate in presence of acid, during a period of 30 minutes in a sealed glass tube. After this time and when the tubes are at room temperature Sodium Metabissulfite was added. After 3 minutes, the reactant 93767-0 was introduced. After 2 minutes, 2 mL of this digested sample was added to one Reagent Vial, and after 5 minutes the test was performed. During the oxidation process time, it could be noticed the change in the color of the chromotropic acid from translucent to yellow. After this process, the vials were cooled to room temperature

Through the spectrophotometer HANNA HI 83224, the color changes were measured directly providing TN data in terms of mg $L^{-1}$.

### III.1.9 Total Phosphorous

Total Phosphorous Phosphorous content was determined in accordance with the protocol given by HANNA INSTRUMENTS.

This method is referred as an adaptation of the EPA method 365.2 and Standard Methods for the Examination of Water and Wastewater, 4500-EP, ascorbic acid method. It permits to quantify all forms of phosphates through a persulfate digestion that converts organic and condensed inorganic phosphates into orthophosphates that react with the existent reactants changing the color to blue. The change is measured with a HANNA HI 83224 spectrophotometer given the concentration of TP in terms of mg.$L^{-1}$.

The test procedure involves the heating to an elevated temperature (150°C) of a known sample volume and the content of a packet of potassium persulfate is added. After 30 minutes of digestion, the vial is cooled at room temperature. Sodium Hydroxide is added, and the zero is measured. After adding a packet of HI 93758-0 Phosphorous reactant, it is stirred to dissolve well and past 3 minutes one proceeds to its measurement trought spectrophotometetryc mesurement.

It should be taken into account possible interferences with arsenate, residual sulfide and turbidity.

### III.1.10 Iron and Chlorid ion

Iron ions were assed in the liquid phase by atomic absorption (Perkin-Elmer 3300, Waltham, MA).

The Chloride ions concentration was determined by ionic chromatography Water Action Analyser equipped with a conductivity detector Waters 431.

# III.2 Biological Assays

## III.2.1 Biochemical Oxygen Demand ($BOD_5$)

The Biochemical Oxygen Demand (BOD) estimates the amount of biologically degradable organic matter present in a volume of aqueous medium at a defined temperature over a specified time period and expressed in mg $O_2.L^{-1}$. This parameter normally reflects the amount of oxygen consumed by aerobic bacteria in five days ($BOD_5$) at 20°C.

The procedure to obtain $BOD_5$ was as follows. Initially, a buffered solution containing essential nutrients was prepared. The buffered solution consists on $MgSO_4.7H_2O$; $FeCl_3.6H_2O$; $CaCl_2$ prepared previously. This water sample was aerated in a period of 24 hours to ensure oxygen saturation.

The used microorganisms came from an activated sludge bio-reactor. The preparation of these consisted on taking a certain volume of activated sludge bacteria solution, decant it, remove the supernatant, and take the bottom layer, which contain the bacteria.

The volume of sample to be tested had to be carefully selected since very high pollutant concentration can lead to a final oxygen concentration below 2 $mgO_2.L^{-1}$, meaning that, after a certain point, bacteria could have been degrading the organic compounds anaerobically. In other hand, very low loads can promote negligible oxygen consumption which increases the experimental error when measuring dissolved oxygen. In this context, as a guideline, one can assume $BOD_5$ equal to COD to select the sample volume to use (Vs).

For each BOD test, a "blank bottle" (B) had to be arranged, containing the bacteria, buffer and nutrient solutions and distillate water. This blank had into account that bacteria still consume oxygen even in the absence of substrate (endogeneous respiration). Moreover, a standard glucose/glutamic acid solution with a known $BOD_5$ range was also prepared to verify if the procedure was well applied.

The biological test consisted of filling an airtight 300 mL (V) BOD bottle with sample, removing the headspace. The bottle sample was incubating for 5 days at 20 °C in the dark. Dissolved oxygen is measured initially ($DO_i$) and following incubation ($DO_f$) using an automatic dissolved oxygen measurement apparatus (WTW INOLab 740 and a HANNA HI 4421). $BOD_5$ was estimated from the difference between initial and final dissolved oxygen (DO) (Equation III.5). All the tests were done in triplicate to minimize the experimental error.

$$BOD_5 = \frac{(DO_i - DO_f) - (DO_i - DO_f)_B}{\frac{Vs}{V}} \qquad \textbf{(III.5)}$$

### III.2.2 Effluent Biodegradability

In order to define, measure or control the effluent treatment processes it is important to evaluate biodegradability. Generally, it is well accepted that the relation between $BOD_5$ and COD, is a good reference of the effluents biodegradability (Equation III.6):

$$\text{Biodegradability} = \frac{\text{BOD}_5}{\text{COD}} \qquad \textbf{(III.6)}$$

If the biodegradability tends to 0, the wastewater biological treatment would be difficult. Instead, if the value tends to 1 the effluent has availability for biological depuration. Usually a biodegradability higher than 0.4, is used as the limit from which effluent is considered to be biodegradable (Esplugas *et al.*, 2004).

### III.2.3 Acute Toxicity Lumistox Bioassay

The commercial Lumistox test is one of the commonly used assays as a bioluminescence-measuring test. It is based on the change of light emission by *Vibrio fischeri* (Photobacterium phosphoreum) when exposed to toxic chemicals. The bioluminescence is directly linked to the vitality and metabolic state of the cells, therefore a toxic substance causing changes in the cellular state can lead to a rapid reduction of bioluminescence.

In concrete, this method measures the concentration that causes the inhibition of 20 and 50% of the bacteria population after a specific time of bacteria-toxic substance contact. These values correspond to the effective concentrations giving 20 and 50% inhibition of light output ($EC_{20}$ and $EC_{50}$, expressed in $mg.L^{-1}$). The toxicity evaluation followed the ISO DIS 11348. The test is carried out in a luminometer (*Lumistox Dr. Lange GmbH, Berlin, Germany*).

The test kits acquired from Dr. Bruno Lange GmbH, Berlin, Germany, were used without modification, and distillated water is applied. The pH of the samples is adjusted to 7.0±0.2. During pH adjustment, the volume of sample should not increase more than 5%. After that, the salinity of the sample was adjusted with NaCl to 2% (w/v). Samples should be kept at 15°C until the beginning of the experiment into the Lumistherm Dr. Lange.

The EC values were determined by combining different dilutions of the potential toxic sample, according with ISO DIS 11348. First, the luminescense intensity was measured and immediately 0.5 mL of diluted sample was added to the bacteria solution. After the selected contact time, generally 15 minutes, the light intensity was measured again. The inhibitory effect of dilution was compared to a control free of toxic sample, and the $EC_{20}$ and $EC_{50}$ values were directly provided by the Lumistox software.

## III.2.4 Respirometry Test

Respirometry is the measurement and understanding of the biological oxygen consumption rate under well-defined experimental conditions. Oxygen consumption is directly related with both biomass growth and substrate removal, and it is a useful technique for modeling and operating the activated sludge process. Respirometric methodology was chosen over other conventional techniques because it allows determining biodegradability, toxicity and inhibitory effects over a real sample of microorganisms, thus being a more realistic analysis than those using a specific strain of bacteria, because there is a heterogeneity of bacteriological communities, which suits the real application conditions of biological treatment.

The respirometric assay was used to determine the Oxygen Uptake Rate (OUR). The OUR determination involves an estimation of the biomass oxygen consumption rate when assimilating organic matter giving the amount of oxygen consumed per time unit.

The measurements were carried out by controlling the oxygen input and output in a liquid-static-static (LSS) respirometer at 25±0.2°C (Greenberg *et al.*, 1985). In this type of reactor, the oxygen measure is performed in the liquid phase by keeping under static conditions the liquid and gas phase. The variation of dissolved oxygen (DO) is plotted versus time and the OUR is then calculated (Equation III.7):

$$\frac{d(V_l \times DO)}{dt} = -OUR \times V_l \qquad \textbf{(III.7)}$$

Where $V_l$, is the volume of the liquid phase expressed in $dm^3$, and DO is the concentration of dissolved oxygen expressed in mg $DO.dm^{-3}$, with OUR expressed in mg DO $dm^{-3}s^{-1}$.

The activated sludge used as inoculums of the respirometer was directly obtained from an aerobic stage from a wastewater treatment plant (WWTP). 250 mL of the active sludge suspension were placed in the reactor and air flowed until dissolved oxygen reaches 7 mg $L^{-1}$. After this, the air diffuser was removed and the reactor is sealed. The OUR of the microorganisms in absence of any nutrient gives the $OUR_{endogenous}$ measured by plotting the DO vs time. This measurement was required prior to any other because it permits obtaining the exogenous consumption of the organic matter of the sample (Equation III.8):

$$OUR_{exogenous} = OUR_{sample} - OUR_{endogenous} \qquad \textbf{(III.8)}$$

From this point on, the OUR of a sample is referred to its $OUR_{exogenous}$.

Thus, for biodegradability assessment it was done a quantification of OUR corresponding to a completely biodegradable standard (acetic acid) which was used as a reference ($OUR_{acid\ I}$) to compare with the OUR of the potentially toxic sample with the same COD content. A pulse of acetic acid was firstly added and $OUR_{acidI}$ was calculated after its complete assimilation by the microorganisms. After that, the biomass was decanted and some of the supernatant is replaced with the wastewater sample with the pH previously adjusted to 7.0±0.2. Finally OUR of the sample was measured and biodegradability is calculated (Equation III.9):

$$Biodegradability\ (\%) = \left(1 - \left(\frac{OUR_{acid\ I} - OUR_{exogenous}}{OUR_{acid\ I}}\right)\right) \times 100 \qquad \textbf{(III.9)}$$

Toxicity was also evaluated by means of respirometry. To assess toxicity, the OUR of a new acetic acid solution ($OUR_{acid\ II}$) was measured once biomass has been in contact with the potential toxic sample. If the solution does not have a toxic effect on the biomass, the OUR of the same biomass exposed for a second time to acetic acid ($OUR_{acid\ II}$) would be the same as the OUR of the same reference solution in contact with the fresh biomass ($OUR_{acid\ I}$). Consequently, toxicity is calculated as follows in Equation III.10:

$$Toxicity\ (\%) = \left(\frac{OUR_{acid\ I} - OUR_{acid\ II}}{OUR_{acid\ I}}\right) \times 100 \qquad \textbf{(III.10)}$$

### III.2.5 Sludge Biotic Index (SBI)

In order to evaluate the effectiveness of the biological treatment and relate it with the microorganism consortium present in the reactor, the biological community was observed by to microscopy and its evolution was assessed through the calculation of the Sludge Biotic Index (SBI.)

The SBI was calculated considering the protozoan community dominant in the activated sludge, and the performance of the biological reactor was classified according to this value.

A mixed liquor drop is deposited on a glass slide and covered with a slip to avoid any stress on the microorganisms. Microscopic observations were held weekly in 25 uL samples using a microscope Motic BA210 with magnification 10X / 0.25. After identification and enumeration of the microorganisms the Sludge Biotic Index (SBI) was determined according to the method described by Madoni (2004). This parameter gives the possibility of defining the biological quality of the sludge using numerical values (biotic index) of 0-10. Thus, SBI is divided into four quality classes Class I (SBI 8 - 10) - biological reactor has well colonized and stable sludge, optimal microbial activity and high removal efficiency; Class II (SBI 6 - 7) - biological reactor has well colonized and stable sludge, almost optimal microbial activity and good removal efficiency; Class III (SBI 4 - 5) - biological reactor presents an insufficient biological activity and mediocre efficiency of removal; Class IV (SBI 0 - 3) - biological reactor with low biological activity and little efficiency of removal.

# III.3 Experimental Procedure

## III.3.1 Coagulation Set-Up

The coagulation/flocculation and sedimentation tests were performed in a standard jar test apparatus from Velp Scientifica FC6S. It consisted on six beakers with a volume of 500 or 2000 mL and stirrers, which could be adjusted to the same stirring conditions for all the beakers. The beakers were filled with the sample and the coagulant/flocculant was added. During the test, no chemical was added to control the pH.

When polymers were applied, mixing time and mixing intensity are of major importance for the effectiveness of the process. Mixing after the addition of coagulants generally consisted of two successive phases:

- The first one, a short, intensive mixing phase aimed at optimizing conditions for particle coagulant interactions.
- The second one, a longer, less intensive phase aimed at flocculation of the activated particles to grow strong, large and separable flocs.

Finally the formed flocks/sludge were allowed to settle during a settling time between 15 and 60 min.

## III.3.2 Fenton Set-Up

Chemical oxidation by Fenton's of industrial wastewaters was conducted in a stirred jacketed glass batch reactor, at ambient temperature.

The reactor (0.5 or 1.5 L capacity) was equipped with a magnetic stirrer for continuous stirring of the reaction mixture (500 rpm), and a thermocouple and a pH meter were used to assess the temperature and the pH in the liquid phase. In other studies, the Fenton experiment was performed in a jar-test (Velp Scientifica FC6S with a maximum speed of 250 rpm). The pH is monitored, using a pH-meter. Samples were taken periodically Fenton oxidation experiments started by correcting the effluent's pH to the desired value. Apart from the pollutants, the initial solution also contains Fe (II) which was added in the form of iron sulphate heptahydrate. The iron concentration in the solutions was calculated taking into account that hydrogen peroxide would be added later, bearing in mind the molar (at lab scale) or massic (at industrial scale$[H_2O_2]$: $[Fe^{2+}]$ ratios and $[H_2O_2]$: [COD] relations. Special attention has to be paid when surfactants are present in the initial effluent in order to avoid foaming during its preparation. Iron hydrolysis was found to affect Fenton's process efficiency (Pignatello *et al.,* 2006). In order to avoid it, the mixtures are immediately used after their preparation. A known volume of hydrogen peroxide 30% w/v commercial solution was added to start the reactions. Simultaneously, blank experiments without hydrogen peroxide were performed. Fenton reaction, due to the homogeneous nature of the catalyst, can continue in sample vials. Thus, samples alkalinizationat pH 11-12 can be used to rapidly decompose hydrogen peroxide and precipitate iron, instantaneously stopping the reaction after the withdrawal of samples. Pre determinate volumes of NaOH 3M solution were added into the sample vials prior to introduce the sample.

### III.3.3 Ozonation Set-Up

The experiments were carried out in a lab-scale reactor (ca. 1 L or 1.5L) with magnetic stirring. In each test the reactor was filled with 700 mL or 1000 mL of wastewater, at the desired pH. Ozone was produced from a pure oxygen stream in a BMT 802N ozone generator. The experiments were performed at constant gas flow (500 $cm^3$ $min^{-1}$, measured at room T and P) and constant inlet ozone concentration.

The concentration of ozone in the gaseous phase was monitored with a BMT 963 vent ozone analyzer. In other studies a C-Lasky C-L010DS (AirTree) was used, with a concentration of 5 $g.h^{-1}$, also producing ozone from a pure oxygen stream. The ozone leaving the reactor was destroyed by passing the outlet gas stream through a KI solution (2%) (Martins and Quinta Ferreira, 2009).

When hydrogen peroxide was added, it was always fed after the ozone flow starts to enter into the system.

### III.3.4 Biological Reactors

Aerobic biological oxidation experiments were completed in a 1.5L and 0.5 L stirred tank reactors. The reactors were equipped with an air diffuser in which an airflow rate is continuously supplied and distributed uniformly all over the reactor, also assisted by agitation that makes the solution inside the reactor homogenous.

The biomass used was activated sludge from an agro industrial wastewater treatment plant. For the bio-oxidation the procedure was as follows:

The reactor was operated at semi-continuous mode and was initially charged with the following mixture:

- biomass from a WWTP:
- wastewater.

Daily procedure with the reactor was as follows:

- The magnetic stirring was stopped and the reactor air feeding was stopped to allow the biomass to settle down during 1 hour;
- A determined volume of solution was taken out;
- The reactor was fed with fresh solution equal to the corresponding wastewater solution/macronutrients mixture, previously neutralized at pH 7-8;
- The liquid level was still maintained constant by the addition of water;
- The air flow and the stirring were restarted.

In order to enhance the system performance, specifically selected bacteria provided by Bio-System Europe (Bioaugmentation) were added to the sequencing batch reactors (SBRs), and the comparison between the attained efficiencies of the simple and the bio augmented system was performed.

## III.4 References

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# IV. EXPERIMENTAL RESULTS AND DISCUSSION

## IV.1 Introduction

The industrial production promotes the release of diverse effluents containing an almost incalculable variety of pollutant compounds into the environment. Thus, it reveals to be an intense source of pollution with aconsequent devastating impact in aquatic life. Some of these compounds, due their stability, some inherent toxicity but mainly non-biodegradable nature, are not able to be treated under usual treatment methods as separation and aerobic biological processes. Due to this refractory effect, it is necessary the application of specific treatment methodologies in order to accomplish the enforceable legislation.

In this context, the Advanced Oxidation Processes (AOPs) have arisen as options of remediation treatment to destroy the recalcitrant pollutants existents on these wastewaters. It is possible to attain the main goal through the single use of these processes; however they should be integrated with biological processes to reduce reactants and energy requirements. Among the existent AOPs, the homogeneous processes as Fenton and Ozonation are of notable interest. In fact, these systems accomplish the intended degradation extension with an acceptable operational cost

One of the crucial points in the development of these works is that the research carried out had as main objective the development of a complete treatment system that can effectively remediate each specific effluent. Usually a coagulation step is required when delaing with real effluents since the solid content may affect the oxidative reaction.

As mentioned above, even if the proposed oxidative process is able to reach the main goal leading to an effluent able to be discharged, the verification of the possibility of applying a biological process is essential in order to not only achieve an economically and viable treatment.

In the present section, the studies involving both Fenton and Fenton-like Processes applied at bench scale to depurate three different effluents as Olive Mill, Elderberry and Winery processing wastewaters are present in Sections IV.2. - IV.5. Below is given a resume of the develop works.

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## Section IV. 2. Integration of traditional systems and AOP´s technologies on the industrial treatment for the olive mill wastewaters

**(Nuno Amaral-Silva, Rui C. Martins, Sérgio Castro-Silva and Rosa M. Quinta-Ferreira, Environmental Technology (submitted))**

This study evidence a treatment system involving the integration of coagulation/flocculation and Fenton processes to depurate a two phases olive oil production mill effluent, where the removal efficiencies obtained from the coagulation/flocculation experiments showed similar phenol and COD results (82 and 84% respectively) as well as a $BOD_5/COD$ improvement (0.20 against the initial 0.05).

Furthermore, the combination of the physical separation stage followed by the chemical Fenton's oxidation, allows a COD and TPh reduction up to 90% and 92% respectively. The treated stream biodegradability ($BOD_5/COD$) reached 0.52 and the Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) decreased 95% and 69% respectively.

Section IV.3 presents a complex and refractory to biological oxidation agro-wastewater coming from elderberry juice production, where the effectiveness of the Fenton's process was investigated.

## Section IV.3: Fenton's treatment as an effective treatment for elderberry effluents: economical evaluation

**(Nuno Amaral-Silva, Rui C. Martins, Sérgio Castro-Silva and Rosa M. Quinta-Ferreira, Environmental Technology (http://dx.doi.org/10.1080/09593330.2015.1107624))**

The present research work main goal was the selection of adequate cost-effective operating conditions suitable to lead to a final treated wastewater within the legal thresholds to be discharged into the natural water courses. . The Fenton's oxidation was able to decrease at least 70 % of COD (corresponding to a final value below 150 $mgO_2.L^{-1}$, achieving the total phenolic content degradation). The results showed average removal efficiencies of COD, TSS and color of about 78%, 90% and 63%, respectively, and a $BOD_5/COD$ improvement of 600%, from 0.05 to 0.3.

Within these conditions, the resulting effluent is able to be directly discharged into the natural hydric channels. Nevertheless, the costs may be reduced if the aim is to reach a biodegradable stream able to be directed to the municipal wastewater treatment plant that can successfully biologically further amend the effluent.

Section IV.4 presents the study of a physicochemical pre-treatment to enhance a posterior biological depuration of a Winery Wastewater (WinW).

## Section IV. 4: A new winery wastewater treatment approach during vintage periods integrating ferric coagulation, Fenton Reaction and activated sludge

**(Nuno Amaral-Silva, Rui C. Martins, Cláudia Paiva, Sérgio Castro-Silva and Rosa M. Quinta-Ferreira, Environmental Technology (submitted))**

A two stage process, involving coagulation and Fenton's-like oxidation, was used for the treatment of winery wastewater. The main objective of this sequence was to enhance biodegradability so that a posterior aerobic biological depuration could be possible. The chemical processes (initial pH of 3, $[Fe_2 (SO_4)_3]$ = 1500 ppm, $[H_2O_2]$ = 1.18 $L.m^{-3}{}_{effluent}$) led to global COD removal of 56.6 %. Besides, a biodegradability enhancement of 60% was attained reaching a $BOD_5$/COD ratio of 0.4. The operation costs were assessed for this stage, showing that the proposed methodology entails a cost of 0.27€ per kg of COD removed. Moreover, the further refining of the effluent using a Sequential Batch Reactor (SBR) had a mild positive effect over COD removal. The final COD abatement was 74% (145 mg $O_2.L^{-1}$). Moreover, dissolved iron reached a value below 1 $mg.L^{-1}$ after the biological treatment. Under these conditions, the final stream was within the legal limits for direct discharge into the hydrological resources. Thus, it was concluded that the proposed methodology is able to satisfactorily treat winery wastewater even during the peak period of winery effluent production.

The section IV.5 presents the extrapolation of the lab test results to an Industrial WWTP, showing that a simplified process combining the Fenton oxidation coupled to a previous coagulation stage is able to depurate the OMW.

## Section IV.5: From a lab test to industrial application: scale-up of Fenton-process as real treatment to olive mill wastewater

**(Nuno Amaral-Silva, Rui C. Martins, Paulo Nunes, Sérgio Castro-Silva and Rosa M. Quinta-Ferreira, Journal of Water Process Engineering (Submitted))**

This work studies the integration of ferric coagulation, Fenton oxidation, at lab and industrial scale on the treatment of olive mill wastewater. The first stage, an iron based coagulation promotes 40% of solids removal (laboratorial) and COD abatement of 38% to laboratorial and 43% $_{average}$ to industrial scale. The Fenton oxidation where iron (II) and hydrogen peroxide were added attains COD removals of 75% at laboratorial and 62%$_{\text{average}}$ at industrial scale.

At the industrial WWTP the ferric coagulation followed by Fenton's peroxidation was completed with consequent neutralization/flocculation, achieving mineralization efficiency up to 90% and a final COD of 200 $mgO_2.L^{-1}$. Moreover, biodegradability was improved (from initial BOD5/COD$_{\text{average}}$=0.03 to final $BOD_5$/COD$_{\text{average}}$=0.37) favoring a posterior biological treatment. The result of the integration of the industrial treated wastewater with biological oxidation performed at laboratorial scale shows that the microorganisms need an adaptation time, reaching an average efficiency of 68% until the day 23. However, at the end of the 60th day, the biomass was totally adapted, presenting a high efficiency treatment, supporting 86% of COD removal increasing from this day on until the end with a final a remarkable degradation of 95%.

The following sections presents the performed works where the ozone was the main oxidant in order to treat three different wastewaters: landfill leachate, high refractory industrial automotive coating tubes, chemical production wastewater, but also carrot washing wastewater.

Section IV.6 presents the study in order to develop a treatment to Landfill Leachate coming from a Reverse Osmosis system.

## Section IV.6: Ozonation and Perozonation on the Biodegradability Improvement of a Landfill Leachate

**(Nuno Amaral-Silva, Rui C. Martins, Sérgio Castro-Silva and Rosa M. Quinta-Ferreira, 2015 Journal of Environmental Chemical Engineering )**

Landfill leachate effluent as the permeate stream from a reverse osmosis treatment presents a very low biodegradability ($BOD_5$/COD = 0.05) being resilient to biological processes. The leachate is characterised by moderate COD value, 1880 mg $O_2.L^{-1}$, very low biodegradability ($BOD_5$/COD = 0.05 and 2 % for respirometric measurement) and an intense dark brown colour.The depuration of the landfill leachate by ozone was favored when high pH values were applied or when hydrogen peroxide was used as co-oxidant.

The best achieved result was derived from the $O_3/H_2O_2$ process using 4 g $H_2O_2.L^{-1}$, with a COD depletion up to 44%, and an increment of a $BOD_5$/COD to 0.27, with a respirometric biodegradability of 29% and colour removal of 87% at pH 9 that enables the treated wastewater discharge for the local sewage collector. Moreover, single ozonation also promoted a removal of the recalcitrant organic matter of 43% of COD and increased leachate biodegradability, $BOD_5$/COD to 0.22, which makes this process a viable option as a pre-biological treatment.

The study showed that single ozonation and ozone combined with hydrogen peroxide are efficient methods to treat this leachate. Biodegradability indicated by $BOD_5$/COD and respirometric tests can be significantly enhanced when ozone is applied.

Section IV.7 presents a different objective of treatment aiming the availability of the wastewater reuse. Two distinct effluents (Vegetable Wash (VW) and Chemical Production (CP) wastewaters) were tested.

## Section IV.7: Utilization of Ozone Based Techniques for Industrial Effluents Depuration and Reuse

**(Nuno Amaral-Silva, Rui C. Martins, Sérgio Castro-Silva, and Rosa M. Quinta-Ferreira, 2012, Journal of Advanced Oxidation Technologies, 15 (1) 1-9)**

The present scarcity and the augment with the costs of water acquisition increase the interest and need of water savings, reclamation and reuse in industry. The search for an efficient and economical method to the depuration of two different effluents was investigated by advanced oxidation processes as direct ozonation and $O_3/H_2O_2$ focusing in the evaluation of their effectiveness for decomposing COD and TOC aiming water reuse.

The $O_3/H_2O_2$ combined system (with hydrogen peroxide concentrations of 3.6 $mmol.L^{-1}$ and 35.7 $mmol.L^{-1}$ were selected for VW and CP depuration), showed the highest oxidizing power amongst the two ozonation methodologies with stronger COD and TOC degradation degrees corresponding to 100% (0 $mgO_2.L^{-1}$) and 33% (38 $mgC.L^{-1}$) after 120 min for the VW and 96% (38 $mgO_2.L^{-1}$) and 66% (62 $mgC.L^{-1}$) for the CP after 180 minutes of oxidizing procedure. In other way the single ozonation leads to COD reductions of 87% and 41%, TOC content removals of 13 and 26% and a TSS decrease of 70 and 66% for VW and CP respectively.

At the end of treatment, the treated water could be reintroduced in the washing vegetables operation, and the final CP effluent could be used in the irrigation or in the other applications existent in the factory layout.

Environmental constraints, especially in relation to existing hydric resources in protected areas, have been raising serious problems to comply with respect to legislation imposed on diverse types of industry. Section IV.8 presents one of these cases, where suddenly appears a huge problem related with the discharge license, from a factory that produce wastewater from the production of automotive coating pipes.

## Section IV.8: Integration of advanced oxidation processes and activated sludge for the treatment of high refractory industrial wastewater

**(Nuno Amaral-Silva, Rui C. Martins, Sérgio Castro-Silva, Cláudia Paiva and Rosa M. Quinta-Ferreira , 2015, Journal of Chemical Technology and Biotechnology DOI 10.1002/jctb.4845)**

During the evaluation of the best methodologies to treat this complex wastewaters, several approaches were taken, as such as Coagulation, Fenton’s reaction and Ozonation integrated or not with biological processes.

Physical-chemical treatment as coagulation presents a maximum removal of 23.5 and 6.2 % of TSS and COD, respectively. On other way, the Fenton oxidation leads to a COD value of 2370 $mgO_2.L^{-1}$. The unique depurative methodology that would be able to attain an effluent with so lower level of organic matter was ozonation. Several parameters affecting Ozonation, such as pH, the addition of hydrogen peroxide as co-oxidant and the contact time, were optimized.

It was concluded that the best efficiency is attained with ozone using a multi-stage pH. After 1200 min of reaction, this system with different stages induced by pH variation, led to 98.2 % of COD degradation with a final COD value of 220 $mgO_2.L^{-1}$to and the final effluent presented a biodegradability improvement of about 260%. It seems that the initial acidic conditions are able to remove radical scavengers which will enhance hydroxyl radicals’ action during the alkaline stage.

## IV.2 Integration of traditional systems and AOP´s technologies on the industrial treatment for the Olive Mill Wastewaters

### IV.2.1 Introduction

Olive oil production is one of the most important agro-industries in countries located near the Mediterranean Sea. However, such mills are normally located in areas with long plains and dry climate, where water stress is an issue (Rizzo *et al.,* 2010). Moreover, during olives processing the generation of enormous quantities of wastewaters (OMW - olive mill wastewater) and solid wastes occur, whose management, treatment and safe disposal (Mavros *et al.,* 2008) becomes a serious problem arising the apprehension of local environmental institutions. Those wastewaters (OMW) are characterized by high organic content involving pollutants, such as polyphenols, that may exhibit toxic properties (Andreozzi *et al.*, 2008) with strong resistance towards the degradation by activated sludge microorganisms. In that way, OMW direct release can generate numerous risks to the environment and it is necessary to develop suitable treatment schemes.

Nowadays, one of the most common applied methods is the OMW storage in lagoons, followed by evaporation during the summer season (Erses Yay *et al.,* 2012)**.** However this procedure reveals serious drawbacks such as low efficiency and sludge-disposal problems since it can only concentrate OMW to the extent of 70-75%; besides, it favors the separation/dehydration (Jarboui *et al.,* 2010) and not as much organic matter degradation (Diamadopoulos *et al.,* 2006). Other used processes are biological treatments, ineffective in practice. However, when combined with chemical or physical systems, the reduction of the OMW pollutants can be drastically improved (Erses Yay *et al.,* 2012). In the last few years, a great effort of the scientific community was performed in order to develop efficient treatments schemes for OMW. In this sense, several methods have been proposed with a main incidence in physical-chemical methodologies (Mavros *et al.,* 2008)**.** Initially, a preliminary step to remove solids, color and odor is needed which is usually associated to the elimination of compounds like polyphenols, therefore reducing the initial polluting load on the formed sludge (Rizzo *et al.,* 2010; Agalias *et al.,* 2007). Nevertheless, the treated wastewater is unlikely to meet discharge limits and it is necessary to incorporate chemical and/or biological oxidation approaches (Andreozzi *et al.,* 2008). Such is the case of electrocoagulation treatment (García-García *et al.,* 2011)**,** Fenton (Bautista *et al.,* 2008), ozonation (Cañizares *et al.,* 2007)**,** peroxidation techniques (Ginos *et al.,* 2006) and electrochemical oxidation (Gotsi *et al.,* 2005; Deligiorgis *et al.,* 2008).

The advanced oxidation processes (AOPs) are arising as suitable technologies able to degrade bio-refractory pollutants through hydroxyl radicals that are powerful oxidants leading to very efficient oxidation processes. The AOPs have potential to achieve total degradation of the pollutants. However, with proper optimization, these processes can be applied with the objective of improving biodegradability due to the partial oxidation of the initial contaminants rather than aiming total mineralization. This approach may lead to lower operating costs. In this context, it is worthwhile to strengthen that no additional energy input is required to activate $H_2O_2$, hence this is a cost effective method to generate ($HO^\bullet$) (Bautista *et al.*, 2008; Lucas and Peres, 2009). On the other hand, Fenton's reaction involves reagents like iron and hydrogen peroxide that are safe, nontoxic, easy to store and easy to handle without environmental danger.

However, AOPs can also origin products more toxic than the original compounds if reactions are incomplete. This is the case of the Fenton reagent, a cost effective method, easy to apply, involving a mixture of hydrogen peroxide whose decomposition into those radicals is promoted by iron salts (Lucas and Peres, 2009).

Fenton's application generally entails four stages: pH adjustment, oxidation, neutralization, coagulation and precipitation (Benatti *et al.,* 2006). This type of technique may not guarantee that the resulting treated water is suitable to be disposed into the natural hydrological resources, but in most of the cases, the partial oxidation of the parent pollutants enhances the effluents' biodegradability, that permits the posterior application of a biological system to finally fulfill the legal limits for discharge (Martins and Quinta-Ferreira, 2009; Kallel *et al.,* 2009).

The economic factor is another restriction due to the high operational costs when high strength wastewaters are involved, that would require great amounts of catalyst and oxidant (e.g. $H_2O_2$). Moreover, the costs associated with the disposal of the sludge produced at the end of the Fenton's process must be considered as well (Cañizares *et al.,* 2007).

The aim of this work focused the optimization of an industrial unit that suffered a sudden variation in the inlet OMW composition namely in what regards parameters such as Total Phenol Content (TPh), Chemical Oxygen Demand (COD). In this ambit, one of the main objectives is to observe the possibility of avoiding the pH adjustment before the Fenton process and if it is possible to reduce the final amount of ferrous sludge by dispensing chemical precipitation through a simple coagulation, in order to evaluate whether pH adjustment and respective alkalization would be unnecessary steps. Those proposed modifications have the main purpose of simplifying the industrial procedures and reduce the investment and operational costs, through the reduction of chemicals dosage and equipment, as well as to improve and reduce the required operational time into the different stages. So an alternative to the OMW treatment was proposed based on the combined use of coagulation and a modified Fenton oxidation. In this context, the operating conditions effects, such as type and concentration of coagulants and flocculants were assessed besides the importance of Fenton's reactants load. The efficiency of the different methodologies was analyzed regarding TSS, TPh and COD removal as well as biodegradability enhancement in order to permit the wastewater disposal into the local collector to be further refined in the biological municipal wastewater treatment plant.

Within this context, the main goal of this research was to achieve a full scale treatment methodology to improve the efficiency of an existent Wastewater Treatment Plant. For this purpose, all the treatment methodologies must be assessed taking into account operational cost restrictions, and ensuring that all processes can be performed without high investments. The aim was to reach a treated effluent within the limits for discharge in the sewage so that a proper biological refining would be possible in a municipal wastewater treatment plant.

## IV.2.2 Materials and methods

This research work aimed to study the efficiency of commercially available coagulants and flocculants provided from a company that is our spin-off. It should be strengthened that the goal was to reach a treatment scheme able to be industrially implemented. Thus, it was necessary to rely on chemicals that are easily available.

All chemicals were of analytical grade, and were used without further purification. Stock solutions were prepared in double-distilled water. pH of reaction solutions was adjusted using $H_2SO_4$ 30% (w/w) and NaOH 3M aqueous solutions.

### *IV.2.2.1 Olive Mill Wastewater (OMW)*

The effluent used in this study comes from a two-phase extraction procedure, with a dark red-brown color, was taken from an Olive Oil Production Plant (OOPP) located in Extremadura region of western central Spain. The physicochemical characterization of this Olive Mill Wastewater is presented in Table IV.2.1. This effluent comes from the end of the process and presents a high pH due to the use of caustic soda for cleaning boilers and the production machinery, and was collected in March, two months after the end of olive oil production. The wastewater comes from the storage lagoon that receives all the waters streams from the olive oil mill operation and installations layout. This stream is characterized by an elevated phenolic content, 547 $mg.L^{-1}$, a very high organic load, 12180 mg $O_2.L^{-1}$, and a very poor biodegradability¸ $BOD_5/COD=0.05$.

*Table IV.2.1- OMW characterization*

| pH | COD ($mgO_2.L^{-1}$) | $BOD_5$ ($mgO_2.L^{-1}$) | $BOD_5$/COD | TPh ($mg.L^{-1}$) | SST ($mg.L^{-1}$) | SDT ($mg.L^{-1}$) |
|---|---|---|---|---|---|---|
| 10 | 12180 | 615 | 0.05 | 547 | 2060 | 7075 |

### *IV.2.2.2 Coagulation/flocculation procedure*

The efficiency of the coagulation/flocculation process was considered under several pH conditions (5, 7 and 10), and different coagulant dosages (in the range 0.25 to 2 $g.L^{-1}$). The pH and coagulant concentration ranges were imposed by the company responsible for the industrial treatment plant in order to reduce costs associated with those reagents. Coagulant concentrations bellow 0.25 $g.L^{-1}$ showed no removal of any of the parameters under consideration.

Coagulation and flocculation experiments were carried out in a jar-test apparatus equipped with six beakers of 600 mL capacity. The effluent pH was adjusted to the desired value. In a typical coagulation run, the appropriate load of coagulant in the range 0.25-2 $g.L^{-1}$ was added directly to 300 mL of OMW and the flocculants were inserted afterwards in order to promote the aggregation of the colloidal and solid particles, by enhancing flocks formation (Diang *et al.*, 2007). After 1 min of agitation at 150 rpm, the coagulant was introduced drop by drop and left for 5 min to coagulate particles. The stirring speed was then reduced to 30 rpm for 15 min to allow flocks growth. For the flocculation of the coagulated suspension, the flocculants were added under rapid mixing before the flocks are left to settle down during 30 min. After, the supernatant was separated off for the relevant analysis. This experimental procedure is similar and adapted from the proceeding reported by (Eckenfelder, 2010).

### *IV.2.2.3 Fenton Oxidation Procedure*

The Fenton tests were executed using ferrous iron sulfate ($FeSO_4.7H_2O$) and hydrogen peroxide ($H_2O_2$, 30% w/w) at ambient temperature. Wastewater samples were introduced in a beaker and stirred; pH was adjusted to fixed values if necessary, the $Fe^{2+}$ dosage was achieved by the addition of the necessary amount of $FeSO_4$ $.7H_2O$ and reaction started when a known volume of 30% (w/w) $H_2O_2$ solution was added in a single step. Afterwards, some runs were conducted with partial $H_2O_2$ addition in equal aliquots during the reaction time.

To all withdrawn samples a pre-quantified NaOH 3M volume was added in order to raise the pH to 12, to decompose the residual hydrogen peroxide and precipitate the iron sludge before performing the necessary analysis.

#### *IV.2.2.4 Analytical Methods*

The removal and transformation of recalcitrant organic matter, by coagulation-Fenton oxidation processes, was evaluated by measuring COD, TPh, $BOD_5$, TSS and TSD. The procedures proposed by the Standard Methods for the Examination of Water and Wastewater (Greenberg *et al.*, 1995) were used to determine the Chemical Oxygen Demand (COD), Biochemical Oxygen Demand ($BOD_5$), Total Suspended Solids (TSS) and Total Dissolved Solids (TDS), while for Total polyphenol content (TPh) determination, Folin-Ciocalteau protocol was followed as described in detail elsewhere (Martins *et al.*, 2008). Changes in solution pH were detected with a Crison micropH 2000 pH-meter.

For the COD, TPh, $BOD_5$, TSS and TSD measurement, the withdrawn samples were analyzed in triplicate to minimize the experimental error. The deviations between runs were always lower than 2% and 5% for COD and TPh. In what regards $BOD_5$, TSS and TSD, the highest deviation was lower than 16%**.**

## IV.2.3 Results and discussion

#### *IV.2.3.1 Coagulation/flocculation*

For the coagulation/flocculation tests four coagulants, 19F, P19, P20 and POLIPAX, were used while the flocculants so-called 2045-SJO and 4490 -SH were kindly provided by ADVENTECH.

##### *IV.2.3.1.1 pH selection*

Preliminary experiments were performed to assess the more efficient pH for the coagulant P19, previously used at the real scale OOPP from where the effluent comes. For different coagulants doses three tests were executed at different pH (10, 7 and 5). Indeed, to be able to use pH below 5, pipes, pumps and tanks made of more resistant materials would be required, increasing the installation costs. The removals of COD and TPh with P19 are depicted in Figure IV.2.1a) and IV.2.1b), respectively.

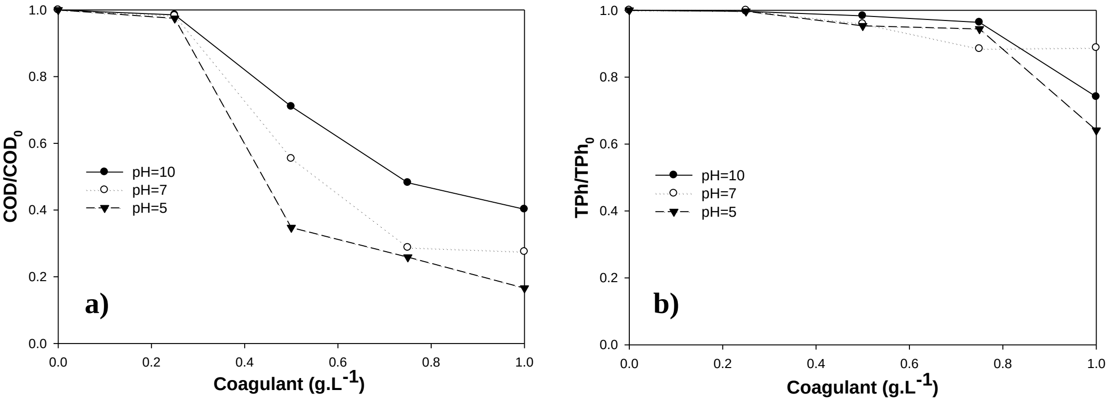


*Figure IV.2.1- Effect of pH on the COD a) and TPh b) removal efficiency during the OMW coagulation with the P19 coagulant*

It can be observed that concentrations of coagulants lower than 0.5 g.L$^{-1}$ are ineffective to cause significant COD decrease. The best results were obtained for pH =5 and a coagulant content of 0.75 g.L$^{-1}$ which enables a COD removal around 80%. For the remaining pH values tested a COD reduction was also possible to be obtained, but the treated wastewater still presented a dark color and some organic matter in suspension. In what concerns TPh abatement, similar behavior was presented for pH 7 and 10 until 0.75 g.L$^{-1}$. The optimal was attained with 40% degradation being achieved for pH 5 and 0.75 g.L$^{-1}$ of coagulant, most likely due to the fact that the effluent pH controls the hydrolysis species that endorse positive or negative charges. These species are positively charged at acidic pH and negatively charged at neutral and alkaline pH. The positively charged hydrolysis species can absorb on the colloidal particles surface originating the destabilization of the colloidal particles, being this mechanism entitled as ‘charge neutralization’. These formed precipitates can physically agglomerate the colloidal particles in suspension resulting in cleaner wastewater and stable flocks leading to quick sedimentation. In fact, the majority of colloidal particles are negatively charged and a lower pH contributes to destabilization (Moghaddam *et al.,* 2010) consequential agglomeration and posterior sedimentation as it was desired.

#### *IV.2.3.1.2 Coagulant Selection*

To the best selected pH value (5), four coagulants, P19, 19F, P20 and POLIPAX, were now considered. To determine the more favorable coagulant dosage, the wastewater was treated with various concentrations of each reactant and the supernatants were compared in Figure IV.2.2 for TPh and COD.

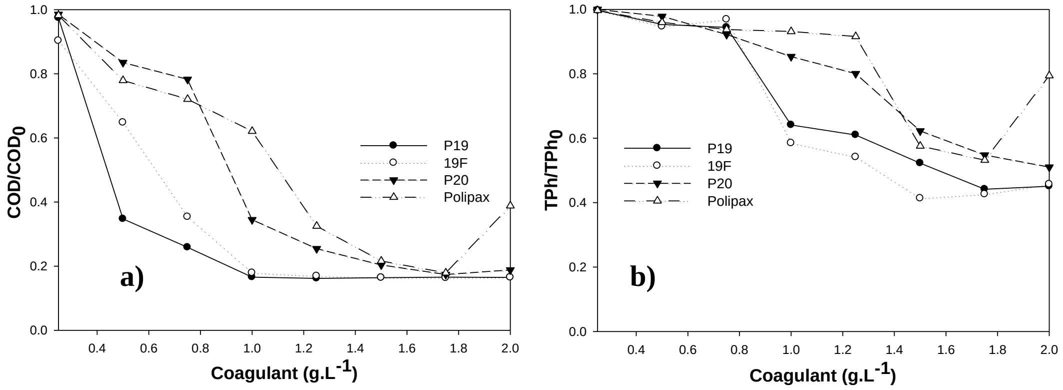


***Figure IV.2.2- Effect of different coagulants on the COD and TPh removal efficiency during the OMW coagulation process at pH=5***

In these experiments the coagulant dosage was increased stepwise (0.25 g.L$^{-1}$ each time) in order to evaluate the minimum amount required to achieve separation. Increasing those quantities from 0.25 g .L$^{-1}$ to 1.5 g .L$^{-1}$ led to a COD removal augment to more than 80% in all the cases. While for P19 and 19F, 80% COD decay was observed at 1 g.L$^{-1}$, for the other coagulants this value was only reached for dosages higher than 1.75 g.L$^{-1}$. A special behavior could be observed for POLIPAX with less efficiency for 2 g.L$^{-1}$, with only 60% reduction, when compared with lower coagulant dosages.

In what concerns TPh degradation, similar profiles were obtained, with the coagulants P19 and 19F achieving almost 60% of polyphenol content removal when using 1.75 g.L$^{-1}$. Higher coagulant concentrations also affected TPh elimination decreasing it to 50% for 19F.

For all tests, as a consequence of particles removal, the observed turbidity decreases for higher coagulant concentrations until it reaches a minimum value, then it increases with the addition of more coagulant. This is often called partial re-stabilization of colloid systems by addition of an excess of coagulant (Sarika *et al.*, 2005)**.** Since it was intended to identify the best concentration range for the next tests the range between 1±0.25 g.L$^{-1}$ (0.75 and 1.25 g.L$^{-1}$) was selected.

#### *IV.2.3.1.3 Flocculant Selection*

Sarika *et al.,* (2005) and Ginos *et al.,* (2006) reported that the flocculants application after coagulation increased the organic matter removal efficiency; more specifically originated a COD and TPh depletion improvement and a better TSS removal as well. In this work the influence of flocculants addition in the effluent purification was also evaluated. Initially, for the previously selected pH (5), two flocculants (2045-SH and 4490-SJO) were applied to the raw effluent.

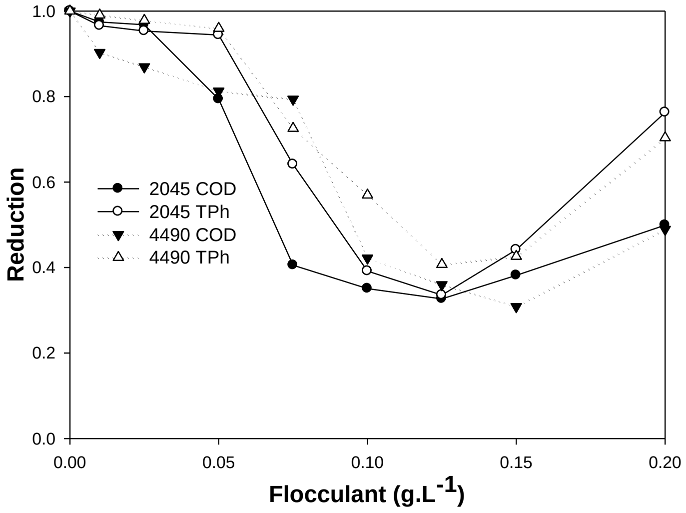


***Figure IV.2.3- Effect of different flocculants on COD and TPh removal efficiency during the OMW flocculation***

Figure IV.2.3 shows the extent of TPh and COD reduction using different concentrations of the flocculants yielding 65% and 60% removal of the COD content and 60% and 45% of TPh decrease for 0.1 g.L$^{-1}$ of the flocculants 2045-SH and 4490-SJO respectively. In fact, one can observe that a minimum amount of 0.05 g.L$^{-1}$ is needed to allow particles aggregation and flock formation, and that the process efficiency increases when the flocculant load raises up to 0.15 gL$^{-1}$. Nevertheless, a maximum concentration was reached after which the addition of more flocculants had practically no effect, decreasing even further the process efficiency what is normally attributed to colloids re-stabilization (Sarika *et al.,* 2005)**.** From these results it was concluded that the flocculant 2045-SH was more favorable in what regards solids and respective organic matter removal from the effluent.

Moreover, concentrations between 0.1and 0.125 g.L$^{-1}$ lead to similar removals; however, as the reagents saving is paramount and it was intended to observe the synergistic effects of the selected coagulant and flocculant, the selected interval was 0.075 and 0.125g.L$^{-1}$ for the combination of coagulation and subsequent flocculation experiments.

The addition of the organic flocculant 2045-SH after using coagulant P19 was then examined and the corresponding results are presented in Figure IV.2.4 showing the effect of the overall coagulation/flocculation process. Several tests were performed aiming to optimize the reactant savings and the higher COD removal was attained when 0.1 g.L$^{-1}$ of 2045-SH flocculant was applied to a previously treated wastewater with 1 g.L$^{-1}$ of P19 coagulant leading to 82% elimination. Similarly for TPh, that revealed to be more sensitive to the coagulant concentration, those were also the best values with 84% abatement.

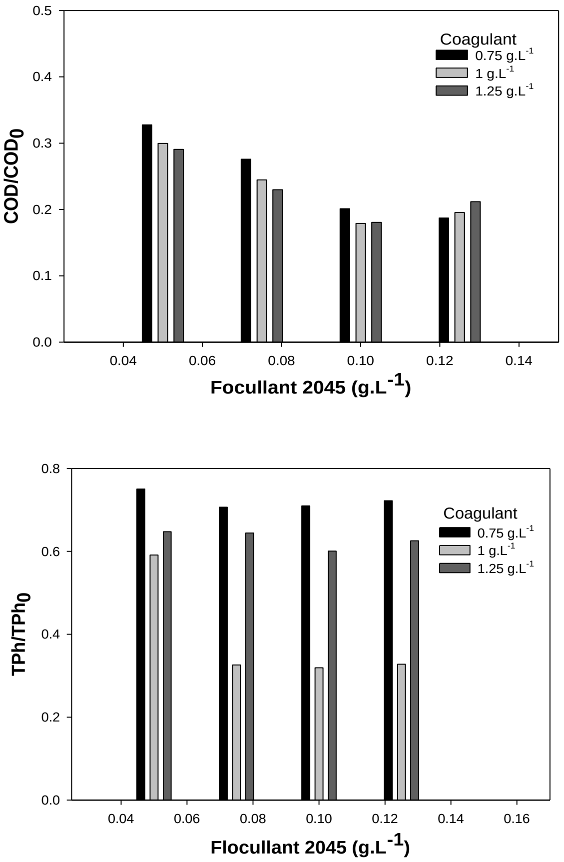


***Figure IV.2.4- Effect of coagulant P19 and flocculant 2045 dosages combination on COD and TPh removal efficiency during the OMW coagulation/flocculation process***

It can also be observed that the experiments with a higher dose of coagulant achieved a smaller COD removal, except on COD removal when 1.25 g.L$^{-1}$ of coagulant was used, demonstrating that the interactions are dependent on the coagulant concentration in addition to the pollutant effluent content. Indeed, there was an increase in COD and TPh depuration when compared with coagulated wastewater without flocculant addition (not presented), but also the improvement in the formation of large flocks, which leads to an easy sludge sedimentation and a much cleaner effluent, achieving an treated wastewater with 2180 mgO$_2$.L$^{-1}$ of COD and 234 mg.L$^{-1}$ TPh, with a BOD$_5$/COD ratio of 0.20 employing 1 g.L$^{-1}$ of P19 coagulant and 0.1 g.L$^{-1}$ of the 2045-SH flocullant.

Total Suspended Solids suffered a sharp reduction of more than 90% and Total Dissolved Solids had a decrease of 35%.

These results show how essential it is to apply a coagulation/flocculation process for solids and associated organic matter removal, showing that the pollutant content at the solids fraction is substantial and responsible at least for 82% of the COD and 59% of TPh.

Even if coagulation was able to lead to a significant COD removal (it was concluded that the COD content on solids was considerable), the treated effluent still did not fulfill the required thresholds for discharge in the municipal sewage. Besides, biodegradability was still insufficient to endorse a posterior biological process. Although coagulation/flocculation appears to be a promising technology for OMW treatment, it is obvious that special care must be paid to guarantee that the resulting liquid and solid phases are suitable for further treatment, disposal or use. In this sense, the water stream will still require some form of further handling possibly by means of advanced oxidation or biological processes or a combination of both.

### *IV.2.3.2 Fenton Oxidation*

The pre-treated coagulated wastewater (Operational conditions: pH= 5, [Coagulant] = 1 g.L$^{-1}$ of P19 and [Flocculant] = 0.1 g.L$^{-1}$ of 2045-SH) was submitted to Fenton's oxidative treatment.

#### *IV.2.3.2.1 Iron and hydrogen peroxide dosage selection*

The Fenton oxidation process can be suitably applicable for the removal of most organics at room pressure and temperature. The main parameters, that can affect this system, are operating pH, besides Fe (II) and $H_2O_2$ concentrations. In what refers to the Fenton oxidation, it is well known that higher hydrogen peroxide to substrate ratios result in more extensive substrate degradation, while higher concentrations of iron ions yield faster rates (Lucas and Peres, 2008), and the described optimum pH for the Fenton process is given as around 3 (Deng, 2007). Though this, in order to maximize the efficiency of the process, it is necessary to determine the optimal operational [$H_2O_2$]: [$Fe^{2+}$] molar ratio (Pignatello *et al.,* 2006) which is usually specific for each type of pollutants. In fact, the Fenton's reagent (Equation IV.2.1) is used to produce the hydroxyl radicals required to oxidize organic matter. Distinctive issues to be aware are the $Fe^{2+}$ and $H_2O_2$ dosages in order to avoid the resulting undesired $HO^{\bullet}$ scavenging reactions happening in the presence of an excess of each of the two reagents. In this case, an optimal ratio between $H_2O_2$ and $Fe^{2+}$ must be fixed in order to minimize scavenging effects (Lucas and Peres, 2008; Kallel *et al.*, 2009)**.**

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + \ OH^- + \mathrm{HO}\bullet \qquad \textbf{(IV.2.1)}$$

In order to assess such a ratio, maintaining constant the concentration of $Fe^{2+}$ four tests were carried out gradually increasing the dosage of $H_2O_2$ and this way the respective $[H_2O_2]$: $[Fe^{2+}]$ ratio. The initial value of $H_2O_2$ was calculated according to the stoichiometric relationship between the COD and $H_2O_2$ proposed by (Lucas and Peres, 2009) (1 g COD = 0.065 mol $H_2O_2$) and a start point was determined as 10% of that estimated amount, 0.0127 mol of $H_2O_2$ per liter of effluent.

The initial trials were performed with the $[H_2O_2]$: $[Fe^{2+}]$ ratio of 2, 4, 6 and 8 to limit the amount of spent iron and in the same way to try to minimize the amount of hydrogen peroxide. The best two ratios were selected for the following stage, the screening of different hydrogen peroxide dosages and $Fe^{2+}$ respective concentration. This range molar ratios was efficient for this kind of treatment (Lucas and Peres, 2009) with a ratio of 7.5 for the greatest COD removal to treat a different OMW.

One of the effects to consider in this treatment is the abatement of pH at the reaction start. A well-known fact is the pH evolution with the iron load, as greater the amount of iron promotes higher pH variation. During the oxidation process, the pH decreases when the iron sulfate is added, and then a bigger abatement at hydrogen peroxide addition as it is represented in equations (IV.2.2- IV.2.3):

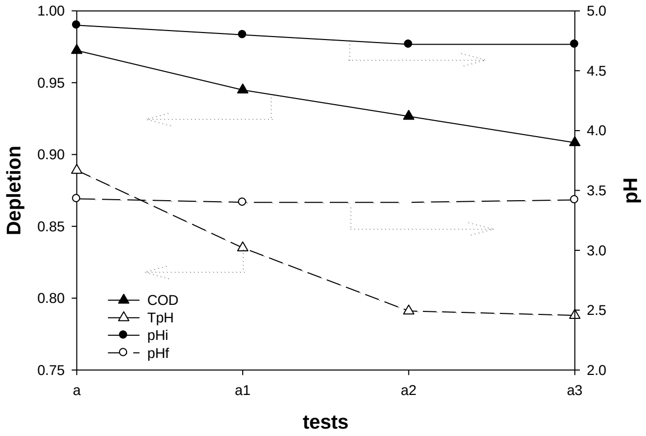
$$Fe\ (III) + H_2O_2 \rightarrow Fe\ (II) + \ \mathrm{HO_2}\bullet + H^+ \qquad \textbf{(IV.2.2)}$$

$$Fe\ (III) + \mathrm{HO_2}\bullet \rightarrow Fe\ (II) + \mathrm{O_2} + H^+ \qquad \textbf{(IV.2.3)}$$

Another fact that contributes for pH reduction during the oxidation procedure is the transformation of a wide range of organic material into intermediary compounds such as organic acids and/or hydrogen ions formed by the redox reactions during Fenton oxidation (Deng, 2007). This pH drop indicates that the mechanisms listed above are present in the reaction medium (Pignatello *et al.*, 2006).

Given this, tests were performed at an initial pH = 5, the pH of the effluent coming from the coagulation/flocculation stage without any modification, and the natural variation of pH with the addition of Fenton’s reagents was studied. All the experiments were carried out fixing a reaction time of 2h at no controlled pH.

As shown in Figure IV.2.5, regardless the initial wastewater pH and amount of reagents added the pH of the effluent at the beginning of treatment tends always to the same value near 3.4.

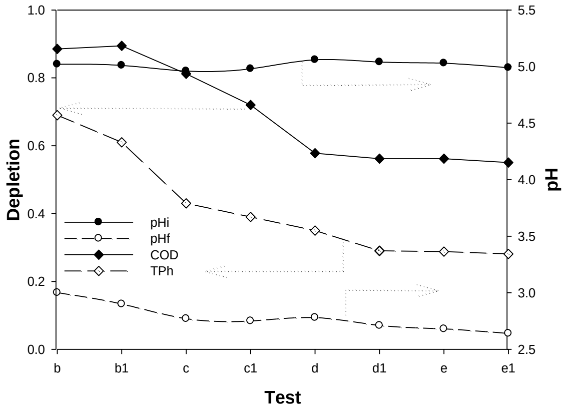


| | $M(Fe^{2+})$ | $M(H_2O_2)$ | $H_2O_2$: $Fe^{2+}$ ratio |
|---|---|---|---|
| a | 0.0032 | 0.0063 | 2 |
| a1 | 0.0032 | 0.0127 | 4 |
| a2 | 0.0032 | 0.0190 | 6 |
| a3 | 0.0032 | 0.0253 | 8 |

*Figure IV.2.5- Effect of different [H2O2]: [Fe2+] molar ratios on initial pH and COD removal during the OMW Fenton oxidation*

It is observed that with higher hydrogen peroxide levels, which means an increase in the $[H_2O_2]$: $[Fe^{2+}]$ ratio, there is an improvement in the pollutants degradation. For the different tests we obtained a removal of COD only between 4 and 9%. Regarding TPh reduction, its efficiency increases with the amount of $H_2O_2$. However, with the use of ratio 8 (the largest amount, IV.2.5, test **a3** there is a very small improvement in the elimination of these compounds, when compared with the previous run with ratio 6, reaching a maximum of almost 22% of the total polyphenol abatement.

Given the small efficiency obtained, four trials were conducted further with different loads of iron. The results are shown in Figure IV.2.6 with the respective monitoring of pH after the addition of reactants.



| | $M (Fe^{2+})$ | $M (H_2O_2)$ | $[H_2O_2]$:$[Fe^{2+}]$ ratio |
|---|---|---|---|
| b | 0.0064 | 0.0254 | 4 |
| b1 | 0.0064 | 0.0381 | 6 |
| c | 0.0096 | 0.0380 | 4 |
| c1 | 0.0096 | 0.0570 | 6 |
| d | 0.0128 | 0.0507 | 4 |
| d1 | 0.0128 | 0.0760 | 6 |
| e | 0.0160 | 0.0634 | 4 |
| e1 | 0.0160 | 0.0951 | 6 |

*Figure 0.1- Effect of different $Fe^{2+}$ dosages on initial and final pH, as well as on COD and TPh removal during the OMW Fenton oxidation*

Figure IV.2.6 shows the the extent of COD depletion using different concentrations of iron and two different [$H_2O_2$]: [$Fe^{2+}$] ratio (4 and 6) consequently involving two different hydrogen peroxide loads for each iron dosage. The increase in iron load permits a better COD removal. However when concentration **d** was reached**,** COD elimination attains a plateau between 42-45%, where higher iron concentration promotes an adverse effect on the performance rate, possibly due to the $Fe^{2+}$ induced radical scavenging (Lucas and Peres, 2008; Gulkaya *et al.*, 2006). On the other hand the radical scavenger effect of $H_2O_2$ is not present because the increased load of this oxidant promotes a slight improvement of the oxidation procedure (as seen previously in Figure IV.2.5). In this way it is possible to obtain a treated effluent with a COD of 1140 $mgO_2.L^{-1}$ and a TPh concentration of 65 $mg.L^{-1}$. The treated wastewater biodegradability was also improved to 0.52. In what regards the solids, these decreased considerably, enabling a reduction of 50% for TSS and 41% for TDS for test **d1** (0.0128 mol of $Fe^{2+}$, and 0.0507 mol of $H_2O_2$).

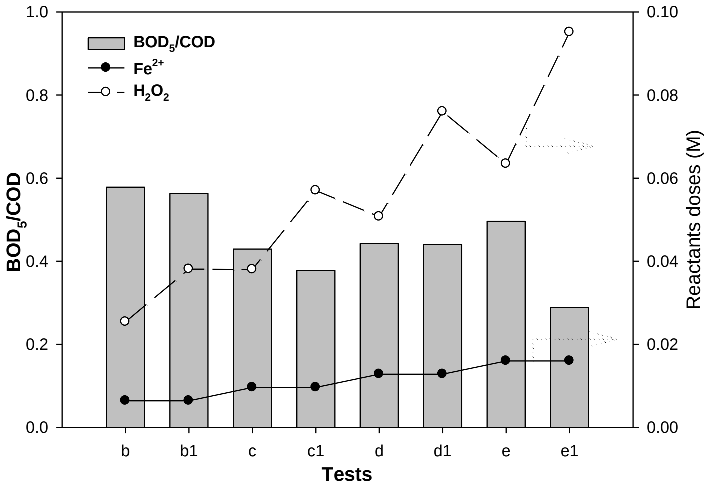


*Figure IV.2.7- Biodegradability for the different iron and hydrogen peroxide doses*

An interesting feature shown in Figure IV.2.7 was $BOD_5$/COD ratio. It is observe that for the same iron dose, the major amount of hydrogen peroxide promotes less biodegradable treated wastewater, showing that there is an increase on mineralization instead of the formation of biodegradable products, or moreover the formed biodegradable species are posteriorly oxidized (Trujillo *et al.*, 2006)**.**

For a better consumption of the used reagents it is appropriate to optimize the reaction time, parameter of vital importance in this process (Diamadopoulos *et al.*, 2006). For this purpose a long-term test (24h) was conducted with the analysis of the temporal profile of COD. This allowed us to conclude that there is an increase on COD removal up to 180 minutes of reaction, but for longer times there is not an improvement, so the experiments carried out from now on will have this duration in opposition at the previously applied 2 hours.

### *IV.2.3.2.2 $H_2O_2$ addition methodology effect*

The Fenton reaction rate tends to increase when rising the hydrogen peroxide concentration, as happened with our previous tests with the same concentration of iron and different loads of $H_2O_2$. Exists; however, a limit for the peroxide dose, above which the process performance does not improve and may even worsen by the referred radical scavenger effect (Pignatello *et al.*, 2006). In this sense two tests were carried out: $H_2O_2$ was either initially totally introduced into the reaction medium or added periodically along the process with the total volume of $H_2O_2$ divided in five aliquots. The used reactants dosages were those that attained the best results with the smallest amount possible, the **d1** test, with 0.013 and 0.051 mol of $Fe^{2+}$ and $H_2O_2$ respectively. Additions were made immediately after withdrawing samples and the results are presented below in Figure IV.2.8. The curves subtitled as t=t0 represent the situations where the addition of the oxidant was carried out at a single time in the beginning of the reaction, and t=d (t) defines the tests where $H_2O_2$ was gradually added in five doses.

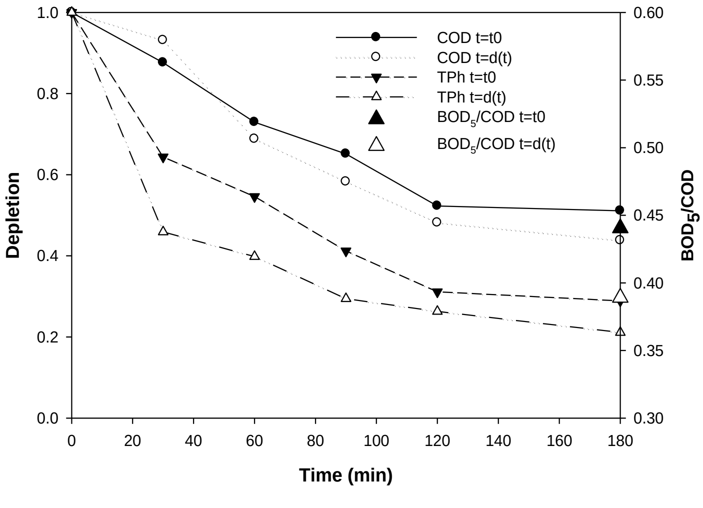


***Figure IV.2.8- COD and TPh removal along Fenton's oxidation operating time and biodegradability improvement for unique hydrogen peroxide load (t=t0) and with aliquot dosage (t=d(t)).***

As can be seen in the early period up to 30 minutes of reaction the initial highest concentration of hydrogen peroxide increases the reaction rate reaching 10% of COD removal while the test with progressive additions attained 6%. However, though during the first hour of reaction, the removal rate of t=d(t) is lower, after this operation time the difference decreases reverse, reaching an overall improvement of 10% with 55% COD reduction at the end of treatment, while the test t=t0 revealed 45% degradation. In what regards TPh, a higher abatement is observed when the oxidant is added gradually, and after 30 minutes of reaction around 50% is eliminated while for t=t0 only 35% is achieved. Towards the end there is an overall improvement with a marked removal of almost 80% of Total Phenolic content compared with the 71% obtained when $H_2O_2$ is added in a single moment.

Nonetheless, the biodegradability is lower at the end of the t=d (t) test, with a final $BOD_5$/COD ratio of 0.39 against the 0.44 observed for t=t0, possibly due to the fact that some formed biodegradable organic matter have been degraded during the oxidation process in this trial, given the fact that COD decreased to 1050 $mgO_2.L^{-1}$, and thus, the biodegradable matter is also substantially less.

This process improvement is probably due to the fact that with successive additions of $H_2O_2$ the hydrogen peroxide scavenger effect is avoided. The excess in the case where the overall quantity is initially added could lead to the unwanted consumption of hydroxyl radicals, with subsequent formation of hydroperoxyl radicals that present a lower oxidation power. In fact, it is well known that hydrogen peroxide may be active as radical generator and as scavenger or both in simultaneous (Gogate and Pandit, 2004).

Therefore, the hydrogen peroxide scavenger effect towards hydroxyl radicals can be decreased by keeping its concentration at a low level. This can be carried out by periodically adding hydrogen peroxide to the Fenton reactor, decreasing the oxidant waste during the treatment thus promoting a higher rate of oxidation and its procedural efficiency.

#### *IV.2.3.2.3 Controlled pH effect*

Literature refers that an adequate control of pH would increase oxidation efficiency (Gogate and Pandit, 2004; Neyens and Baeyens, 2003), even if this would increase the operating costs. In order to prove this effect, one test with pH control was performed, where pH was adjusted when necessary in order to be kept in the range 3.0 ± 0.1, and the hydrogen peroxide was added in five doses, keeping the operating conditions described previously. The removal profiles of TPh and COD are presented in Figure IV.2.9.

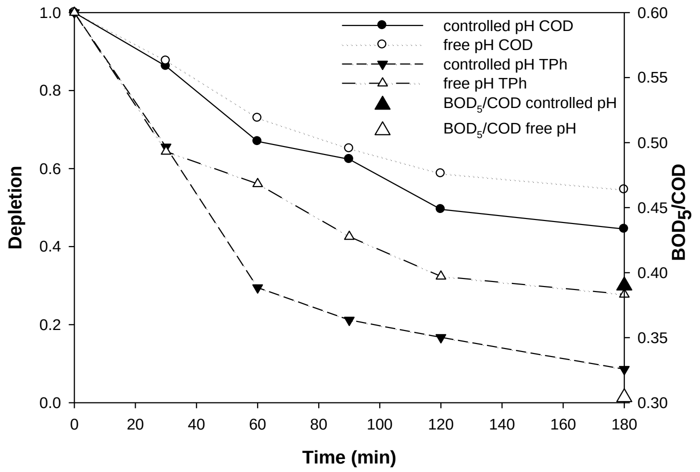


*Figure IV.2.9- COD and TPh removal along Fenton's oxidation operating time for free and controlled pH*

As it is shown, the pre-adjustment of pH and its maintenance within the selected range enhanced the COD and TPh reduction rates by Fenton oxidation.

For the initial 30 minutes of oxidation all the results are similar; however, after 60 minutes the TPh degradation is favored by maintaining a constant pH leading to 81% removal against 71% obtained by the experiment where pH ran freely. In what regards COD, there is a greater improvement after 90 minutes of reaction showing an enhancement of around 10%, enough to reach a COD value of 900 mg $O_2.L^{-1}$ (53% of COD and 92% of TPh). This allows to achieve the aim of this treatment that is focused on the discharge of the treated effluent into a municipal sewage collector, which demands a COD threshold value lower than 1250 mg $O_2.L^{-1}$. However, as occurred in the previous test, there was a reduction in the effluent biodegradability when compared with the higher attained value (0.39), achieving a $BOD_5/COD$ ratio of 0.30, presumably for the same reason involving the degradation of the formed biodegradable compounds.

Comparing the referred two tests, there is a slight improvement when the pH was controlled. This fact would be expected, given that during the reaction, the organic acids formed as by-products of the degradation of the polluting compounds endorse the pH abatement to a value that encourage the formation of iron complex species, which react slower with the hydrogen peroxide. Also, this oxidant gets solvated in the presence of high concentration of $H^+$ ion yielding a stable peroxone ion that reduces the reactivity with ferrous ion reducing the oxidation extent (Eckenfelder, 2000). On the other hand, the cited organic acids could be subsequently degraded, thus promoting the pH increasing of the effluent (Gogate and Pandit, 2004), which can lead to a decrease in the process oxidation efficiency.

#### *IV.2.3.2.4 Coagulation vs NaOH precipitation*

The Fenton's treatment has two main stages, oxidation which is promoted by hydroxyl radicals ($HO^{\bullet}$) formation and ferric coagulation afterwards (Gulkaya *et al.,* 2006). The recurrent procedure is that at the end of the oxidation treatment the discharge from the Fenton reactor passes to a neutralization tank (Bautista *et al.,* 2008) where, by increasing the medium pH until an alkaline value (>7), the dissolved iron can be removed by precipitation, and consequently any residual $H_2O_2$ is decomposed into $O_2$ and $H_2O$ with the advantage of removing some organic matter at the same time that solid sludge is formed (Cañizares *et al.,* 2007; Deng, 2007).

With the purpose of avoiding the neutralization and posterior acidification for accomplishing the wastewater discharge, the addition of a coagulant into the treated mixture by Fenton's was analyzed, aiming to enable the possible replacement of the final chemical precipitation stage in order to simplify the process and reduce the expenses with reactants and equipment required for their dosage. Thus, different concentrations of the previously selected coagulant (P19) used on the pre-treatment coagulation/flocculation process were tested, at the end of the oxidation procedure. Quickly, it was noticed the formation of a film and in few minutes (5-10 min) a high quantity of red mud (about half of the volume of the sludge formed by precipitation) was deposited at the bottom of the reactor. The results obtained for the COD in the supernatant at the end of the integrated process described are then shown in Figure IV.2.10.

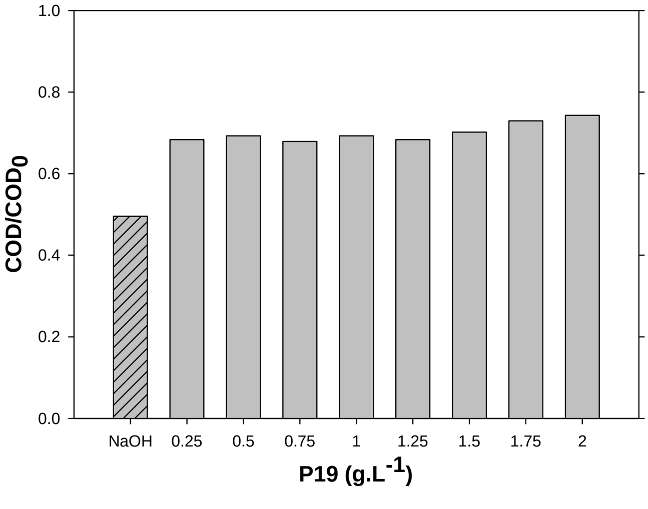


***Figure IV.2.10- COD abatement for different coagulant dosages compared with NaOH precipitation***

Iron sludge precipitation was only achieved for concentrations of coagulant higher than 0.25 g.L$^{-1}$.The results prove that the COD removal is more efficient when chemical precipitation is obtained with NaOH. But it is our belief that coagulant addition instead iron precipitation is an option that may be considered for other types of effluents depending on the final treatment purpose. This way, the alkalization-acidification step can be avoided.

The global results integrating coagulation and Fenton's process are shown in Figure IV.2.11 depicting COD and TPh depletion as well as the $BOD_5$/COD evolution during the two-step process.

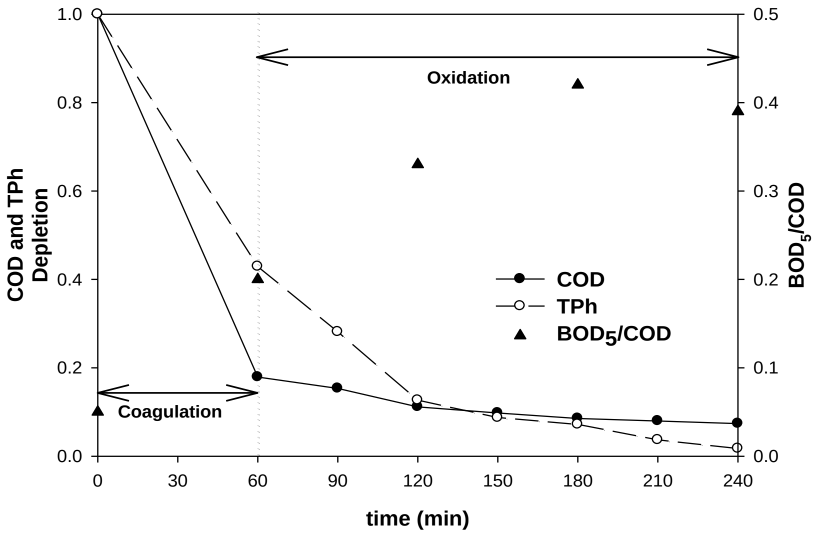


*Figure IV.2.11- COD, TPh depletion and BOD5/COD ration for the coagulation- optimized Fenton oxidation (d1) test during the integrated procedure at controlled pH and with H2O2 gradually added in aliquots*

From Figure IV.2.11 analysis it is possible to conclude that in the first hour, where the coagulation stage takes place, 82 % of the COD was removed, the total phenol content depletion attains 57% and the biodegradability was just improved to 0.20. In the oxidation process, COD decreases 58.7 % while 96% of TPh was reduced. Moreover, a biodegradability improvement to 0.39 was possible. This reveals that Fenton's process is an effective methodology to promote organic load reduction leading to biodegradability improvement.

The integrated coagulation-oxidation system allows to attain a robust process where COD and TPh removals globally reach 92.6 and 98.3 % respectively. Besides, $BOD_5$/COD ratio was improved from 0.05 to 0.39.

### *IV.2.3.2.5 Reactants Cost Evaluation*

An important factor that may restrict the process applicability is related with the operating costs.

For this reason it is necessary to perform their evaluation before conceptualizing the physical structure of the wastewater treatment plant and determine the investment costs. The costs associated with the treatment implementation (construction, mechanical instrumentation and maintenance) were excluded, mainly because they depend on the site that is available for the plant installation, existing equipment, the variability of the wastewater characterization and the volume to treat (Martins *et al.*, 2010). For this purpose the coagulant, iron sulfate, $H_2O_2$ and flocculant amounts as well as NaOH and sulfuric acid necessary to prepare the wastewater for the different stages (coagulation, oxidation and pH correction) to allow the wastewater discharge (attained at test d1) were determined. Besides, when the main target is an improvement of the effluent biodegradability with the increase of $BOD_5$/COD ratio the costs associated with that experiment should also be assessed (test b1).

In order to carry out the coagulation treatment with the referred doses to achieve the discharge limits it was necessary 1 $g.L^{-1}$ of coagulant as well as 0.1 $g.L^{-1}$ of flocculant. The pH correction to achieve the value of 5 requested 2$mL.L^{-1}$ of $H_2SO_4$ 30% (w/w).

In what regards the oxidation procedure under test d1, it was necessary to use 1$ml.L^{-1}$ of $H_2SO_4$ 30% (w/w) to change the pH to 3.0 ±0.1 and a 1.5 $mL.L^{-1}$ of NaOH to keep it in the range 3.0 ±0.1. The oxidation treatment required 7.14 $ml.L^{-1}$ of $H_2O_2$ and 3.5 $g.L^{-1}$ of $FeSO_4.7H_2O$ (29.5 % w/w). At the end of the oxidation 2 $mL.L^{-1}$ of NaOH were needed to adjust the final pH. For test b1 half of the $H_2O_2$ and $FeSO_4.7H_2O$ doses were requested.

The price of the hydrogen peroxide 50% was 0.6041 € $L^{-1}$, the costs of NaOH (50% w/w) and $H_2SO_4$ were 0.366 € $L^{-1}$ and 0.141 € $L^{-1}$ and the one of the iron sulphate (29.5% w/w) was 0.2 € $Kg^{-1}$, being each reactant acquired in Portuguese market. The coagulant and floccullant had a price of 2 and 4 €.$kg^{-1}$ respectively.

***Table IV.2.2- Costs for the different scales treatment***

| | **Reactants** | | | | | | **Cost** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Coagulant** | **$FeSO_4$** | **$H_2SO_4$** | **NaOH** | **$H_2O_2$** | **Flocculant** | **KgCOD /$m^3$** | **€/ $m^3$** | **€/ $KgCOD_{removed}$** |
| ($kg.m^{-3}$) or ($l.m^{-3}$) | 1 | 3.5 | 3 | 3.5 | 7.14 | 0.1 | | | |
| **d1** (€).$m^{-3}$ | 2 | 0.7 | 0.42 | 1.28 | 4.31 | 0.4 | 11.28 | 9.11 | 0.81 |
| **b1** (€).$m^{-3}$ | 2 | 0.35 | 0.42 | 1.28 | 2.16 | 0.4 | 10.60 | 6.61 | 0.62 |

Table IV.2.2 shows the costs associated with the reactants and the global investment required for the **d1** and **b1** tests. As it is possible to conclude, the treatment of each cubic meter of effluent through test d1 costs 9.11 € which corresponds to 0.81 € for each kg of COD removed. The hydrogen peroxide has a significant relevance on the total budget corresponding to almost 50% of the total reactants charge. If it is intended to increase the biodegradability for a subsequent biological treatment (test b1), it was possible to achieve a cost of 0.62 € for each kg of COD removed with a global cost of 6.61 €.m$^{-3}$. Comparing both processes, from **b1** to **d1** it is necessary to spend almost more 30% with reactants to remove only 5% more of COD. This shows that the main reasons imposing processes integration are predominantly economic aspects, due to the fact that complete mineralization by AOPs treatment results in extremely high costs.

## IV.2.4 Conclusions

In this study, integrated coagulation/flocculation and Fenton processes were applied for olive oil mill wastewaters treatment. The presented results indicate that physical, chemical and posterior biological processes are able to treat OMW.

It was observed that such coagulation stage coupled to flocculation promotes, when compared with single coagulation, the solids formation and a subsequent major organic matter removal by gravitational settling; in this physical process the operational parameters that were studied were pH and the added dosages of coagulant/flocculants, being achieved a removal of 82% of COD and 57% of TPh, with a $BOD_5$/COD ratio improvement to 0.20 spending only 1 $g.L^{-1}$ of P19 coagulant and 0.1 $g.L^{-1}$ of the 2045-SH flocculant.

The further combination with the Fenton process revealed that it is possible to reach larger COD and total phenol content abatement (90% and 92%) and a biodegradability enhancement to 0.52 in relation with the raw wastewater.

pH adjustment along Fenton's oxidation can be avoided at a full scale plant; however when compared with pH-controlled trials, efficiency decreases slightly probably due to the formation of intermediate compounds of acid character, that promote a pH decrement. This will lead to oxidation rate decrease due to the formation of complex species $[Fe (H_2O).6]^{2+}$, which reacted slower with hydrogen peroxide. On the other hand, the addition of hydrogen peroxide in small aliquots over the time reaction prevents the promotion of the radical-scavenger effect increasing the effectiveness of the overall treatment.

The final Fenton's precipitation step also removes organic compounds, indicating that in addition to precipitate ferrous sludge, it acts as a polishing stage in what regards to COD removal.

The optimized integrated system allows to remove 92.6% of COD and 98.3 % of TPh, improving as well the $BOD_5$/COD ratio to 0.39.

Consequently, the Fenton process showed a satisfactory COD and phenol depuration performance as well as biodegradability improvement revealing therefore that their integration whit a biological treatment step can be an economically viable choice for the OMW before discharge into municipal sewages.

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# IV.3 Fenton's treatment as an effective treatment for elderberry effluents: economical evaluation

## IV.3.1 Introduction

Currently there is a worldwide need to treat the huge volumes of wastewater caused by massive industrial production in order to minimize the associated severe environmental impacts. The direct release of these streams is threatening our sensitive and continuously scarcer hydrological resources. Therefore it is essential to find depuration methodologies able to efficiently remove pollutants. However, the costs associated to these technologies are normally a limiting factor for any company.

In the last decades, Advanced Oxidation Processes (AOPs) have been developed and are emerging as potential wastewaters treatment techniques (Jordá *et al.,* 2011) showing to be attractive for polluting content destruction and consequential COD and/or TOC removal (Padoley *et al.,* 2011), biodegradability improvement as well as odour and color abatement (Chu *et al.,* 2012).

Amongst AOPs, effluents depuration by Fenton's process is receiving great attention as a promising methodology showing high efficiency for the degradation of a large number of organic pollutants and hazard materials. Besides, it is a technology involving low investment costs and simple proceedings demanding non-toxic reagents (Fu *et al.,* 2009). Moreover, it still has the advantage that can be used as a pre-treatment stage in order to increase the biodegradability of refractory pollutants and diminish wastewaters toxicity allowing the final application of a traditional activated sludge depuration (Cañizares *et al.,* 2009; Mandal *et al.,* 2010).

This technology is based on the oxidant power of hydrogen peroxide catalysed by iron ions under acidic pH (2-4), which promotes chain reactions and consequently endorses an effective degradation of pollutants through the production of free radicals such as $HO^{\bullet}$ and $HO_2^{\bullet}$ . Hydroxyl radicals are well known as strong oxidants and can oxidize many recalcitrant organic compounds (Martins *et al.,* 2010a).

As $Fe^{2+}$ and $Fe^{3+}$ ions are coagulant species, the Fenton process shows a dual function in effluents depuration, involving both oxidation and coagulation steps, being the sedimentation triggered after the neutralization of the treated water originating coagulation of the originated ferric hydroxo complexes (Xing and Sun, 2009; Badawy *et al.,* 2009; Karthikeyan *et al.,* 2011).

The major drawback of Fenton's treatment appears to be the requirement of large concentrations of $H_2O_2$ and $FeSO_4$ which can be costly reactants (Molinos-Senante *et al.*, 2010). Moreover, the sludge encompassing iron and organic matter formed at the end of the process entails management constituting thus another shortcoming of this treatment technology (Rossi *et al.*, 2011).

This technique is usually successful in the depuration of agro industrial wastewaters, leading to an efficiently COD reduction and increase in the $BOD_5$/COD ratio, as it was concluded when applied to milk whey effluents (Martins *et al.*, 2010b) and olive mill wastewaters (Lucas and Peres, 2009; Martins *et al.*, 2010a). Diverse applications have already been reported for other types of liquid wastes, such as industrial wastewater (Mandal *et al.*, 2010), textile wastewater (Karthikeyan *et al.*, 2011; Rodrigues *et al.*, 2009) and landfill leachate (Zhang *et al.*, 2005; Cortez *et al.*, 2011).

In this context, it is proposed to use this oxidative system to favour the depuration of an agro-industrial effluent, resulting from elderberry juice production. In this industry almost 40% of the elderberry initial weight leads to solid and liquid pollutants (Seabra *et al.*, 2010).

Economic evaluation of treatment units has been reported in the literature with a greater prevalence in recent years (Shaalan *et al.*, 2007; Rodriguez-Garcia *et al.*, 2011). This demonstrates the scientific and commercial interest in this type of technology for future applications. However, significant cost issues like construction, mechanical instrumentation and maintenance were omitted in order to simplify the analysis, especially because each treatment unit has its equipment requirements and components depending on the wastewater characteristics, and therefore could not be considered as orientation (Cañizares *et al.*, 2009). In this sense, only operating costs have been accounted, as they demonstrate if the proposed treatment scheme is viable or not.

The main objective of the present investigation addressed the remediation of an industrial wastewater coming from an elderberry juice production by using the Fenton technology, aiming to attain a stream legally able to be discharged into the natural hydrological resources. Moreover, the operational costs, considering the used reactants were assessed.

## IV.3.2 Material and Methods

### *IV.3.2.1 Wastewater*

The wastewater was characterized by a dark-brown color, high amount of suspended solids (inducing turbidity, a moderate COD value (620 $mgO_2.L^{-1}$), low TPh (29 $mg.L^{-1}$) content and an extremely low biodegradability (0.05) are presented at Table IV.3.1. In this Table are also described the limit values to perform a discharge into the hydrological resources, where one can observe that all parameters with the exception of $BOD_5$ are well above the legal limit of discharge.

*Table IV.3.1- Wastewater characterization and discharge legal limits*

| | **pH** | **COD (mg $O_2$. $L^{-1}$)** | **TPh (mg. $L^{-1}$)** | **$BOD_5$ (mg $O_2$.$L^{-1}$)** | **TDS (mg.$L^{-1}$)** | **TSS (mg.$L^{-1}$)** | **$BOD_5$/COD** |
|---|---|---|---|---|---|---|---|
| **Wastewater** | 6.7 | 680 | 29.1 | 33 | 1160 | 370 | 0.05 |
| **Discharge legal limits** | 6-9 | 150 | 0.5* | 40 | - | 60 | - |

*** Phenol ($C_6H_5OH$)**

### *IV.3.2.2 Reagents*

All reagents were of analytical grade and were used without any additional purification process, such as hydrogen peroxide (50%), ferrous sulphate, mercury sulphate, silver sulphate, potassium dichromate, magnesium sulphate, sulphuric acid and sodium hydroxide (Merck, Germany).

### *IV.3.2.3 Oxidation Procedure*

The experiments were performed in a jar-test system allowing various runs to be performed simultaneously using ferrous iron sulfate ($FeSO_4.7H_2O$) and hydrogen peroxide ($H_2O_2$, 50% w/w) at ambient temperature. Each 600 mL batch reactor was filled with 300 mL of wastewater and continuously mixed at 200 rpm. The experiments were carried out at different $Fe^{2+}$ and $H_2O_2$ concentrations in the range of 5-50 mM and 20-250 mM, respectively (Dogruel *et al.*, 2009). Beyond these concentrations, the associated cost by using higher reactants concentrations triggers for not bearable prices for further commercial application of the use as discussed later.

The oxidation procedure was carried out with the following steps: pH was adjusted around the value of 3 (Lucas and Peres, 2009; Martins *et al.*, 2010b; Padoley *et al.*, 2011) by the addition of sulphuric acid ($H_2SO_4$, 1M) and sodium hydroxide (NaOH, 3M). At this time $FeSO_4.7H_2O$ was dissolved and then slowly mixed with $H_2O_2$. The reaction was considered finished after 4 h. Higher reaction times, led to a wastewater purification increase in the order of barely 10%.

### *IV.3.2.4 Analysis*

During the experimental period, samples were withdrawn in certain intervals of time to analyze Chemical Oxygen Demand (COD), Biochemical Oxygen Demand ($BOD_5$), Total Phenol Content (TPh), Color, Total Suspended Solids (TSS) and Total Dissolved Solids (TDS).

Chemical Oxygen Demand was acquired by the method specified in Standard Methods 5220 D: closed reflux, colorimetric method. The samples were digested during 2h at 148 ºC in a WTW CR3000 thermoreactor (Weilheim, Germany) and the COD value measured in a WTW MPM3000 photometer. The Folin-Ciocalteau reactant was used to determine total soluble phenolics (TPh) as described elsewhere (Martins *et al.,* 2008). The dissolved oxygen was assessed by a WTW Inolab (Martins *et al.,* 2010c). Color was determined by spectroscopy using a T60 (PG instruments) spectrophotometer and the pH was attained using a Crison micropH 2000.

The Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) were determined by Standard Methods: “2540 D: Total Suspended Solids Dried at 103 - 105 °C” for TSS assessment and “2450 C Total Dissolved Solids Dried at 180ºC” for TDS evaluation (Greenberg *et al.,* 1985). To check repeatability, some experiments were randomly run in duplicate and the samples withdrawn were analyzed in triplicate to minimize the experimental error and to check the results reproducibility. The deviations between runs were always lower than 5% for COD, TPh and color, respectively, below the inherent errors to the employed techniques.

## IV.3.3 Results and Discussion

This study was carried out in response to an existing problem, where the main requirement and the most limiting factor for the process acceptance were constraints of economic nature, mainly associated with the related operational costs, as well as the need to discharge the treated wastewater into a natural water courses. Thus, in accordance with the manufacturer industry, it was set initially a maximum value to be expended in reactants (3 € per cubic meter of effluent) and by this value the amounts of iron and $H_2O_2$ were assessed. However, after the first assays sequence, it was noted that a higher oxidation level was required to attain the proposed objective (a treated wastewater with a COD lower than 150 mgO$_2$. L$^{-1}$).

To make the assessment and selection of the finest operational conditions was initially selected the better ratios [$H_2O_2$]: [$Fe^{2+}$]. Afterwards, were evaluated certain experimental procedures in order to establish whether they increased efficiency and subsequently, in a 3rd stage, were selected the best chemicals concentrations in order to enhance the efficiency and diminish the operational costs. Therefore, the charges of reagents had to be augmented and so the cost of the process ranged from 1.183 until 9.822 €.m$^{-3}$. These costs are referred to the sum of the two main reactants, $H_2O_2$ and $Fe^{2+}$, and its amount depends on the [$H_2O_2$]: [$Fe^{2+}$] ratio. The operational conditions, the resume of obtained results referents to COD and BOD$_5$ as well the costs for each proposed Test are presented in Table IV.3.2.

*Table IV.3.2- Reactants concentration for each test; * no pH adjustment; ** controlled pH;*** 4 aliquots*

| **Test group** | **1** | | | **2** | | | **3** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Test** | **1** | **2** | **3** | **4*** | **5**** | **6***** | **7** | **8** | **9** | **10** | **11** | **12** |
| **[$Fe^{2+}$] (mmol.$L^{-1}$)** | 10 | 10 | 10 | 10 | 10 | 10 | 5 | 5 | 20 | 20 | 50 | 50 |
| **[$H_2O_2$] (mmol.$L^{-1}$)** | 20 | 50 | 100 | 50 | 50 | 50 | 10 | 25 | 40 | 100 | 100 | 250 |
| **[$H_2O_2$] : [$Fe^{2+}$]** | 2 | 5 | 10 | 5 | 5 | 5 | 2 | 5 | 2 | 5 | 2 | 5 |
| **$COD_f$ (mg $O_2$.$L^{-1}$)** | 240 | 220 | 330 | 350 | 310 | 310 | 435 | 390 | 210 | **150** | 200 | 250 |
| **$BOD_5$ (mg $O_2$.$L^{-1}$)** | 60 | 64 | 67 | 58 | 63 | 48 | 87 | 72 | 43 | **45** | 33 | 46 |
| **Biodegradability ($BOD_5$/COD)** | 0.25 | 0.29 | 0.20 | 0.18 | 0.20 | 0.13 | 0.20 | 0.18 | 0.20 | **0.3** | 0.16 | 0.18 |
| **Reactants Costs (€.$m^{-3}$)** | **1.608** | **2.571** | **4.176** | **2.252** | **2.681** | **2.571** | **1.183** | **1.665** | **2.458** | **4.384** | **5.008** | **9.822** |

### *IV.3.3.1 Effect of [$H_2O_2$]: [Fe2+]*

Taking into account that $H_2O_2$ is the reactant that has more relevance in the cost of the process (Bautista *et al.*, 2008), with the commercial cost of € 200 per ton, the best [$H_2O_2$ and $Fe^{2+}$] concentrations were defined to minimize the required amount of Fenton's reagents in view of its cost, taking into account what the greatest amount until the sum of the costs of these two reagents do not exceed the 3€ per cubic meter of raw wastewater treated.

Below and above the optimal [$H_2O_2$]:[$Fe^{2+}$] ratio, the treatment is inefficient or less effective due the well know scavenger effect instigated by the excess of reactants. Moreover, as it is well known, the Fenton process is comprised by two distinct purification paths, oxidation and coagulation where chemical coagulation prevails at a lower [$H_2O_2$]:[$Fe^{2+}$] ratio, whereas chemical oxidation is dominant at higher [$H_2O_2$]:[$Fe^{2+}$] ratios (Karthikeyan *et al.*, 2011). The hydrogen peroxide concentration was varied keeping the ferrous sulphate concentration constant at 10 mM, in the ratio of 2:1, 5:1 and 10:1 (mol/mol) respectively.

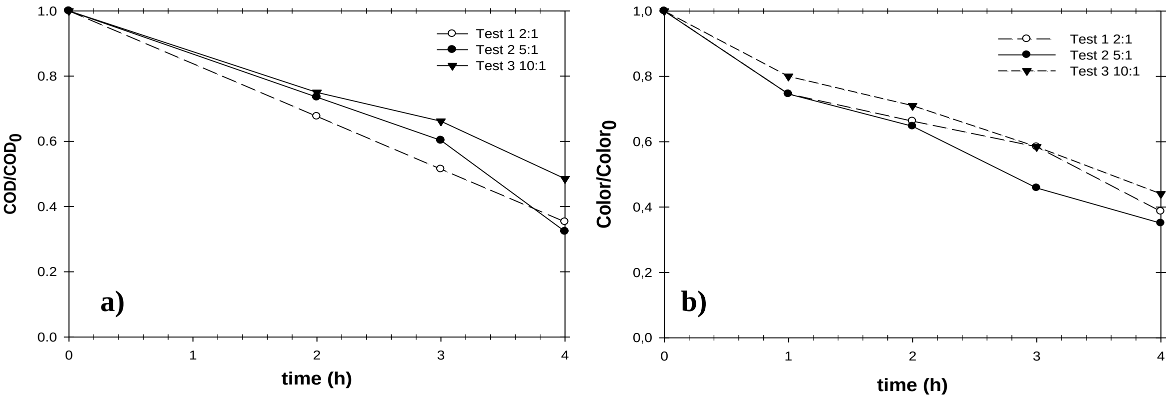

***Figure IV.3.1- Reduction of COD a) and Color b) with treatment time. Conditions: pH initial=3.0, Temp= 20 °C***

The results depicted in Figure IV.3.1 a) point out that it was possible to attain a COD removal of 65% when a 2:1 ratio (Test 1) was applied and a slight final increase to 68% was detected as the ratio reached 5:1 (Test 2) after 4 hours of oxidative procedure. However, for the ratio 10:1 (Test 3), the COD abatement decreased considerable reaching only 51%.

Initially, trial 1 shows a greater removal rate; however, after 3 hours of reaction, the rate of oxidation of the second trial enhances awarding a higher wastewater treatment at the end of 4 hours of reaction. In fact, this outcome may be originated by the fact that the second trial initially presents a greater $H_2O_2$ concentration, which may show a slight inhibition resulting from the effect of oxidant scavenging, which reduces the amount of hydroxyl radicals available for oxidation, forming hydro peroxide radicals, $HO_2•$, with a much lower oxidizing power. During the oxidation, hydrogen peroxide concentration drops, reaching a value that might encourage the increase of the reaction efficiency.

From these results it is then observed that using $[Fe^{2+}]$ =10 mM (Table IV.3.2) the higher concentration of $H_2O_2$ (100 mM) is not favorable to the oxidation, achieving almost less 10% of removal in COD and color when compared with the two other tested loads, showing the scavenger effect of hydrogen peroxide. In fact, increasing the hydrogen peroxide quantity may change its character from being initiator for the production of hydroxyl radicals that enhance the oxidant power of the system to inhibitor of this kind of reactions when in excess.

For this reason two $[H_2O_2]$: $[Fe^{2+}]$ratios were selected, 2:1 and 5:1 as the best concentrations providing 65% and 68 % on COD removals as it is seen in Figure IV.3.1.

In what regards color removal, 1(b), similar results were obtained; the degradation increased from 61% (2:1) until 65% (5:1) but for the higher ratio (10:1) the removal is much lower, attaining only 55% of color reduction. It is important to refer that the Phenol Content was always totally degraded during the first hour of reaction.

### *IV.3.3.2 Effect of Different Operational Procedures*

Frequently it is mentioned that an adequate control of pH would increase Fenton's process efficiency (Mandal *et al.*, 2010), since this is a key parameter on the reaction, playing an important role in $HO^•$ production; nevertheless, the system pH adjustment increases the operating costs.

In order to prove this gain, a test with pH control was performed, where pH was adjusted within the range 3 ± 0.1 (test 5). In opposition to this assay, a run without any kind of pH control was performed (test 4) and the reactants were added at the raw pH of the effluent (6.7), trying to safeguard the operational costs. Moreover, an experiment where pH was only adjusted to 3 initially and afterwards left to run freely was performed. It was expected a pH decrease due to the formation of some $H_3O^+$ from the reaction of some iron complexes, such as ferric hydroxo with hydroxide ions (Ma and Xia, 2009; Martins *et al.*, 2010b). Complementary, a sequential hydrogen peroxide dosages added from time to time with the total volume of $H_2O_2$ divided in four aliquots (test 6) at each hour of reaction was also tested to ascertain whether there might be an improvement in process efficiency. The removal profiles of COD and color are presented in Figure IV.3.2.

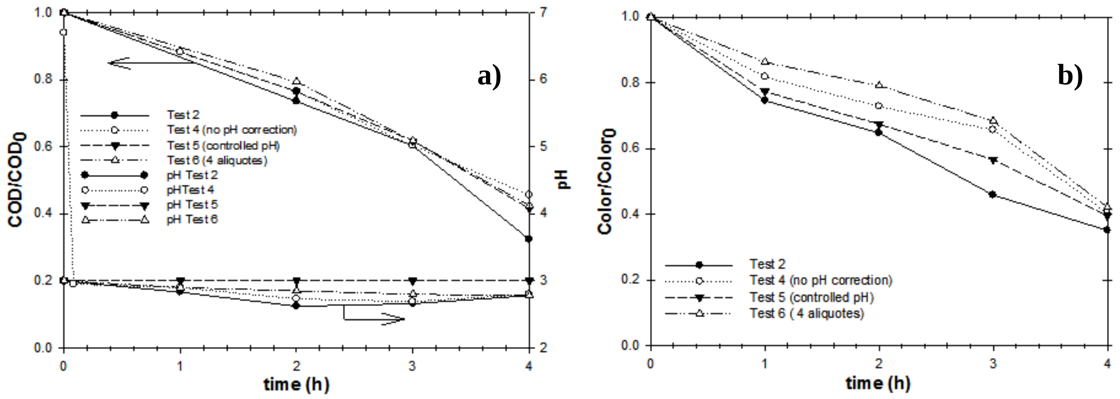

***Figure IV.3.2- COD and color reduction for different oxidation conditions. Conditions: Temp= 20 °C; [$H_2O_2$]=50 mmol..$L^{-1}$; [$Fe^{2+}$]= 10mmol..$L^{-1}$***

As it is shown in Figure IV.3.2 a), the pH maintenance (Test 5) within the selected range seems not to be an indispensable factor regarding Fenton's efficiency to depurate this effluent, since no significant differences regarding COD and TPh removals were observed when comparing the results of Test 4 (no pH correction) and with Test 2 (where pH was corrected only at the oxidation begin). After 3 hours of oxidation all the removals are similar; however, from this time on, the COD degradation is favored by a free pH in a wastewater with previous pH correction (Test 2).

For the Test 4, where any kind of pH adjustment was performed, it is observed a decrease in pH as expected; but with the development of the oxidation, there is a decrease on the process efficiency. In fact, there is a consumption of $H_2O_2$ to favour the formation of $H^+$ leading to the production of less efficient hydroperoxyl radicals (Equation IV.3.1). Furthermore, as the wastewater was about pH 7, some hydrogen peroxide self-decomposition may have been favoured (Martins *et al.*, 2010c).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \qquad \textbf{(IV.3.1)}$$

In what concerns the case where pH was controlled during time and comparing it with Test 2, the oxidative systems showed a similar profile and achieved practically the same removal, almost 40% of COD. In fact, to the pH adjustment a certain quantity of NaOH was added which can favor the formation of small quantity of iron hydroxide Fe $(OH)_3$ which, due to his difficult to solubilize, causes the reduction of ferric ions in solution and therefore a decrease in the process efficiency (Peres *et al.,* 2004).

In fact, during the oxidation, the pH reaches 2.6 ± 0.1 and is maintained in this value along two hours of reaction. Then the pH rises and reaches 2.8 ± 0.1 that is kept constant till the end of the process. This fact would be expected, given that during the oxidation organic acids formed as by-products of the pollutants degradation origin a drop in pH, but its posterior oxididation, will promote the slight pH increase (Gogate and Pandit, 2004).

Surprisingly, the hydrogen peroxide addition along time does not present an efficiency improvement, in disagreement with was related by Martins and collaborators (2010a), attaining only 54% of COD removal beside the degradation of 67% attained for a single oxidant addition (Test 2). This result is justified with the fact that a minor concentration of $H_2O_2$ is present during the first two hours of oxidation, since only ¼ of the dose of the Test 2 was added, and consequently the latest amount could not get reaction time to a proper consume.

It is observed, in comparison with all tests that the initial pH adjustment and let it run freely afterwards it is preferable before the reaction starts and the pH's runs freely after its initial correction, where it was achieved 43% of COD degradation. Besides, all $H_2O_2$ should be initially added.

In Figure IV.3.2 b) it is perceived that there is a relationship between operating conditions and the final color achieved. Tests with controlled pH led to a higher coloration removal considering that during the Fenton's reaction with uncontrolled pH its value decreased below 3, resulting in the formation of iron complexes, keeping a more intense coloration (Mandal *et al.,* 2010).

In the aliquots (Test 6) and pH controlled tests (Test 5, pH during all the reaction and Test 2, corrected before the oxidation), this effect was not observed, and the smallest removal is detected. In fact, the profile indicates a smaller color degradation rate along time, showing that the lower amount of hydrogen peroxide represents a minor degradation on this parameter.

All the tests assumed an analogous degradation rate profile, indicating that oxidation was dependent of the reactants doses, instead of different operational conditions so that in the following sections the effect of $Fe^{2+}$ and $H_2O_2$ will be discussed.

For all the performed tests total phenolic content was removed at the first hour of reaction.

### *IV.3.3.3 Effect of $Fe^{2+}$ and $H_2O_2$ Concentration*

In order to assess a better COD depletion, capable of reaching a value below 150 $mgO_2.L^{-1}$ that permit the treated wastewater discharge to the hydrological resources, a third sequence of tests, where the effect of an increment on the iron dosage was evaluated, maintaining the same studied ratios 2:1 and 5:1 was performed. The reactants concentrations used in each experiment are present in Table IV.3.3. The ferrous sulphate dose for this effluent depuration was varied in the range of 5 until 50 mM (in order to guarantee a catalyst dosage up to a maximum where is expected that more oxidizable organic matter is not present) and the hydrogen peroxide dose was varied according to the selected $[H_2O_2]$: $[Fe^{2+}]$ ratios. The reaction time was maintained (4h) and pH was initially corrected to the value of 3 ranging freely during the oxidation experiment.

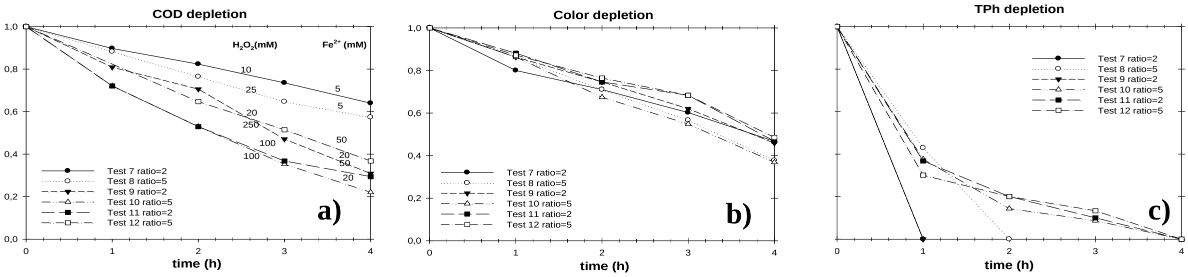

***Figure IV.3.3- COD a), Color b) and TPh c) depletion for different iron dosages. pH initial=3.0, Temp= 20 °C***

Figure IV.3.3 shows COD, color and TPh abatement (residual fraction in the liquid-phase) for the referred experiments, Tests 7-12, and Table IV.3.3 summarizes the main results obtained for the different applied ratios at different iron concentrations.

As it can be observed in Figure IV.3.3 a), there is an improvement on COD removal for Test 10 ($[Fe^{2+}]$ = 20 mM, $[H_2O_2]$: $[Fe^{2+}]$ = 5:1 and the test with the pH innitialy corrected at a value of 3 reaches a remarkable 78% fulfilling the principal objective of this work: a final COD value of 150 $mgO_2.L^{-1}$.

***Table IV.3.3- Main obtained results summary for the different tests with [$H_2O_2$]: [$Fe^{2+}$]= 2 and 5***

| **$Fe^{2+}$ (mmol)** | **Test** | **[$H_2O_2$]: [$Fe^{2+}$]** | **$H_2O_2$ (mmol)** | **COD removal** | **Color removal** | **TPh total removal** |
|---|---|---|---|---|---|---|
| **5** | 7 | 2 | 10 | 36% | ± 45% | 1h |
| | 8 | 5 | 25 | 43% | ± 65% | 2h |
| **10** | 1 | 2 | 20 | 65% | ± 60% | 1h |
| | 2 | 5 | 50 | 68% | ± 65% | 1h |
| **20** | 9 | 2 | 40 | 69% | ± 55% | 4h |
| | 10 | 5 | 100 | 78% | ± 65% | 4h |
| **50** | 11 | 2 | 100 | 71% | ± 50% | 4h |
| | 12 | 5 | 250 | 63% | ± 50% | 4h |

In Table IV.3.3 is possible to observe that for higher iron concentration, 50 mM, (Tests 11 and 12) it is possible to observe a decrease in the COD degradation. Knowing that the Test 11 had the same hydrogen peroxide dosage (100 mM $H_2O_2$) that was applied in assay 10 (20 mM $Fe^{2+}$) one can conclude that the differences observed are due to the iron scavenger effect, since there is no improvement in the COD removal with a higher iron dosage, but a divergent effect, where is present a decrease in the efficiency of the oxidation procedure. For doses lower than 10 mM of $Fe^{2+}$, COD removal diminished remarkably for different ratios (Tests 7 (2:1) and 8 (5:1)), where a higher oxidant dosage promotes a major depuration, as expected. The worse result was obtained for the Test 12, where the higher reactant dosages were used. Comparing the Tests 11 and 12, for the same iron concentration, increasing the hydrogen peroxide dosage did not improve COD removal, otherwise seems to decrease due to the scavenging effect of $H_2O_2$ on $HO^{\bullet}$ radicals (Padoley *et al.*, 2011) previously described. Thus, considering that an increased concentration of reactants does not potentiate the oxidation rate, the test 11 conditions with 20 mM of iron and 100 mM peroxide seem to be the most favorable to depurate this wastewater.

For $Fe^{2+}$doses lower than 10 mM, COD removal diminished remarkably for both ratios (Tests 7 and 8). These results reveal that to get a satisfactory COD degradation even if the required [$H_2O_2$]: [$Fe^{2+}$] ratio is important; the amounts of $H_2O_2$ and $FeSO_4$ applied are also imperative to produce adequate amount of $HO^{\bullet}$ and consequent depuration improvement**.**

In what concerns color abatement, from Figure IV.3.3 b) it is possible to see that the higher used iron concentration attains only 50 % of color reduction (Tests 11 and 12). This result was expected since a higher iron dose leads to a higher iron concentration left in solution that in turn provides some color to the treated effluent (besides the higher amount of sludge produced), evidenced by the fact that the Test 7 in spite of leading to less COD removal, achieves higher color depletion. In fact, the best color removals were perceived when lower iron concentrations were applied, namely test 8 where was attained 65%, the same value accomplished at the tests 2 and 10, both with a [$H_2O_2$]:

$[Fe^{2+}]$ ratio of 5 (Table IV.3.3). There is the exception of test 7, where only 45% of color depletion was accomplished which may be explained by the also low COD abatement detected. Anyway, it is emphasized that within those same iron concentrations, tests with higher concentrations of $H_2O_2$, provide an upper color removal, because a greater oxidation implies a possible higher degradation of the chromospheres compounds and consequently, a major reduction in color.

In opposition with the other tests sequence (1 and 2) where was reached the total TPh removal, this parameter degradation was not obtained at the first reaction hour for higher dosages of iron (Tests 9-12) most probably due to the abovementioned scavenger effect (Figure IV.3.3 c)). In fact, our results show a decrease on TPh removal when the catalyst load increases from 20 to 50 mM. For those conditions, complete removal was achieved only after the 4 hours of oxidation while for tests with lower iron concentrations (5 mM at Test 8) this was assessed after 2 hours of reaction.

### *IV.3.3.4 Biodegradability Enhancement*

Figure IV.3.4 exhibits the initial effluent biodegradability (· · —) and the minimum value requested for posterior biological treatment (·-----), assuming that when the ratio of $BOD_5/COD$ is greater than 0.3, the wastewater is partially biodegradable (Chun and Yizhong, 1999).

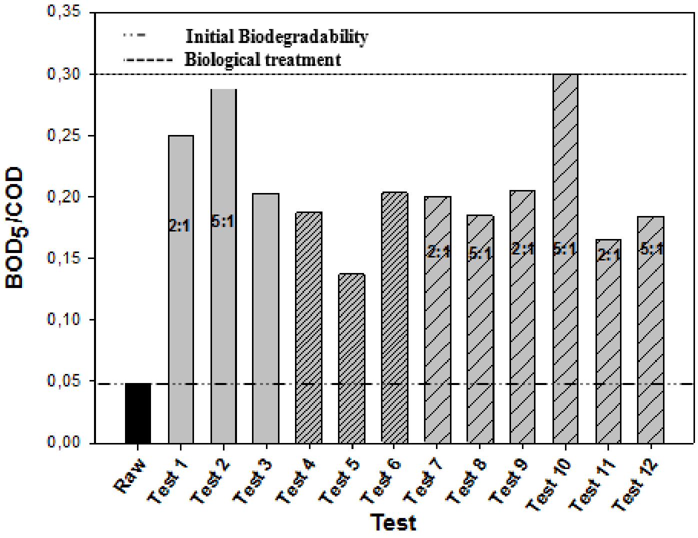

*Figure IV.3.4- Biodegradability of all homogeneous Fenton Tests*

For all tests the biodegradability was improved. However, only in two of them (Test 2 and 10), the treated wastewater, seems to be suitable to be depurated by a posterior biological treatment.

In what respects to the used ratios (2:1, 5:1 and 10:1) in Tests 1, 2 and 3 respectively, one can observe that it exists an increase in the effluent biodegradability for the two first proposed ratios values, but for the highest of them (Test 3) the biodegradability accomplished is smaller than the previous ones (Test 2). This is a classic example of the reactants over dosage effect, namely of the hydrogen peroxide scavenger impact, because in addition to the smaller COD removal also lower biodegradability enhancement occurred (Badawy *et al.*, 2009).

In which refers to the many operative conditions studied, for all the tests with the same reactants concentration, $[Fe^{2+}]$ = 10 mM and a 5:1 ratio (Tests 2, 4, 5 and 6), significant differences are found regarding the biodegradability attained. The highest value, 0.29, was accomplished during the experiment where pH was corrected before the oxidation procedure, and the worst value, 0.13, was reached during the run where hydrogen peroxide was gradually added. The gradual addition of hydrogen peroxide could promote the degradation of the formed biologically degradable compounds in the remaining solution leading to a more bio-refractory effluent lessening the COD and the $BOD_5$ values.

Figure IV.3.5 a) and b) represents the COD removal and the $BOD_5$/COD profiles resulting from the oxidation reaction in function of iron and hydrogen peroxide doses, respectively. From these results it is possible to observe that higher ratios (5:1) favors the COD reduction as well as the biodegradability improvement when compared with the 2:1 ratio, except for the test with lower iron dosage, that also attained the small COD removal value.

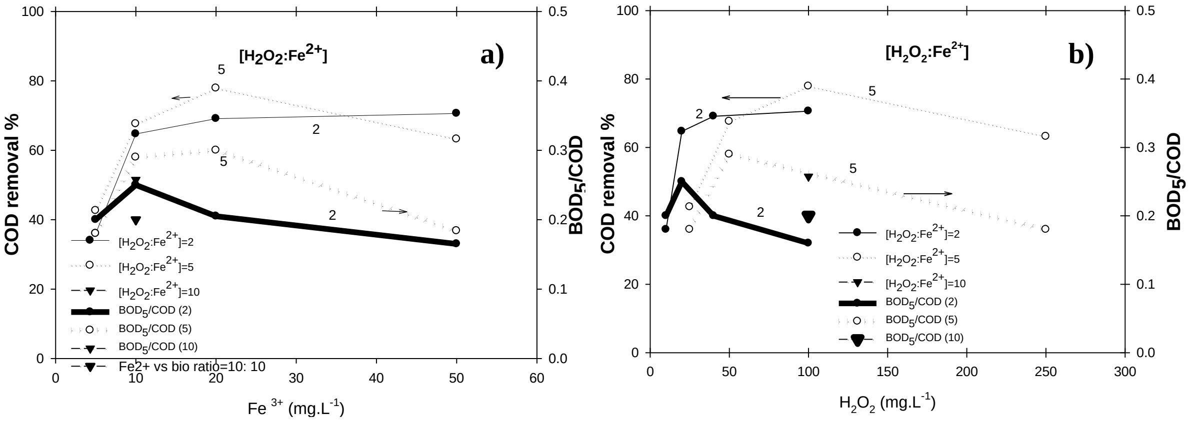

*Figure IV.3.5- COD and $BOD_5$/COD in function of iron a) and $H_2O_2$ b) dosages*

According to these biodegradability results, in what regards to the influence of iron concentration it is possible to conclude that for a 5:1 ratio, similar effluents biodegradability is attained when iron concentrations of $[Fe^{2+}]$ = 10 and 20 $mmol.L^{-1}$ are used (Tests 2 and 10), but for higher loads an adverse effect exists and less biodegradable by-products are formed (Tests 12). This probably derives from the iron scavenger effect, where higher concentrations of this reagent consume hydroxyl radicals enhancing the formation of Fe (III) and $OH^-$ (Karthikeyan *et al.*, 2011). Moreover, it is reported harmful effects of the iron excess over microbiological systems which can also contribute for the decrease of measured biodegradability in treated effluent. For the lower iron concentration, 5 mM, the degradation of organic compounds (COD) is slighter, and the obtained $BOD_5$/COD ratio also follows this trend, reaching a value below 0.2 but even somehow higher than the one achieved with the greatest iron concentration (50 mM).

For the $[H_2O_2]$:$[Fe^{2+}]$ = 2:1 the behavior related to the removal of COD and biodegradability obtained is similar to the ones referred before, but the values attained for biodegradability are considerably shorter for the intermediate concentrations and very similar at the extremes (5 and 50 mM).

For the Figure IV.3.5 b) it is possible to conclude that for the 2:1 ratio, for a concentration of hydrogen peroxide above the 25 mM, there is a slight COD removal improvement, opposed to the $BOD_5$/COD of the treated effluent that goes down sharply. A different behavior is observed for the ratio 5:1 where after reaching the 100 mM $H_2O_2$, there is a reduction in COD removal that in turn is accompanied by a decrease of the effluents bio-amenability.

As mentioned above, the ratio between hydrogen peroxide and iron concentration has a strong influence over Fenton process efficiency. As smaller ratios favor the coagulation mechanism, although the COD decrease, there is no oxidation of primary compounds and subsequent formation of biodegradable materials, reducing the biodegradability of the effluent. For higher $[H_2O_2]$:$[Fe^{2+}]$=5, there is also a maximal concentration that enables purification, from which the oxidant excess provides a decrease in the efficacy through the effect of the $H_2O_2$ scavenging behavior already mentioned. However, with the reduction of the removal of COD, there is a decrease in the same proportion of $BOD_5$/ COD.

### *IV.3.3.5 Solids Evaluation*

The results regarding Total Suspended Solids, TSS, and Total Dissolved Solids, TDS derived from the Fenton’s process resultant supernatant. Besides the amount of produced settable iron sludge after alkalization of the reaction medium is present in Figure IV.3.6 for the different tests performed. As depicted in that Figure, there is a strict relationship between TSS and TDS. With the removal of suspended solids by this process, there is dissolution of a significant part of them, providing a substantial increase (express at negative removal percentage) in the amount of dissolved materials.

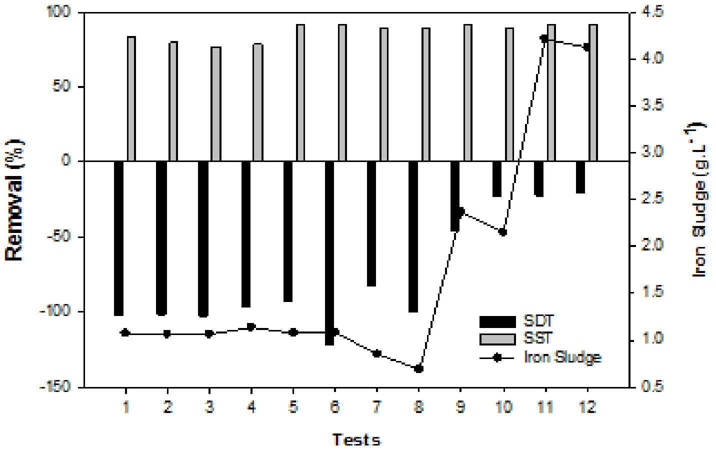

*Figure IV.3.6- Total Suspended and Dissolved Solids removal during Fenton's Process (left axis), and respective formed Iron sludge (right axis)*

This rise is greater than the amount of removed solids, which suggests that in addition to dissolution of the suspended solids there is the formation of solids compounds not sedimentable. Bearing in mind that the main target pollutants of Fenton's oxidation are organic substances as nucleophile and aromatic substances, in opposition to the colloids compounds present in wastewater (Dogruel *et al.*, 2009), it was expected that the colloidal and suspended matter was removed at a later stage throughout pH re-adjustment and favored by the ferric coagulation during the neutralization and consequent ferrous sludge formation (Zhang *et al.*, 2006). In opposition, the formed larger particle as iron salts, but not large enough for a natural sedimentation, shall remain in suspension contributing to the increase of TDS (Deng and Englehardt, 2006).

However, when a higher hydrogen peroxide dosage is used, for the same iron load (major [$H_2O_2$]: [$Fe^{2+}$]), a minor quantity of iron sludge was produced. This effect is present in the tests 7-8, 9-10 and 11-12, where different $H_2O_2$:$Fe^{2+}$ were used (2 and 5 respectively), in accordance to what is reported **(**Neyens and Baeyens, 2003**)** where is referred that chemical coagulation prevails at lows ratios, while higher ratios promote the chemical oxidation and consequent reduction of sludge volume. This case could be justified by a higher mineralization and consequently a smaller amount of settable organic matter available.  It is also remarkable, that for iron dosages higher or equal than 20 mM, the TDS concentration drops more than 50% when compared with the amount formed at the test were 10 mM were added. In fact, with the increase of iron concentration is promoted the decrease the of TDS quantity, showing that this parameter is strictly related with the coagulation stage, and it is necessary to optimize this dosage in order to take advantage of the synergistic effects of both phases (oxidation and coagulation) in the Fenton process.

One important aspect that can be observed is that increasing the amount of iron, provides an increase on the quantity of formed sludge. As might be expected, for Fe concentrations of 5 mM less than 1g.L$^{-1}$ of sludge was formed, while for 10 mM resulted to between 1-1.5 g.L$^{-1}$ and for concentrations of 20 mM and 50 mM produced about 2-2.5 g.L$^{-1}$ and 5 g.L$^{-1}$, respectively.It is possible to observe that the increase in iron load endorses firstly a better COD removal until 20 mM, where the COD elimination seems to attain a maximum between 70-78% (Tests 9, 10). Afterwards an adverse effect is detected on the performance rate (Tests 11, 12), possibly due to the $Fe^{2+}$ induced radical scavenging (Lucas and Peres, 2009). In the other hand, the difference between the higher $H_2O_2$ doses means a more marked improvement on the oxidation efficiency when the lowest iron range is used, 5 mM in tests 7 and 8, than for higher values 10 and 20 mM at tests 1, 2, 3 and 9, 10, respectively, with a reverse scavenger effect for the highest iron concentration (50 mM) in the tests 11 and 12, where trough the selected ratios, the amount of hydrogen peroxide was significantly superior, and a scavenger effect is present induced by the excess of oxidant.

For the strongest COD reduction (78%), in Test 10, a purified effluent with a COD concentration of 150 mg$O_2$ L$^{-1}$, total TPh removal, and wastewater biodegradability improved to 0.3 ($BOD_5$ < 40 mg$O_2$ L$^{-1}$) was possible to be attained. Also for solids, a considerable decrease was observed, enabling a reduction of 90% for TSS (< 60mg L$^{-1}$, that is the legal threshold that must be accomplished by a wastewater for this parameter). This means that the stream is now able to be discharged into the hydrological resources entailing an operating cost of 4.384 € m$^{-3}$.

However, for test 2, 52 % of COD removal, a $BOD_5$/COD improvement to 0.29 and 30% of TSS removal was achieved requiring only 2.571€.m$^{-3}$. Nevertheless, for direct hydric discharge a biological step treatment would be necessary to further refine the wastewater before disposal.

### IV.3.4 Chemical costs evaluation

In this section it is intended to estimate the operating costs associated to the depuration of elderberry juice wastewater by Fenton's peroxidation. Only the cost of reagents used per m$^3$ of treated effluent are considered. In fact, these are the only cost that we can infer from the carried activity because the associated costs related to the acquisition of equipment and its installation, maintenance, electricity, employment and associated costs such as transportation and treatment of the originated sludge (Molinos-Senante *et al.*, 2010), would only be possible to estimate, in accordance with the specific needs of each industrial installation, as volume to treat, wastewater characterization and site and area available for the WWTP.

It should be noticed that it was had into account the amount of sulfuric acid to acidification of the medium before the treatment, and the addition of NaOH to terminate the reaction and precipitate ferrous sludge. Moreover, the doses of $H_2SO_4$ and NaOH applied were the same in all experiments, except the acid at the Test 4 and the NaOH at Test 6. The costs of the spent reactants per $m^{-3}$ of treated wastewater are present in Table IV.3.4.

***Table IV.3.4- Reactant Costs for each test***

| **Test** | **Fe.m$^{-3}$ €** | **(%€) Fe** | **$H_20_2$.m$^{-3}$ €** | **(%€) $H_20_2$** | **$H_2SO_4$.m$^{-3}$ €** | **(%€) $H_2SO_4$** | **NaOH.m$^{-3}$ €** | **(% €) NaOH** | **Total (€.m$^{-3}$)** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.208 | 12.9 | 0.642 | 39.9 | 0.319 | 19.8 | 0.440 | 27.3 | 1.608 |
| 2 | 0.208 | 8.1 | 1.605 | 62.4 | 0.319 | 12.4 | 0.440 | 17.1 | 2.571 |
| 3 | 0.208 | 5.0 | 3.210 | 76.9 | 0.319 | 7.6 | 0.440 | 10.5 | 4.176 |
| 4 | 0.208 | 9.2 | 1.605 | 71.3 | 0 | 0.0 | 0.440 | 19.5 | 2.252 |
| 5 | 0.208 | 8.1 | 1.605 | 62.4 | 0.319 | 12.4 | 0.440 | 17.1 | 2.571 |
| 6 | 0.208 | 7.8 | 1.605 | 59.9 | 0.319 | 11.9 | 0.549 | 20.5 | 2.681 |
| 7 | 0.104 | 8.8 | 0.321 | 27.1 | 0.319 | 27.0 | 0.440 | 37.1 | 1.183 |
| 8 | 0.104 | 6.2 | 0.802 | 48.2 | 0.319 | 19.2 | 0.440 | 26.4 | 1.665 |
| 9 | 0.416 | 16.9 | 1.284 | 52.2 | 0.319 | 13.0 | 0.440 | 17.9 | 2.458 |
| 10 | 0.416 | 9.5 | 3.210 | 73.2 | 0.319 | 7.3 | 0.440 | 10.0 | 4.384 |
| 11 | 1.04 | 20.8 | 3.210 | 64.1 | 0.319 | 6.4 | 0.440 | 8.8 | 5.008 |
| 12 | 1.04 | 10.6 | 8.024 | 81.7 | 0.319 | 3.2 | 0.440 | 4.5 | 9.822 |

Figure IV.3.7 shows the final COD and $BOD_5$ improvements for different tests as well as an economical evaluation considering the costs of sulfuric acid, NaOH, Iron sulphate, and $H_2O_2$. The price of the hydrogen peroxide 50% was 0.6041 € .$L^{-1}$, from Portuguese industrial sources, the costs of NaOH (50%) and $H_2SO_4$ were 0.366 €.$L^{-1}$ and 0.141 €.$L^{-1}$ and the iron sulphate has a cost of 0.2 €.$Kg^{-1}$ per ton of each reactant acquired in Portuguese market. The fundamental costs are fixed per $m^3$ of wastewater (€.$m^{-3}$).

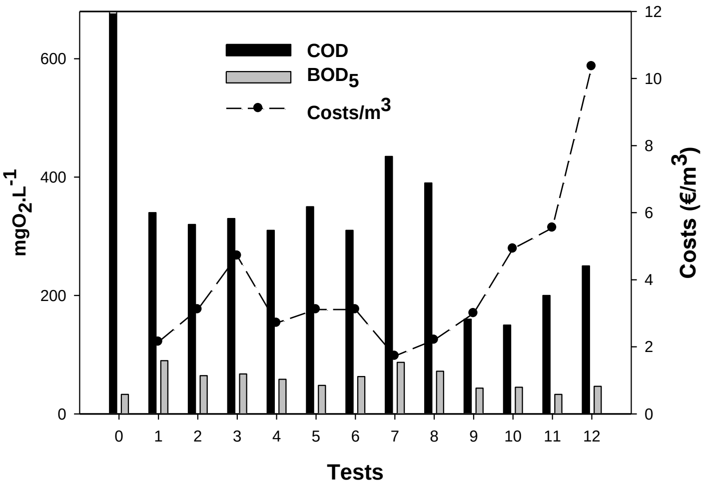

***Figure IV.3.7- COD, $BOD_5$ and the operational reactants cost achieved for each test***

As it turns out, a significant portion of the cost comes from the amount of $H_2O_2$, standing between the 27.1% of the Test 7 until the maximum achieved of 81.7% of the test 12 (Table IV.3.4). Overall, with the $[H_2O_2]$: $[Fe^{2+}]$ ratio increase, these cost associated percentage increases in the process.

It is possible to observe that the increase in iron load permits firstly a better COD removal until 20 $mmol.L^{-1}$, where the COD elimination seems to attain a maximum removal between 70-78% (Tests 9, 10). Afterwards an adverse effect is detected on the performance rate (Tests 11, 12), possibly due to the $Fe^{2+}$ induced radical scavenging. In the other hand, the difference between the higher $H_2O_2$ doses means a more marked improvement on the oxidation efficiency when the lowest iron range is used, 5 $mmol.L^{-1}$ in tests 7 and 8, than for higher values (10 and 20 $mmol.L^{-1}$ at tests 1, 2, 3 and 9, 10, respectively, with a reverse scavenger effect for the highest iron concentration (50 $mmol.L^{-1}$) in the tests 11and 12.

Thus we can prove that the homogenous Fenton process is effective in this wastewater treatment in order to permit to be discharged into ditch water, but it should be consider the possibility of a subsequent biological treatment stage in order to reduce the reactants costs. So the advanced oxidation process followed by biological process can be an environmental and economic advantageous for the treatment of this industrial wastewater.

## IV.3.5 Conclusions

The effectiveness of the Fenton's process as a method for elderberry juice production wastewater treatment was investigated. The extent of purification of the treated wastewater was dependent on the $[H_2O_2]$: $[Fe^{2+}]$ ratio, but the major significant improvement is determined by the reactants concentration. The more suitable ratio for this treatment was 1:5 until a determinate maximum iron concentration after which a scavenger effect is promoted and consequential efficiency decrease. The wastewater pre-acidification before the depuration step (pH adjustment to about 3) was beneficial in comparison to when pH control was effectuated during the oxidation process or when any kind of pH correction was done. The stepwise addition of hydrogen peroxide did not provide benefits when compared with the case where this reactant was introduced all at once.

It was verified a biodegradability improvement for the treated streams. The results showed average removal efficiencies of COD, TSS and Color of about 78%, 90% and 63%, respectively, and a $BOD_5$/COD improvement of 600%, from 0.05 to 0.3. The best treated effluent parameters attained with the operational conditions of initial pH=3, $[H_2O_2]$: $[Fe^{2+}]$ =5: 20 mM $Fe^{2+}$ and a retention time of 4h leading to an effluent were within the legal limits allowing its discharge throughout the hydric resources, since the COD and $BOD_5$ and TSS values accomplish the legal limits for those parameters (150 $mgO_2\ L^{-1}$, 40 $mgO_2\ L^{-1}$ and 60 mg $L^{-1}$ respectively). However, this operational system reaches a reactant costs of more than 4 € $m^{-3}$. Nevertheless, the costs may be reduced if the aim is to reach a biodegradable stream able to be directed to the municipal wastewater treatment plant that can successfully biologically further amend the effluent.

Thus, Fenton's oxidation can improve biodegradability and reduce COD content until the discharge limit, and may possibly be successfully applied both as a single method and as a pre-treatment stage for increase the biodegradability and/or remove the wastewater organic content for a posterior biological treatment approach.

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# IV.4 A new winery wastewater treatment approach during vintage periods integrating ferric coagulation, Fenton Reaction and activated sludge

## IV.4.1 Introduction

Water scarcity is raising some important questions related with the obligation of minimizing consume and safeguard the natural water courses. Liquid effluents reutilization for land irrigation or even for public water supply will decisively contribute for a better management of water resources, minimizing the ecological problems associated with the disposal of wastewater into natural hydrological systems (Amaral-Silva *et al.,* 2012).

In wine production, vintage occurs for only 3-4 months. During this stage, wastewaters produced encompass strong organic content and high flow rates when compared with the streams coming from the remaining periods of winemaking.

Winery wastewaters (WinW) are characterized by pH 4-5, high biochemical and chemical oxygen demand (Oller *et al.*, 2011). Moreover, the high seasonal features of these streams difficult management. Over the years different treatment methodologies were proposed. Among them, traditional biological processes are the most widely studied (Arienzo *et al.,* 2009). The wineries wastewater treatment plants (WWTP's) are normally designed for the vintage period. The off season period is characterized by lack of sufficient organic load to maintain an adequate biomass concentration in the biological reactors. Thus WWTP are oversized during most of the year. This design leads to an increase of the foot implantation and high investment costs. Besides, these traditional treatment systems are unable to eliminate recalcitrant or high molecular weight compounds. To solve these issues, the advanced oxidation processes arise as suitable alternatives. It should be referred that usually their efficiency increases when associated with a previous coagulation/floculation stage for solids removal and some COD abatement (Kestioglu, 2005; Ntampou *et al*. 2006; Martins *et al.,* 2012). Among these processes, Fenton's oxidation (Beltran de Heredia *et al.,* 2005; Peres *et al.,* 2004; Martins *et al.,* 2009; Lucas *et al.,* 2009a), ozonation (Lucas *et al.,* 2010), electrochemical oxidation (Rincon *et al.*, 2009),electrochemical coagulation (Kirzhner *et al.,* 2008), solar photo-Fenton (Ormad *et al.,* 2006; Anastasiou *et al., 2009*; Monteagudo *et al.,* 2012) and solar photocatalysis (Rodríguez *et al.,* 2008) can be referred since they operate at room conditions of pressure and temperature.

Fenton oxidation process (using iron and hydrogen peroxide in an acidic solution) is a technique widely used for the destruction of several organic compounds. It is based on the generation of free hydroxyl radicals $HO^{\bullet}$ which have a high oxidation potential. Moreover, at the end of the process, the ferrous/ferric coagulation promoted under alkaline conditions facilitates the separation of some suspended organic matter (Zhang *et al.,* 2005; Wu *et al.,* 2010). Fenton process can be extremely costly when the aim is total mineralization. Thus, usually this technology is designed to promote partial oxidation with a corresponding increase of the wastewater biodegradability favoring a posterior biological treatment (Rodrigues *et al.*, 2009; Martins *et al., 2010a*; Martins *et al.,* 2010c; Oller *et al.*, 2011).

This work has as main purpose to develop a novel methodology able to minimize the impact over the activated sludge reactors due to the harvesting period peak during winery wastewater treatment. This new process can be applied for different wineries, as an integrated and compact technology. This study evaluates the integration of coagulation, chemical oxidation and biological treatment for an application at the real scale. A first stage with iron based coagulants was applied. A certain amount of this iron will remain dissolved and can be directly used as catalyst in Fenton's reaction. The main goal of this oxidation stage was to verify the possibility of enhancing biodegradability, thus endorsing a substantial more efficient and quick posterior biological treatment (Wang *et al.,* 2008*;* Padoley *et al*., 2011; You *et al.*, 2011).

In this context, the novelty of this research relates with the development of a compact treatment system able to be adapted to the flow and composition variations of winery wastewater along the year. Moreover, a coagulation step that will also produce the catalyst for the posterior Fenton's peroxidation constitutes an important step in processes integration. This procedure would allow designing the biological tanks for the off season period and apply the chemical process as a pre-treatment during the harvesting period.

## IV.4.2 Materials and methods

### *IV.4.2.1 Winery wastewater characterization*

Winery Wastewater (WinW) was collected in March 2011 from a winery located near Sabrosa, Portugal. Its main characteristics are present in Table IV.4.1. Briefly, the chemical and physical properties of the WinW were: pH 4.3; Chemical Oxygen Demand (COD) 5180 $mgO_2.L^{-1}$; Total Suspended Solids (TSS) 556 $mg.L^{-1}$; Total Nitrogen Content (TN) 55.8 ($mg.L^{-1}$) and Total Phosphorous Content (TP) 5.49 $mg.L^{-1}$.

*Table IV.4.1- WinW characterization*

| pH | COD (mgO$_2$.L$^{-1}$) | TN (mg.L$^{-1}$) | TP (mg.L$^{-1}$) | TSS (mg.L$^{-1}$) | BOD$_5$ (mg.O$_2$.L$^{-1}$) | BOD$_5$/COD |
|---|---|---|---|---|---|---|
| 4.3 | 5180 | 55.8 | 5.49 | 556 | 1296 | 0.25 |

### *IV.4.2.2 Reagents*

All reagents (Hydrogen peroxide (49.5%), ferric sulfate, ferric chloride, sulfuric acid (30%) and sodium hydroxide) were industrial grade and used as received.

### *IV.4.2.3 Analytical methods*

The liquid samples were analyzed regarding COD, TSS, BOD$_5$, TN and TP. All the parameters were measured in accordance with Standard Methods (Greenberg *et al.*, 1985).

COD determination was performed by the 5220D standard method using a COD thermoreactor (HANNA HI 839800) and a HANNA HI 83224 photometer. The dissolved oxygen for BOD$_5$ analysis was measured using a HANNA HI 4421 measurer while pH was determined using a HANNA HI 4522 pH meter. Hydrogen peroxide concentration was controlled during and after the treatments using test strips. Along the experiments, ammonia (N-NH$_4$), nitrite (N-NO$_2$), nitrate (N-NO$_3$), and phosphates (P-PO$_4$) were analyzed with the specific kits using a HANNA HI 83224 photometer.

Total Total Suspended Solids (TSS) were obtained by Standard Methods: “2540 D: Total Suspended Solids Dried at 103 - 105 °C” (*Greenberg et al.*, 1985). Iron content on the liquid phase was measured by atomic absorption in a Perkin-Elmer 3300 apparatus. Chloride was obtained by ionic chromatography (Waters).

All the referred measurements were determined in non-filtered samples. To check repeatability, some experiments were randomly run in duplicate and the samples were analyzed in triplicate to minimize the experimental error. The deviations between the performed runs were always lower than 5% and 12% for COD and BOD$_5$ results, respectively.

### *IV.4.2.4 Coagulation experiments*

Coagulation experiments were performed at ambient conditions using a jar test. Two iron based coagulants ($Fe_2(SO_4)_3.5H_2O$ and $FeCl_3.6H_2O$) were tested in doses varying within the range 500 and 2000 ppm. The effect of pH (from 2 to 6) over COD and TSS removal was also evaluated. Each coagulant was added to 250 mL of effluent in the mentioned conditions. The experimental process consisted in three steps: flash mixing for one minute (120 rpm) followed by 30 min of slow stirring (20 rpm) in order to promote coagulation. Afterwards, two samples were taken. The first was used to analyze directly the resulting supernatant (after one hour of sedimentation). In the second one, sodium hydroxide was added until reaching a pH value of 10 so that iron precipitation could be promoted. The supernatant was analyzed after 1 h of sedimentation.

#### *IV.4.2.5 Fenton Oxidation*

Iron remaining in solution after the coagulation step was applied as catalyst in Fenton's process. The oxidation was carried out in a jar test system. Briefly, 250 mL of wastewater were introduced in a glass reactor. The initial pH was the one coming from the coagulation stage. This parameter was left run freely during the experiments (between 2.4 and 3.2). The reaction (at room conditions) initiates when a specified amount of $H_2O_2$ was added in the reactor. Along the treatment, samples were withdrawn for analysis. NaOH was introduced to promote the precipitation of iron, removing a fraction of the organic matter (Gulkaya *et al.*, 2006) and quenching the remaining $H_2O_2$ (Martins *et al.*, 2010 c).

#### *IV.4.2.6 Biological treatment*

Aerobic biological treatment was performed at laboratory scale in a Sequential Biological Reactor (SBR) with an operating volume of 150 mL. Agitation was magnetically promoted at a speed of 150 rpm. An air diffuser was used to maintain aerobic conditions. Temperature was kept around 22 ± 2 °C while pH was maintained around pH 7.5-8.5 by adding $H_2SO_4$ 10% and NaOH 1 M.

The biological process was divided into five distinct phases following a controlled time: filling (5 min), aeration-reaction (19-20h), settling (3h), draw and idle (5 min). The reactor was operated with a solids retention time (SRT) of 10 days. The SBR was inoculated with 150 mL of activated sludge (3000-4000 $mg.L^{-1}$ of Volatile Suspended Solids), from the aeration tank of a winery WWTP near Cartaxo (Portugal). For acclimation of the biomass, an HRT of 10 days was used with treated water resulting from the WWTP that was mixed with raw winery effluent at ratios of 1:10, 2.5:10, 5:10 and 10:10.

Analysis of COD of the influent and effluent of the biological reactor were carried out in a daily basis. Besides, iron content after the biological treatment was also assessed. The activated sludge volume was determined. Moreover, the indicator of the sludge conditions was also performed through Madoni classification (Madoni, 2003).

## IV.4.3 Results and discussion

### *IV.4.3.1 Coagulation experiments*

The main purpose of this stage was to achieve an efficient TSS removal and an acceptable COD reduction. Moreover, the resulting conditions should favor the application of a posterior Fenton like reaction. Thus, the final pH should be in the range of 2.5-3.5 (Mandal *et al., 2010*; Karthikeyan *et al*. 2011). Most importantly, this work addressed the possibility of maintaining a final iron concentration after coagulation able to initiate Fenton's reaction without the need of the addition of further catalyst.

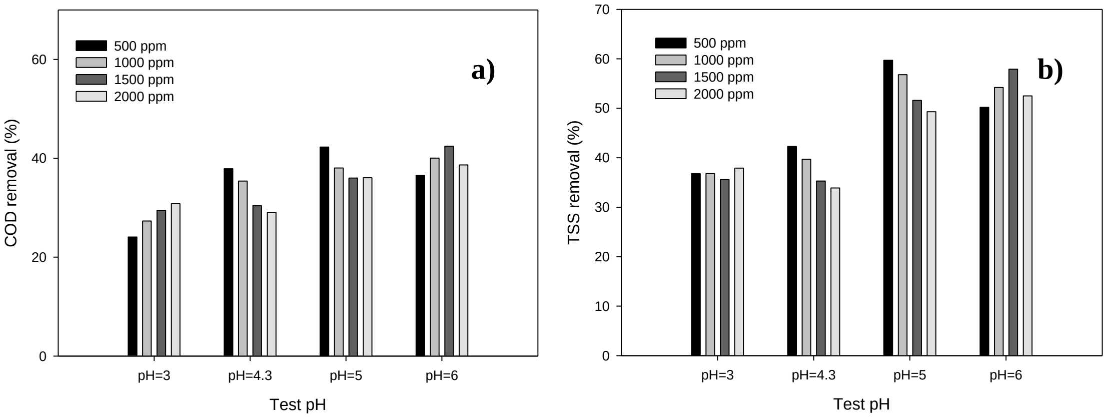

***Figure IV.4.1- a) COD and b) TSS removal at different pH and $FeCl_{3}.{}_{6}H_{2}O$ dosages***

Figure IV.4.1 shows the effect of pH on COD (a) and TSS (b) removal when $FeCl_3.5H_2O$ was used as coagulant. It is possible to observe that COD removal is more effective for a pH range between 5 and 6. Moreover, the best depletion was achieved when 1500 ppm of this coagulant at pH 6 was used. When pH rises from 3 to 6, COD removal efficiency increased from 29.5% to 42.5 %. For the lower tested pH (3), the coagulant dose increase improved COD depletion efficiency from 24 to 30.8%. However, for the raw effluent pH (4.3), as well as for pH 6, the coagulant dosage increase reduces COD abatement, probably due to the fact that pH is the key parameter controlling hydrolysis species. These species promote positive or negative charges depending on the pH. Generally, these species are positively charged for pH lower than 6 and negatively charged for higher values (Tatsi *et al.,* 2003). The positively charged hydrolysis species can absorb on the colloidal particles surface originating their destabilization. This mechanism is entitled as 'charge neutralization'. The formed precipitate can physically agglomerate the colloidal particles in suspension (Liang *et al.* 2009).

At pH 6, COD removal increases with the coagulant dose, leading to a maximum COD abatement of 42.5% when 1500 ppm are applied; however, for further higher dosages COD removal tends to decay possibly due to partial re-stabilization of colloids (Sarika *et al*., 2005; Aygun and Ylmaz, 2010).

In what regards TSS removal, Figure IV.4.1 b) shows that solids abatement increased with pH. Significant differences are found for two pH ranges: values below or equal the effluent raw pH and another for higher pH values. For the lowest pH range, the best removal efficiency was accomplished at raw pH when 500 ppm of coagulant were added (42.3%). The further increase on coagulant load led to a decay on the process efficiency. On the other hand, for higher pH's, the removal efficiency is more expressive. This fact could be justified by the use of NaOH for pH correction. $OH^-$ promote the formation of insoluble compounds that precipitate leading to a more effective settling, improving the process effectiveness (Jiang and Graham, 1998, Peres *et al*., 2004). From the results attained using $FeCl_3.5H_2O$ it is possible to conclude that the best TSS is obtained in the test with 500 ppm at pH 5 (59.7%) and the worst outcome was reached for the same pH but with 2000 ppm (49.3%).

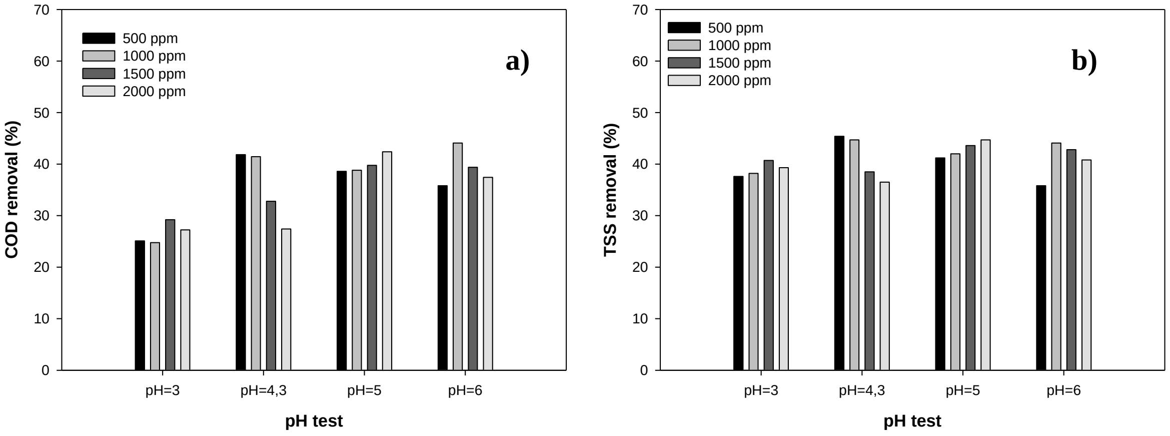

*Figure IV.4.2- a) COD and b) TSS removal at different pH and $Fe_2(SO_4)_3.5H_2O$ dosages*

Figure IV.4.2 COD and TSS removal for several ferric sulfate doses and pH. In what concerns COD removal (Figure IV.4.2 2 a)), best results (44.1%) are attained for an initial pH value of 6 using 1000 ppm of coagulant. For this pH, the removal profile shows that the efficiency increases with the coagulant dose until 1000 ppm; however, higher loads promote a decrease in the treatment effectiveness due to the above mentioned partial re-stabilization of the colloidal system. The worst results were obtained for more acidic pH with only 24.8% of COD elimination for a reactant dose of 1000 ppm.

The TSS removal profiles, represented in Figure IV.4.2 b) are identic to those attained for COD, showing that for this coagulant, the organic matter abatement is dependent on the amount of solids removed. The highest efficiency was observed in the test performed with 500 ppm at raw pH leading to up to 45.4% of COD abatement. The worst conditions for TSS elimination were 500 ppm and pH 6 (35.8%).

Both coagulants show to be effective in the TSS and COD removal. However, the main goal of this investigation is to get a precursor working as coagulant, but also able to lower pH (that must be in the range 2.5 - 3.5) and ensure a final iron concentration allowing a subsequent Fenton-like oxidation.

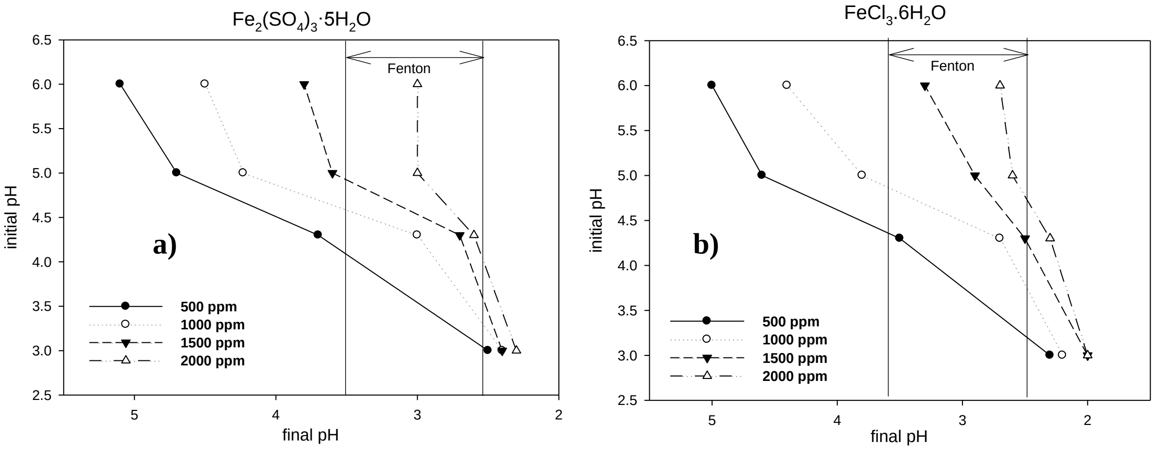

***Figure IV.4.3- pH variation for the differents experiments with the $Fe_2(SO_4)_3.5H_2O$ a) and $FeCl_3.6H_2O$ b) dosages***

The pH change with the coagulant dosage is presented in Figure IV.4.3. The treated wastewater pH value continuously decreased with the increasing dosage of coagulant. For ferric chloride the values ranged from 5 (500 ppm at an initial pH of 6) to 2 (1500 and 2000 ppm at an initial pH of 3). On the other hand, for ferric sulfate the values ranged from 5.1 (500 ppm at an initial pH of 6) to 2.3 (2000 ppm at an initial pH of 3). The decrease of pH values is justified by the acidic character of the tested coagulants promoted by the fact that the $Fe^{3+}$ cations are Lewis acids *(Ntampou et al.,* 2006).

It should be though referred that the counter ions of the coagulants (sulfate and chloride) are still in solution after the coagulation process. As it is well known, chloride interferes in the COD measurement and it is recommended that it should not be used for concentrations above 2000 mg.L$^{-1}$ (Greenberg *et al.*, 1985). Besides, chloride is a legislated parameter with a threshold that must be fulfilled so that an effluent can be discharged. Thus the residual chloride concentration on the coagulated water was followed and it is presented in Figure IV.4.4 for the different pH values.

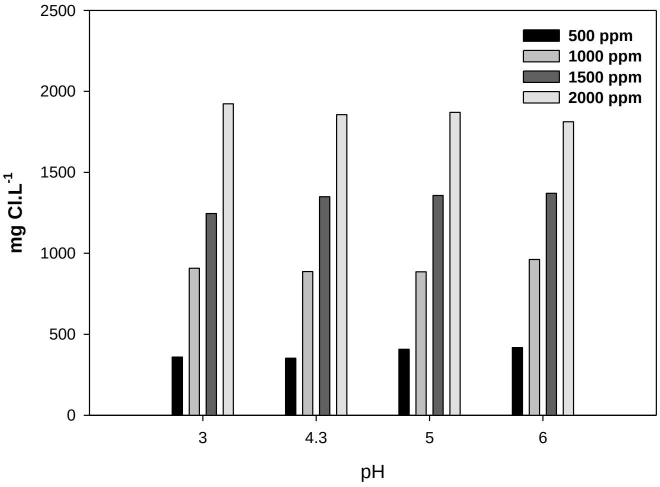

*Figure IV.4.4- Chloride concentration for the different experiments with $FeCl_3.6H_2O$*

The results reported confirm that the chloride concentration in solution was mainly dependent on the amount of coagulant added rather than on the initial pH. In fact, the deviations between the results determined for the same coagulant concentration for different initial pH values do not reach 10%. Due to the high $Cl^-$ concentration found and bearing in mind the possible formation of organochloride compounds with toxic features during oxidation, it was concluded that the best coagulant should be ferric sulfate.

Another important consideration that must be taken for the purpose of this work is the amount of iron in solution after coagulation. It must be a load able to promote Fenton's peroxidation. Thus, for the different assays, the amount of iron in solution was determined. Figure IV.4.5 presents the iron content in solution for the performed coagulated experiments as function of the initial pH.

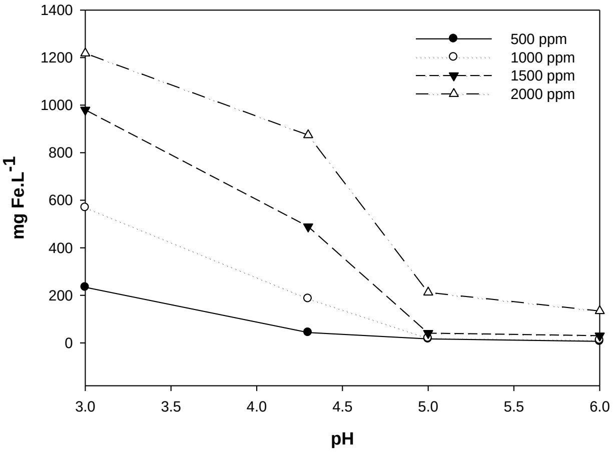

*Figure IV.4.5 - Dissolved iron in the pre-treated water for the $Fe_2(SO_4)_3.5H_2O$ coagulation experiments*

As depicted in Figure IV.4.5, more acidic media promotes higher concentrations of iron (proportional to the added amount of coagulant). In this case, the most favorable pH was the lowest one, maintaining almost 60% of the initial iron in solution. For pH values exceeding the raw effluent value (4.3), iron content is residual and tends for the same value, regardless the added quantity. Considering these findings, the more effective pH to maintain the iron present in solution was 3.

For the abovementioned pH, the remaining iron content as well the COD and TSS removal are presented in Figure IV.4.6.

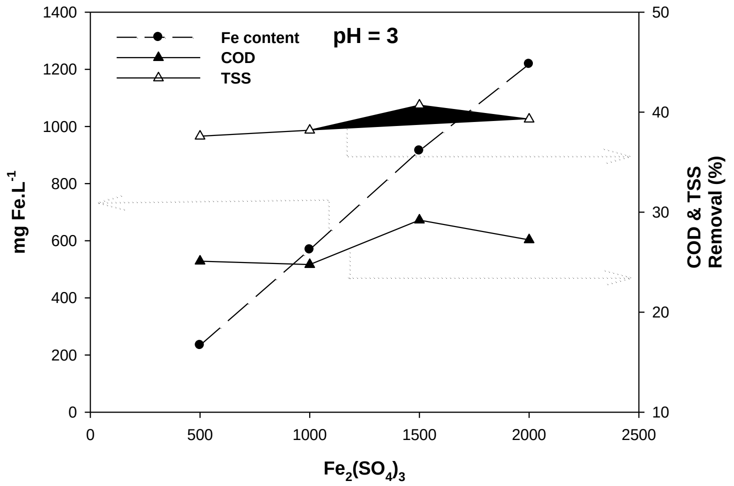

***Figure IV.4.6- COD, TSS and Iron content after iron sulfate coagulation at pH 3 for different coagulant doses***

Through this Figure, it is possible to observe that for the described conditions, the most favorable coagulant concentration, 1500 ppm, attains an efficient removal of organic load (29.2%) and total suspended solids (40.7%), but at the same time, maintains a concentration of iron sufficient (920 ppm) to allow a subsequent Fenton-like oxidation.

### *IV.4.3.2 Fenton-like Oxidation*

The dose of reactants required for Fenton's process is an important factor to consider since it determines the economic feasibility of the treatment. As mentioned, a certain amount of iron remains in solution, resulting from the previous coagulation stage, which allows reducing the costs related with the catalyst. The reaction time was varied in the range of 30-720 min (0.5-12 h). pH of the reaction mixture was maintained at the resulting value from the coagulation stage (pH 2.75). The initial value of hydrogen peroxide dosage was established based in the stoichiometric relation given by Lucas *et al.* (2009b) (1 g COD = 0.065 mol $H_2O_2$). 10% of that amount (1.22 L.m$^{-3}$) was set as starting point. From the results attained with this preliminary test, it was concluded that the oxidation time should be 8 hours, since after that only a slight COD removal improvement of 6% was obtained.

To analyze the effect of hydrogen peroxide dose, this parameter was varied from 5 to 50% of the stoichiometric value using the same conditions (pH 2.75, 480 min of reaction and iron content in the order of 920 ppm).

Figure IV.4.7 a) and b) show the evolution of residual normalized COD and biodegradability, at different doses of hydrogen peroxide.

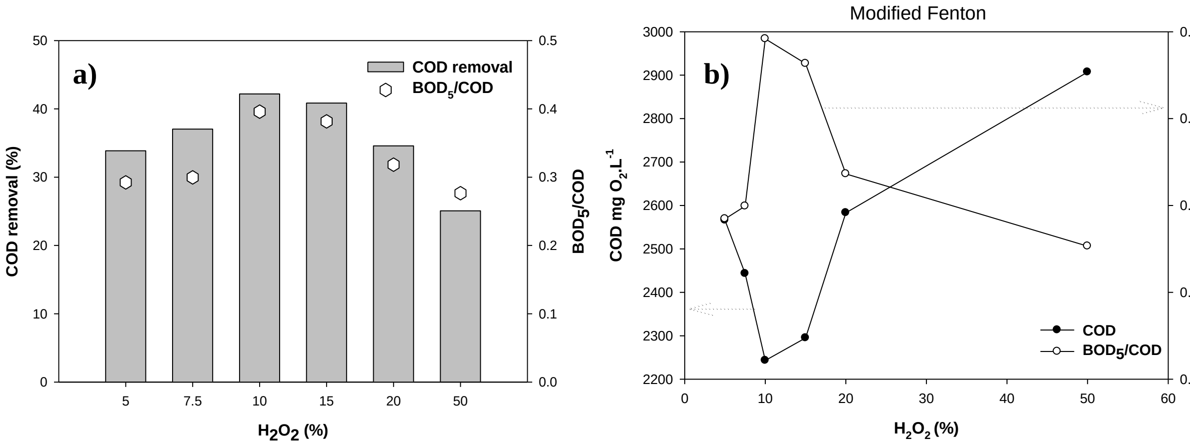

*Figure IV.4.7- a) COD removal and BOD$_5$/COD for the different $H_2O_2$ doses; b) COD and BOD$_5$/COD for the different $H_2O_2$ doses*

During the optimization studies, it was found that the COD removal (Fig. 7a) firstly increases with $H_2O_2$ concentration decreasing afterwards. When in excess, hydrogen peroxide will react with the formed hydroxyl radicals yielding the formation of less reactive radicals or innocuous species (Deng and Englehardt, 2006; Pignatello *et al.*, 2006).

Through the observation of Figure IV.4.7 a) it is possible to conclude that all tests performed led to significant COD abatement besides improving biodegradability. The highest COD removal (42.1%) occurs for the experiment where 10 % of the stoichiometric oxidant dose was added. Besides, those conditions led to a biodegradability improvement of 60% (final BOD$_5$/COD of 0.40).

Figure IV.4.7 b) presents a small interval of optimal dosages, between 10 and 15% of $H_2O_2$ stoichiometric value where the COD abatement and the biodegradability enhancement is observed with higher preponderance, showing that the oxidant dosage control is essential.

The major purpose of this integrated chemical scheme was to facilitate a subsequent biological treatment. So that the posterior biological system can properly operate, it is important to ensure that the required nutrients (COD, N and P) are in a proper ratio (Strong, 2008). Figure IV.4.8 exhibits the resultant COD, P and N for each oxidation test.

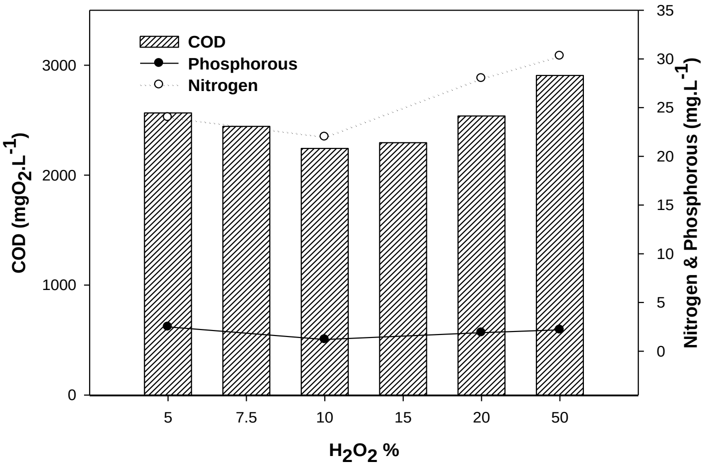

*Figure IV.4.8- COD, Nitrogen and Phosphorous for the different $H_2O_2$ doses*

From the analysis Figure IV.4.8 is possible to conclude that the Total Phosphorous and Nitrogen removal profiles are similar to those attained for COD depletion, achieving the highest abatement for the experiment where10% of the stoichiometric hydrogen peroxide value was used. With those conditions a final COD value of 2243mg.O2.L$^{-1}$, as well as 6 and 1.2 mg.L$^{-1}$ of N and P, respectively are reached.

The global results, integrating coagulation and Fenton's process, are shown in Figure IV.4.9.

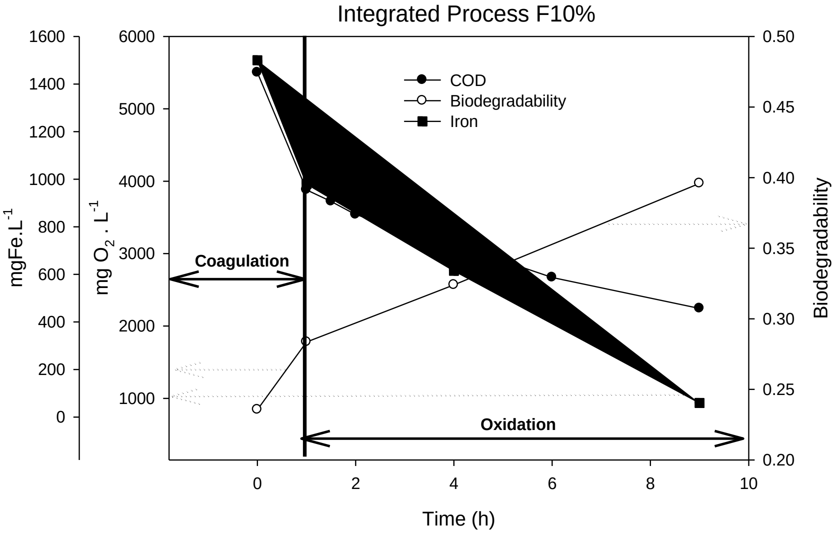

*Figure IV.4.9- COD, $BOD_5$/COD and iron concentration profile for the coagulation- Fenton like (10% of $H_2O_2$) during the integrated procedure time*

It is possible to conclude that in the first hour, where the coagulation stage takes place, 30 % of the COD was removed and the biodegradability was improved up to 0.28. In the oxidation process, the biodegradability increases until 0.4 due to the pollutants partial oxidation. COD removal was about 42.1 % showing that Fenton-like process is an effective methodology to promote organic load reduction besides improving biodegradability.

In what regards the iron content, after the coagulation, 36% was eliminated from the system through the ferric sludge formed in this stage. Moreover, after 8 hours of oxidation only 59 ppm of Fe remains in the system. It should be referred that the biodegradability enhancement and the decay on the iron content until a value that can be assimilated by the microorganisms (60 ppm) may promote an efficient subsequent biological oxidation.

### *IV.4.3.3 Biological treatment*

As previously mentioned, the main goal of this research was to provide a suitable pre-treated wastewater able to be easily further biologically oxidized. Figure IV.4.10 exhibits the bio-reactor efficiency during 3 weeks of treatment.

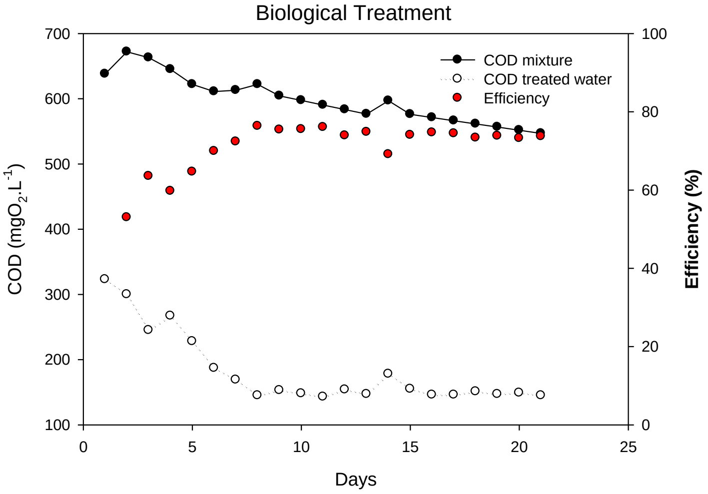

*Figure IV.4.10- COD removal for the raw and treated wastewater and biological efficiency in function of time*

The results show that COD reduction is significant. In fact, 52% of COD is abated for day one while a value above 73% is reached for the seventh day of treatment. This efficiency is maintained until the end of the experiment. The treated water reaches a final COD value of around 145 mg $O_2$. $L^{-1}$. Besides, the biological system shows also an impressive ability to remove the iron from the aqueous media, achieving a final value of 1 mg.$L^{-1}$. Thus, this methodology is able to reduce the iron content remaining after Fenton's process. In fact, dissolved iron is a well-known drawback of this chemical oxidation system. The resulting water has conditions to be discharged in the hydric resources, during the grape harvest period.

Table IV.4.2 presents the microbiological species evolution and the sludge biotic index (SBI). The SBI, according with the Madoni classification, classifies the treatment efficiency as described in the label aside of the Figure IV.4.2.

***Table IV.4.2- Microorganisms evolution - Madoni classification***

| **Days** | **Madoni Classification**<br>**Predominant Species** | **SBI** | **Class** |
|---|---|---|---|
| 1 | CC+SC | 10 | I |
| 2 | FSC | 5 | III |
| 3 | | | |
| 4 | FSC | 5 | III |
| 5 | FSC | 5 | III |
| 6 | | | |
| 7 | SC | 7 | I |
| 8 | SC | 7 | I |
| 9 | | | |
| 10 | SC | 9 | I |
| 11 | SC | 9 | I |
| 12 | | | |
| 13 | | | |
| 14 | SC | 10 | I |

**Label:**

FSC – Free Swimming Ciliate; CC – Crawling Ciliate; SC – Sessil Ciliate;

Class I: Activated sludge well colonized and stable, optimal biological activity and high treatment efficiency.

Class II: Activated sludge well colonized, almost optimal biological activity and sufficient biological activity

Class III: Biological treatment system with insufficient microbial activity and mediocre removal efficiency.

Class IV: Biological treatment system with low microbial activity and low removal efficiency.

From the results it is possible to conclude that an adaptation time of 5 days was needed until the SBR starting to give a satisfactory response. At the 7th day, the process was stable with the microbiological system presenting a positive trend, improving the oxidation rate until day 14. During this period, a high treatment efficiency and a well colonized activated sludge is observed leading to stable and optimal biological activity. This conclusion is in agreement with what was presented in Figure IV.4.10. These results show that the integrated chemical process under study is a suitable technology to be applied during the harvest period, improving the effluent quality and preserving the microorganism’s stability during this period.

## IV.4.4 Cost evaluation

The operating costs are an important factor on stakeholders decision for a new process. Thus, it is necessary to conduct an assessment of the operational costs before conceptualizing the physical structure of the wastewater treatment plant.

The costs related with the construction, mechanical instrumentation and maintenance were excluded, mainly because they depend on the site, existing equipment, the characteristics of the wastewater and the volume to be treated (Martins *et al.*, 2010b). Therefore, with the aim of evaluating the reliability of a possible industrial application of the developed treatment scheme for the studied effluent, only the operating costs were assessed. For this purpose, the amount of reactants required for pH change, the amount of coagulant and the $H_2O_2$ quantity used were determined.

The costs of the referred reactants are present in Table 0.1. The prices of these reactants were: $H_2SO_4$ (50%) = 0.141 €.$L^{-1}$, Ferric Sulfate (49.5%) = 0.24 €. $kg^{-1}$, hydrogen peroxide 50% =0.254 € .$L^{-1}$ and NaOH =0.366 €.$L^{-1}$. The costs associated with the sludge treatment and disposal were not considered.

***Table IV.4.3- Treatment costs of test 10% for the Winery wastewater***

| | **Costs €.$m^{-3}$** | | | | **Degradation** | | |
|---|---|---|---|---|---|---|---|
| | **$Fe_2(SO_4)_3$** | **$H_2SO_4$** | **NaOH** | **$H_2O_2$** | **KgCOD.$m^{-3}$** | **€.$m^{-3}$** | **€.$Kg^{-3}COD_{removed}$** |
| 10% F | 0.36 | 0.11 | 0.12 | 0.30 | 3.325 | 0.89 | 0.27 |

For each cubic meter of raw effluent, it was necessary 0.34 L of $H_2SO_4$ to decrease the pH to 3 and, at the end of the process, 0.45 L was added to reduce the pH to 8 before the biological treatment. The amount of coagulant required was 1.50 L and the most favorable hydrogen peroxide quantity was 1.22 L. Finally, it was necessary 0.32 L of NaOH to conclude the oxidative reaction and consequent iron precipitation.

The operation costs for the proposed treatment scheme are present in Table 3. The costs are fixed per $m^3$ (€.$m^{-3}$) and per kilogram of removed COD (€.kg $COD^{-1}$). As observed, the treatment of each cubic meter would costs 0.89 € corresponding to 0.27 € per kg of COD removed. A significant parcel of the total cost is due to $Fe_2 (SO_4)_3$, corresponding to up to 40% of the total cost. However, it is important to remember that this precursor had two distinct roles, as coagulant and as catalyst in Fenton's process. It is also impressive that the cost resultant from the sum of NaOH and $H_2SO_4$ dosages is very similar to the one related to the oxidant, reaching 26%.

Although the present process brings higher costs when compared with the direct application of the traditional biological treatment, the required time for biological oxidation decreases as well. This will reduce the costs associated with aeration. So, the advanced oxidation process followed by a biological system can be an environmental and economical alternative for the treatment of this kind of agro industrial wastewater especially during the peak period of winery wastewater production.

## IV.4.5 Conclusions

This paper emphasizes the performance of an integrated coagulation-Fenton-like system for the depuration of winery wastewater. The study revealed that the proposed methodology is efficient to treat this effluent, attaining an interesting biodegradability enhancement. The results obtained for the optimal conditions are depicted in Table IV.4.4.

***Table IV.4.4- COD, $BOD_5$/COD, TP and TN for all the stages***

| | **Raw** | **Coagulation** | **Oxidation** | **Biological** | |
|---|---|---|---|---|---|
| **COD($mgO_2.L^{-1}$)** | 5180 | 3880 | 2245 | 150 | |
| **$BOD_5$/COD** | 0.25 | 0.28 | 0.40 | --- | |
| **TP ($mg.L^{-1}$)** | 5.49 | --- | 1.2 | --- | |
| **TN ($mg.L^{-1}$)** | 55.8 | --- | 6 | ---- | Global |
| **COD removal %** | | 25 | 42 | 74* | 97 |

The coagulation step leads to 25 % and 40.7 % of COD and TSS removal respectively. This stage leads to a final effluent with a pH and dissolved iron content able to promote a posterior Fenton's peroxidation. The oxidation step leads to a COD reduction of 42%, and a $BOD_5$/COD improvement of 60%, with a final content of 59 ppm of iron. At the end of this pre-treatment scheme were also removed 89% and 80% of Total Phosphorous and Nitrogen.

The integrated oxidative process endorses a global COD removal of 56.6% and enhanced the wastewater biodegradability ($BOD_5$/COD = 0.4), showing that it could be efficiently used as prior treatment before a biological system. The operating costs inherent to the reactants required for the overall process are 0.89€.$m^{-3}$ which corresponds to 0.27 € per kg of COD abated.

The biological system needs an adaptation time and at the end of the 7th day up to 74% of COD removal was achieved along with the reminiscent iron elimination.

The described chemical processes when integrated with a posterior biological treatment reach the legal limits for the effluent disposal into the natural water courses during grape harvesting. Thus, the SBR can be designed to the average flow charge of the off season leading to a smaller reactors.

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## IV.5 From a lab test to industrial application: scale-up of Fenton-process as real treatment to olive mill wastewater

### IV.5.1 Introduction

In the last two decades great emphasis has been given to the problem related with the disposal and treatment of olive mill wastewaters (OMW), namely at countries producers of olive oil. Currently, the most used methodology to treat OMW is the storage in lagoons, and posterior evaporation by natural convection (Ginos *et al.,* 2006; Kallel *et al.,* 2009a). However, this approach contains severe drawbacks as low efficiency and sludge-disposal problems since it can only concentrate the effluent and does not promote the organic matter degradation, leading to an environmental problem to the surrounding populations due to the smell and possible water contaminations (Jarboui *et al.,* 2010). The main difficulties allied to the olive mill wastewater treatment are generally associated with the seasonal operation, high organic loading, and presence of organic compounds which are hard to biodegrade, such as phenolic compounds and long chain fatty acids (Mert *et al.,* 2010). For this reason, the biological processes are often times unsuccessful (Gonçalves *et al.*, 2007). However, when combined with chemical or physical systems, the pollutants reduction can be extremely improved (Khoufi *et al.,* 2006). There have been many works in literature to find efficient and cost effective treatment alternatives for OMW treatment including coagulation/flocculation/precipitation (Ginos *et al.*, 2006), chemical (Cañizares *et al.,* 2007), aerobic and anaerobic biological treatment (Mert *et al.,* 2010; Azabou *et al.,* 2010), membrane separation (Akdemir and Ozers, 2006; Ochando-Pulido *et al.,* 2013a) and their combinations (Andreozzi *et al.*, 2008; Ochando-Pulido *et al.*, 2013b). In particular, new trends are focused on integrating advanced oxidation processes (AOPs), which may be able to remove recalcitrant compounds (Martins and Quinta-Ferreira, 2009) . Truthfully, in the last years, AOPs have been applied to industrial wastewater as a polishing step (Khoufi *et al.*, 2006) integrated with conventional chemical (Ginos *et al.*, 2006) and/or biological processes (Bressan *et al.,* 2004) (Zorpas and Costa, 2010) in order to increase the overall treatment effectiveness.

The advanced oxidation processes are arising as suitable choices competent to degrade the bio-refractory pollutants for agro industrial wastewater (Kallel *et al.*, 2009b; Hodaifa *et al.,* 2013). In these systems the hydroxyl radicals formation is promoted, a very powerful oxidant that leads to effective oxidation. This is the case of the Fenton reagent, a process that is receiving great attention as a promising methodology for wastewater processing based on the oxidant power of hydrogen peroxide catalyzed by iron ions to enhance the formation of hydroxyl radicals, which promote chain reactions and consequently endorse an effective degradation of pollutants (Martins *et al.*, 2010). The

Fenton process (Zorpas and Costa, 2010; Lucas and Peres, 2009b) and Fenton-like process (Hodaifa *et al.,* 2013; Nieto *et al.,* 2011) were studied and described as effective treatment able to degrade the OMW refractory pollutants, nonetheless with some restrictions in its application. Compared to other AOPs, Fenton's oxidation presents several advantages, besides the $H_2O_2$ be environmentally friendly because it may be decomposed into oxygen and water, the $Fe^{2+}$ (catalyst) exists in abundance, has lack of toxicity and it is easy to remove from water, what makes this process a suitable technology (Kallel *et al.,* 2009b; Zorpas and Costa, 2010).

Additionally, a previous treatment could endorse a more effective oxidative treatment. Several studies propose the integration of a pre- coagulation stage that enables the solids removal, some organic matter subtraction, but above all promotes a more consistent effluent without large variations of organic and inorganic loads, allowing an improved oxidation (Rizzo *et al.,* 2008) (Papaphilippou *et al.,* 2013). Other possibility is the integration with a biological treatment, normally a more economical option that for itself would be inefficient, but could be favored by the biodegradability enhancement promoted by the chemical reaction (Lafi *et al.,* 2009; Zorpas and Costa, 2010).

The main objective of the present work was to investigate the depuration of an industrial wastewater from an olive oil production coming from a storage lagoon using the Fenton technology. The aim was to attain a stream legally able to be discharged to the local sewage collector (COD $\leq$ 1250 $mgO_2.L^{-1}$). Thus, lab tests were effectuated in a jar test apparatus and posteriorly were scaled up to a continuous industrial scale WWTP where the OMW treatment was performed. Whatever the treatment requirements, the economic factor is always superimposed to the operational dimensioning for a future application, and the reagent's required quantity is one of the most important factors to consider, as it could determine the economic feasibility of the process. In fact, the final decisions will take into account the amount of reactants and the simplification of some operational procedures with the intention of obtaining a simple, robust, economic and viable treatment. A strong novelty of this work is the industrial application of the laboratory developed methodology.

## IV.5.2 Materials and methods

### *IV.5.2.1 Olive mill wastewater characterization*

The wastewater was collected in Spain, at the province of Badajoz on the same storage lagoon where later the industrial effluent was treated. The effluent was characterized by dark color, high amount of suspended solids, moderate COD, low/moderate $BOD_5$, Nitrogen (TN) and Phosphorous (TP) content, as well an acidic pH.

*Table IV.5.1- Wastewater Characterization for the lab tests*

| COD ($mgO_2.L^{-1}$) | TN ($mg.L^{-1}$) | TP ($mg.L^{-1}$) | TSS ($mg.L^{-1}$) | $BOD_5$ ($mg.O_2.L^{-1}$) | $BOD_5$/COD | pH |
|---|---|---|---|---|---|---|
| 6450 | 42 | 21 | 3190 | 2130 | 0.33 | 4.9 |

### *IV.5.2.2 Reagents*

All reagents were industrial grade provided from ADVENTECH suppliers and were used without any additional purification process as was the case of the hydrogen peroxide (49.5%), ferric sulfate, ferrous sulfate, sulfuric acid (30%) and sodium hydroxide.

### *IV.5.2.3 Analytical methods*

All analyses were performed according to the standard methods for the examination of water and wastewaters (Greenberg *et al.*, 1985).

The Total Suspended Solids (TSS) were measured by Standard Methods: "2540 D: Total Suspended Solids Dried at 103 - 105 °C". In particular, chemical oxygen demand (COD), was measured by the closed reflux, colorimetric method, using an HANNA HI 839800 thermoreactor and a HANNA HI 83224 photometer. pH (HANNA HI 4522) was adjusted adding $H_2SO_4$ (30%) or 3 M NaOH, when necessary. The dissolved oxygen for $BOD_5$ was measure using a HANNA HI 4421 dissolved oxygen meter. Ammonia nitrogen ($N\text{-}NH_4$), nitrite nitrogen ($N\text{-}NO_2$), nitrate nitrogen ($N\text{-}NO_3$), and phosphates ($P\text{-}PO_4$) were analyzed with a HANNA HI 83224 photometer.

All the referred measurements were determined in non-filtered samples. To check repeatability, some experiments were randomly run in duplicate (with the exception at the industrial scale) and the withdrawn samples were analyzed in triplicate to minimize the experimental error. The deviations between the performed runs were always lower than 7% and 15% for COD and $BOD_5$ results, respectively.

### *IV.5.2.4 Experimental work development*

In this work, two distinct parts were performed; initially at lab scale, the coagulation study that accomplished the solids fraction removal in addition to the pH drop until a desirable value to Fenton oxidation was carried out. Wastewater samples were introduced in a beaker and stirred and the $Fe^{2+}$ dosage was added; the reaction started when a known volume of the $H_2O_2$ was inserted. The oxidation terminated with NaOH addition until a pH of 10.

In a second step the obtained results were scaled up to the industrial wastewater treatment plant, also designed for this purpose and for the mentioned hereafter treatment scheme. In contrast with the laboratorial tests, this installation works continuously with a flow rate of approximately 1.5 $m^3.h^{-1}$.

#### *IV.5.2.4.1 Coagulation experiments*

In this physical-chemical pre-treatment, the experiments were performed through a jar test apparatus and an iron based coagulant $Fe_2\ (SO_4)_3.5H_2O$ was used by applying several dosages, between 500 and 3000 ppm. The coagulant was dosed into 250 mL of wastewater and the experimental process consisted in three steps, a first stage with a flash mixing for one minute (120 rpm) followed by 20 min at 20 rpm in order to promote the agglomeration. Posteriorly, two samples were taken, being the first one the resultant supernatant and the second a sample in which sodium hydroxide was added until reaching a pH value of 11. One hour of sedimentation was promoted and the supernatants were analyzed at the end of sedimentation period by measuring COD and TSS.

For the most favorable conditions, a 2 liters assay was performed, given that the main purpose, besides the COD removal, was also to maintain the pH unchanged in order to avoid the subsequent pH adjusting for the posterior oxidation thus eliminating another procedural step.

#### *IV.5.2.4.2 Fenton Oxidation*

All the experiments were performed at room temperature, without pH control and all the reactants were added in a single step.

The oxidation process was accomplished in a jar test apparatus where each experiment was prepared into a stirred glass reactor using 250 mL of wastewater. The pH value was provided by the coagulation stage, and its value runs freely during the experiments between 2.8 and 3.3 for all the performed experiments. After the addition of a certain iron dose, the reaction starts when $H_2O_2$ was added in the system. Along the oxidative process, several samples were withdrawn during the procedure time for subsequent analysis. Sodium hydroxide was added at the end of the previous established reaction time to promote the precipitation of iron hydroxides and subsequent iron removal in addition to the residual $H_2O_2$ in solution extinguishment. The samples analyses were performed at least after 24 hours. The COD results of a first test with 48 hours oxidation, revealed that for retention times higher than 24h, the organic content degradation improved only 8% until the end, hence limiting the oxidative operation for greater residence times, with respective diminution of treatment capacity.

#### *IV.5.2.4.3 Industrial application*

The industrial application was performed in CASAT SA, and the WWTP simplified scheme is exhibited in Figure IV.5.1. The wastewater resulted from the 2012 campaign was stored in a pond, without any previous treatment. A detailed description of each stage and respective units is also performed.

The process was composed by four distinct stages, all of them dependent and conditioned by the upstream and downstream units, which were adjusted in order to accomplish their specific purpose, as describe below:

- Coagulation: When the effluent was pumped from TH, the coagulating agent is added in line and goes to D1 where is subjected to rapid mixing and then is discharged and submitted to decantation.
- Oxidation: The effluent derived from D1 is forced by action of a pump to go to RT. During this discharge iron sulfate and hydrogen peroxide were added, and the mixture was promoted, being then discharged in RT where the reaction time was performed. When this tank was full, at the same time that enters water from D1, the same volume was expelled to D2.
- Neutralization/flocculation: When the water comes from RT, NaOH was added to correct the pH for a value of 10, cationic flocculant was injected and during the discharge to D2 the mixture was promoted.
- Discharge: In D2, and after the adequate settling, the sludge was removed by action of a mono-pump, the clean water exits through the upper crown, and the pH was corrected to 7-9, in order to discharge to the collector

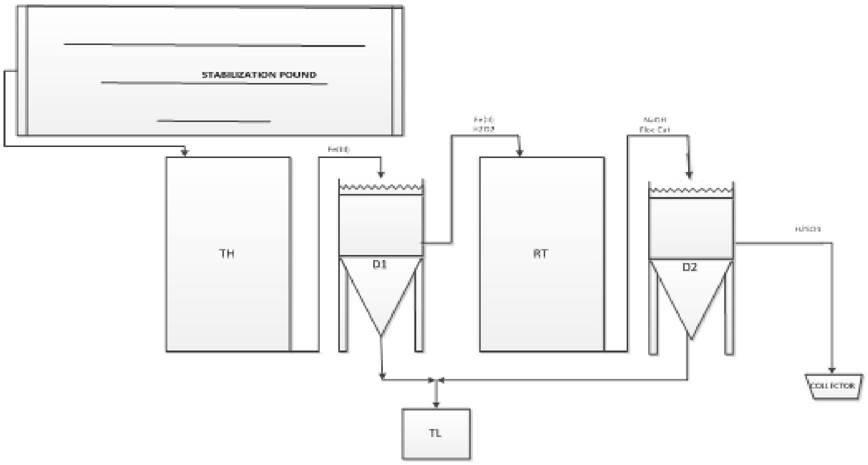

*Figure IV.5.1- Simplified Wastewater Treatment Plant Scheme*

In the following section the main results and the changes in the process will be described. While in the lagoon it was observed that the Chemical Oxygen Demand decrease over time, which might be explained by two facts that were promoted during the stabilization in the lagoon: sedimentation of the organic matter on the bottom, and also the existence of microbiological action (Jarboui *et al.,* 2010). The continuous treatment was carried out with an average flow of 1.5 $m^3.h^{-1}$, with an estimated treated volume of 450 $m^3$ of effluent.

### *IV.5.2.4.4 Biological Treatment*

After the industrial application, samples were taken during the process. The resultant treated wastewater was submitted to Aerobic Biological Treatment performed at laboratory scale and executed in a Suspended Biological Reactor (SBR) of 500 mL with 400 mL of aerobic sludge, equipped with stirring plat and stirred bar at speed rate of 150 rpm and aerated by air diffuser, promoting the biomass diffusion with the aim of providing the necessary oxygen concentration to endorse aerobic conditions. The temperature was kept around 22 ± 2 °C and the internal pH was unchanged within pH 7.6-8.8 depending on the added sample.

The treatment was composed by five distinct sequential phases:  filling (5 min), aeration-reaction (19-20h), settling (3h), withdraw and idle (5 min). The reactor was operated with a solids retention time (SRT) of 10 days, and the SBR was inoculated with 150 mL of biological sludge (1500-2000) $mg.L^{-1}$ of Volatile Suspended Solids), from the aeration tank of a winery WWTP. The tests were executed without any sludge adaptation and regular COD analyses were carried out.

## IV.5.3 Results and discussion

### *IV.5.3.1 Laboratorial experiments*

#### *IV.5.3.1.1 Coagulation experiments*

In the coagulation processes, various inorganic materials such as iron, magnesium and aluminum can be applied and their effect could be potentiated by the use of some flocculants. However, the main aim of this stage, was to attain an effective COD removal and TSS reduction, besides providing the operational conditions that could favor a posterior Fenton oxidation, specifically the pH drop into the desirable range (3-4). For this stated aim the use of flocculants with pH at the neutral region (Ntampou *et al.*, 2006) should be inefficient as also would become expensive an extra acidification stage.

Due to previous tests effectuated on the WWTP, iron sulfate showed to be the more effective coagulant on the case of a winery effluent treatment for the pre-oxidation stage. However, in order to take fully advantage of the existent WWTP equipment without any kind of investment in the olive mill wastewater now under study, it would be impossible to make pH adjustment prior to this stage, so the tests were conducted at raw effluent pH.

Initially, in order to enable substantial solids removal and to provide most favorable water conditions for the subsequent oxidation, the study of the coagulation process has been performed. As result, five trials between 500 and 3000 ppm ferric sulfate were assessed, between the minimum and the maximum reactant amount considered acceptable for industrial application in view of the inherent cost. The main results are presented in Figure IV.5.2.

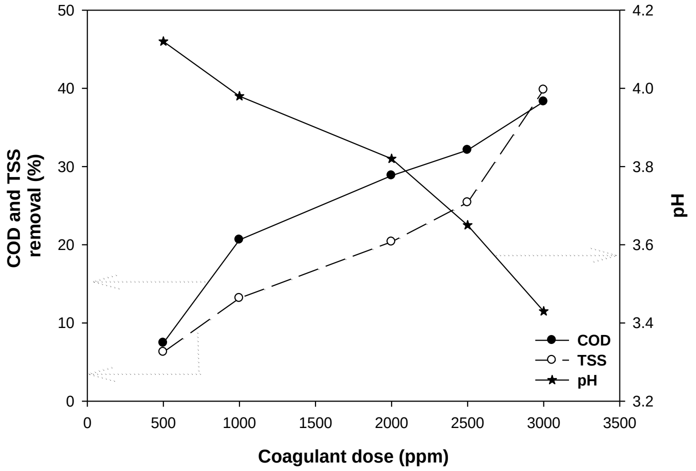

*Figure IV.5.2- Variation of COD and pH according to the coagulant dose*

Figure IV.5.2 represents the obtained COD and pH values correlated to the ferric coagulant added dose. There is a clear trend towards the increase in coagulant concentration with consequent COD reduction and more favorable lower pH values. Nonetheless, this could lead to a decrease to undesirable values lower than 2. In fact, the aim is to directly apply a Fenton's oxidation to the coagulated effluent, but pH < 2 leads to a reduction of the reaction extent (Lucas and Peres, 2009b).

Taking into account the abovementioned factors, the economic, operational and reactive constraints, the best selected conditions were 3000 ppm of coagulant that obtains COD decreased to 3980 $mgO_2.L^{-1}$ that corresponds to 38% of removal, with 40% of TSS depletion in addition to the pH drop until 3.4, a favorable value to the oxidation stage. These data indicate that this step efficiency increases with growing coagulant dose, especially for the higher concentrations were the difference is very significant (25% vs 40% for 2500 and 3000 ppm respectively), presenting a relation between TSS and COD as can be observed by the removal profile.

Such results could be justified by two reasons: in a first step a part of the coagulant added acidifies the medium (Ntampou *et al.*, 2006), and the pH of the effluent approached to the most favorable pH for coagulation; and then the remaining concentration form various hydrolysis products that integrate $Fe(OH)_3$, originating compounds that have high cationic charge which provides the neutralization of the electrostatic charges existent on colloidal material and also to connect to negatively charged particles promoting the formation of a fraction of sludge, (Tatsi *et al.*, 2003) that will settle.

#### *IV.5.3.1.2 Fenton Oxidation*

The economic factor of a process is always superimposed to the operational dimensioning for future application, and the required Fenton's reagent dose is an important factor to consider as it could determine the economic feasibility of the technology.

Contrary to what is normally executed, the doses of reagents are not pre-determined according to the COD complete degradation, but by taking into consideration the minimum amount of reagents liable to achieve the desired removal to the imposed discharge limit. For this reason an array of tests with a fixed concentration of catalyst (500, 1000 and 1500 ppm) was carried out, each with varying [oxidant/catalyst] in weight/weight, being this ratio very important in the effectiveness of the Fenton degradation (Lucas and Peres, 2009b; Hodaifa *et al.*, 2013).

The contact time of Fenton's reagent and wastewater in the reaction mixture was 1320 min (24 h) and intermediary samples were taken; the initial pH was the resulting value provided from the coagulation stage (pH 3.4).

Figure IV.5.3 shows the COD attained for the oxidation lab tests for different concentrations of $Fe^{2+}$ and $H_2O_2$ (ppm) and the respective oxidation efficiency.

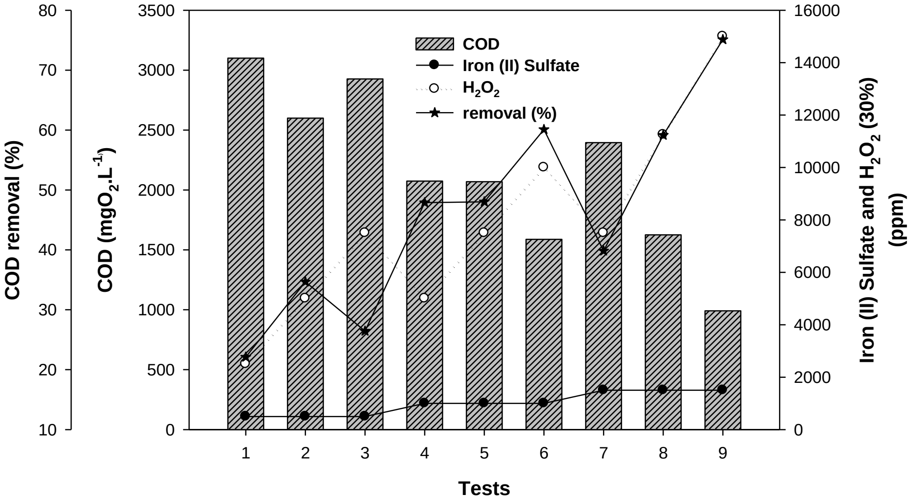

*Figure IV.5.3- COD, removal efficiency and reactants doses used for the oxidation experiments*

It is possible to observe that the increase in the iron load and hydrogen peroxide dose (showed in ppm in the right side of the Figure IV.5.3) led to better COD removal.

Initially 3 tests (1-3) were performed, with the mentioned different ratios (w/w) 5, 10 and 15. The three tests had the same iron content and different oxidant concentrations. By the efficiency analysis it is possible to conclude that the best result arises for intermediate ratio, having a significant gain compared with the first (22 vs 35 %). However, for higher oxidant concentration there was a marked decrease in the efficiency (26%), promoted by the scavenging effect due to the oxidant excess. When the oxidant concentration is quite large there are parallel reactions which lead to the consumption of hydrogen peroxide by reacting with the formed radicals, thereby decreasing both amount of radicals as well as the peroxide concentration (Deng and Englehardt, 2006; Pignatello *et al.*, 2006). For this reason, the ratio 15 was disregarded, appearing in the three further experiments the ratio [$H_2O_2$: ferrous sulfate] equal to 5, 7.5 and 10, for the tests with 1000 and 1500 ppm of catalyst.

The tests sets 4-6 and 7-9, reveal that for the same iron dose, the increase on the hydrogen peroxide dose permits a better COD degradation with a huge gain on the process efficiency. As these tests were performed with the purpose of an industrial application, the trials were carried out aiming to achieve a COD value below 1250, which corresponds to the maximum allowable legal value for discharge in the municipal sewage.

This work involves optimization of the smallest possible amount of the reagents in order to make the process economically acceptable. In this case it was needed 1500 ppm of iron sulfate and 15000 ppm of $H_2O_2$, a ratio of 10, in order to attain best efficiency of 75% for the COD removal that corresponded a final COD value of 995 $mgO_2.L^{-1}$.

### *IV.5.3.2 Industrial Scale UP*

The wastewater was stored in a lagoon during 4 months to stabilize given by some biological activity but also for the solids settling, instigating a pre-treated wastewater more limpid, with a small $BOD_5$, and more homogeneous mixture for the posterior treatment.

#### *IV.5.3.2.1 Coagulation*

This stage was the most difficult to control because its efficiency depends greatly on the effluent constitution. Since the effluent comes from a pond, there is a range of concentration profiles (COD and solids) over the time of treatment, requiring consequently the coagulant dose variation. During this period, efficiency and accuracy of the added amount was carried through the obtained pH value by increasing the concentration if the pH went up and lowering the concentration if the pH falls too much, in order to keep it between 3.2-3.8.

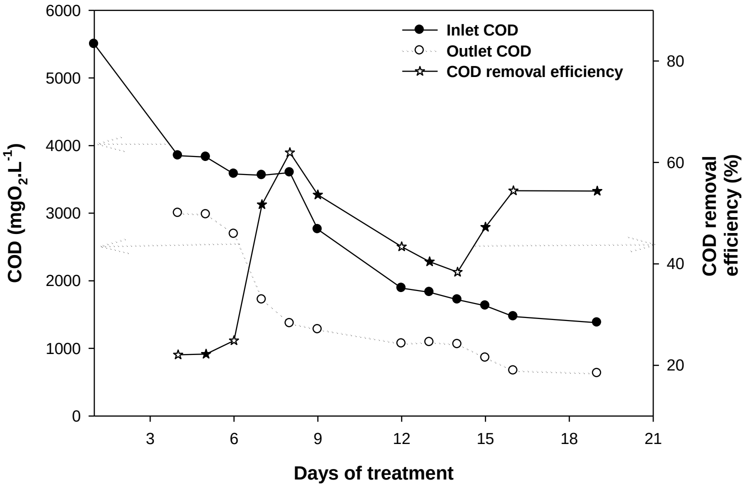

*Figure IV.5.4- Inlet and Outlet COD and removal efficiency for the coagulation stage*

Figure IV.5.4 shows this stage efficiency in the removal of the chemical oxygen demand, as function of the days of treatment. It is observed that the efficiency increases over time, also promoted by the lowering in the chemical oxygen demand of the inlet wastewater.

Initially, until the 3rd day, 3000 ppm of coagulant were added. However, the solid amount formed after coagulation was high and the pH (2.8) was too low, whereby to the 3rd day the dose was reduced to 2500 ppm by keeping afterwards always constant throughout the treatment, lowering the pH to a value of 3.4 ± 0.2. The same happens on the 14th day, and it was necessary to reduce the coagulant concentration to 1500 ppm to attain the described conditions with an effective increment on the process efficiency in the next day.

From this analysis one can conclude that initially there was coagulant in excess, which promoted a re-stabilization of the colloidal load, which in practice causes a dispersion rather than agglomeration and sedimentation resulting solid colloidal particles promoting a decreased efficiency (Sarika *et al.,* 2005). Therefore, diminishing the coagulant dose immediately had a positive effect with an increase of over 200% on the system efficiency, where over 40% of the organic matter was eliminated. The observed results allow to conclude that this stage in the way it was conducted, promotes the preparation of the effluent for the further oxidative process besides being responsible for a significant reduction of COD, thus confirming to be an indispensable step of the overall purifying process.

The added coagulant amount of this incomplete coagulation will provide dissolved iron in solution that will participate later in oxidation (Nieto *et al.,* 2011) (Fenton-like) promoting greater efficiency in the Fenton’s process with especial advantage on the automatic adjustment of the pH to a favorable oxidative process value.

#### *IV.5.3.2.2 Oxidation Treatment*

As expected, there is a certain concentration of iron (Fe (III)) in solution triggered by the coagulation stage. However, given the conditions of the implemented process, it was impossible to determine these quantities, as there were variations caused by the coagulant dosing pump and variations of the effluent flowrate, among others. Besides the remaining iron in solution, iron (II) was added in a solution at 7.5% (w/w) as well the hydrogen peroxide dosage that was pre-established. The organic load from day 1 was associated to the content of the Homogenization Tank (TH), and for this reason its value was slightly higher than the one that was observed for the remaining days.

Figure IV.5.5 shows the COD after coagulation (inlet) and after the oxidative reaction (outlet), the dosage of Fenton's reagent, and the efficiency removal of the oxidation process.

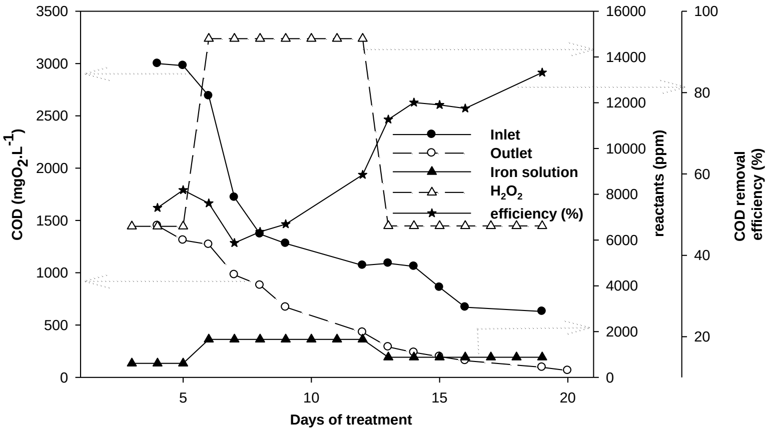

*Figure IV.5.5- Inlet and Outlet COD, removal efficiency and reactants doses used for the oxidation experiment*

Alone for itself, at the end of the performed depuration treatment period, the wastewater had COD very close to 1500 mgO$_2$.L $^{-1}$ due to the partial degradation promoted in the storage lagoon (Khoufi *et al.,* 2008; Jarboui *et al.,* 2010). For this motive it was necessary to adjust the amounts of reagents to avoid the appearance of competing parallel reactions which would reduce the oxidation efficiency (Kallel *et al.,* 2009b). Whereas the proposed target would maintain a COD below 1250 mgO$_2$.L$^{-1}$, being the treated water at the end of coagulation stage with such lower organic load that was necessary (Figure IV.5.5), the reagents dosages at the oxidation step were decreased on the 13th day of operation in order to optimize the overall efficiency for the stipulated output value and thus save on chemicals, making this process economically more favorable.

As can be seen, the outlet COD on the 5th day was insufficient for discharge. For that it was needed to increase the reagents dosages ($H_2O_2$ and iron) to promote a stronger oxidation. The result of this action was observed immediately on the following day; however, it should be noted that the wastewater volume to be treated is much smaller than the volume of the tank (continuous treatment) where the reaction was occurring (RT), and therefore there was a mixture effect of the different treatment days, taking a longer time to reach the efficiency value and consequent final COD value that was expected on the oxidation stage.

On the 7th day, this process reached the desired COD (970 mgO$_2$.L$^{-1}$), being kept the dose of reagents identical until the 13th day with a significant increase in the process efficiency. In this day and considering that the resulting oxidation COD was 430 mgO$_2$.L$^{-1}$, it was decided to lower the $H_2O_2$ and iron amounts, that in turn slightly decreased efficiency removal in the next few days but increased it afterwards considerably up to the maximum value measured over the entire period. Indeed, the effluent organic load considerably decreased, thus justifying efficiency increase towards 100% and for this motive the previous dose could be to have an adverse impact due to competing side reactions taking in the oxidation reaction promoted by excess of reagents, that could be iron, hydrogen peroxide or booth, thereby decreasing the reaction (Babuponnusami and Muthukumar, 2012) efficiency, being necessary a rigorous control and assessment of the treatment conditions during the treatment time (Guieyss and Norvill, 2014). At the end of the treatment the oxidized water had a COD of 65 $mgO_2.L^{-1}$. The samples taken from the reaction tank (oxidation process), were completely translucent with the respective settled iron sludge at the vessel bottom.

#### *IV.5.3.2.3 Neutralization / flocculation*

The last step was the wastewater neutralization and the catalyst precipitation (iron in solution), which also fosters a coagulation of some of the resulting colloids from the purifying process (Kallel *et al.*, 2009a). To facilitate sedimentation, flocculant was added with the purpose of increasing the flock size, yielding a more clean water.

Figure IV.5.6 the resultant output samples taken from the collector from 30 to 30 minutes so as to verify the achieved improvement with cationic flocculant addition.

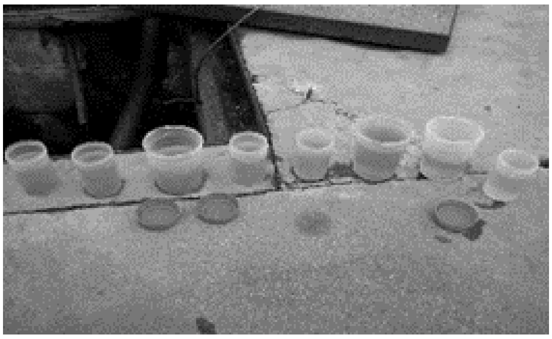

***Figure IV.5.6- D2 samples photos to assess the process efficiency before (left) and after flocculant addition (right).***

According to Figure IV.5.6, it could be observed that the flocculant addition brought an improvement in the process. Being a continuous process, the iron oxides did not have time to settle properly and were subsequently entrained by the wastewater flow coming out of the system, being maintained in suspension over time. After the flocculant addition it was possible to visualize a cleaner supernatant, that is an indicator of less iron flocks, which as shown in from left to right, leads to a significant decrease in coloration of the discharged treated water with consequent lower Chemical Oxygen Demand.

### *IV.5.3.2.4 Overall efficiency*

Regarding the in-situ tests, Figure IV.5.7 presents the COD values of the inlet (In) industrial wastewater from a storage pond without any pre-treatment along time, and those achieved for the effluents after being submitted to the coagulation and Fenton´s oxidation and precipitation stage as well, procedures separately as well as the ones of the outlet treated wastewater (Out) discharged into the sewage collector during 14 days of continuous operation.

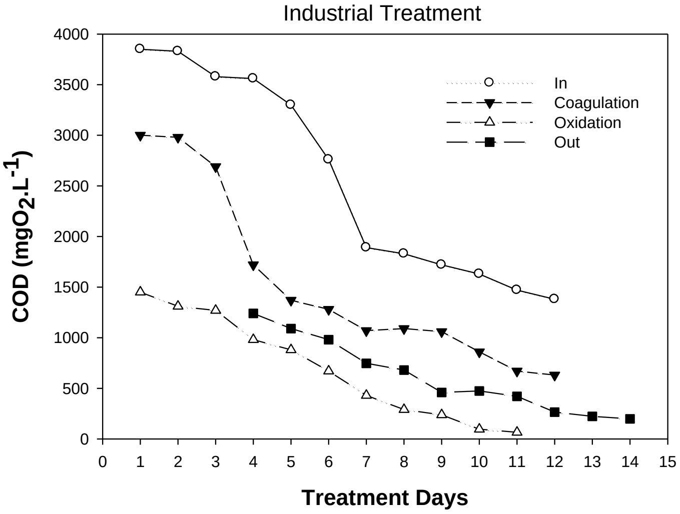

*Figure IV.5.7- COD profiles for the different wastewater streams of the Industrial Plant*

From these results it can be observed that the COD of the inlet wastewater shows a high reduction of the organic load over time to less than half from the start to the end of the tests. This feed stream variation shows that the storage pond enables the organic content reduction, quite possibly due to the sedimentation of pollutants, which led to a raw wastewater with different concentrations in suspended solids, but also due to the microbiological action which manages to remove some biodegradable organic material (Jarboui *et al.,* 2010).

Over the coagulation process there was the need to change from 3000 to 1500 ppm on ferric coagulant addition, which reduces considerably the pH to values that misfits the oxidation. The treatment with coagulation was a qualitative leap when reducing the dosage of coagulant, demonstrating the need for continuous monitoring and correction of the reactants dosage, because when in excess, may cause undesirable adverse effects disabling an aggregation of pollutants and therefore a smaller removal efficiency. By the slope of the different curves it is possible to infer if the efficiency of each step is maintained throughout the process. In order to reduce the overall costs, the chemicals dosages in the oxidation stage were also optimized decreasing the amount of iron and peroxide to 35% and maintaining the final COD close to 300 $mgO_2.L^{-1}$. Presenting the same trend, the Fenton process also enables the COD removal, reaching COD values of 65 $mgO_2.L^{-1}$, proving to be very effective in the degradation of dissolved pollutants resulting from the production of olive oil.

In the overall process, the evolution of the efficiency of each stage of treatment was truly significant. The coagulation was able to remove 30% of COD in the first day and 50% in the last one, while the Fenton´s oxidation ranged from 40 until a remarkable 90% in the last day, also depending on the clotting and operating equipment, thus subject to slight variations. The discharged water started out with 1200 $mgO_2.L^{-1}$ on day 1, because the start-up phase of the system is always more difficult and there is an amount of effluent that is only partially treated; however, with advancing time it stabilized very close to the 300 $mgO_2.L^{-1}$ reaching in the last day of operation nearly 200 $mgO_2.L^{-1}$.

Figure IV.5.8 shows the Chemical Oxygen Demand in the various treatment steps, the overall efficiency of each stage and also the $BOD_5$/COD ratio (biodegradability) that enables to infer the possibility of the treated water being subjected to posterior biological treatment.

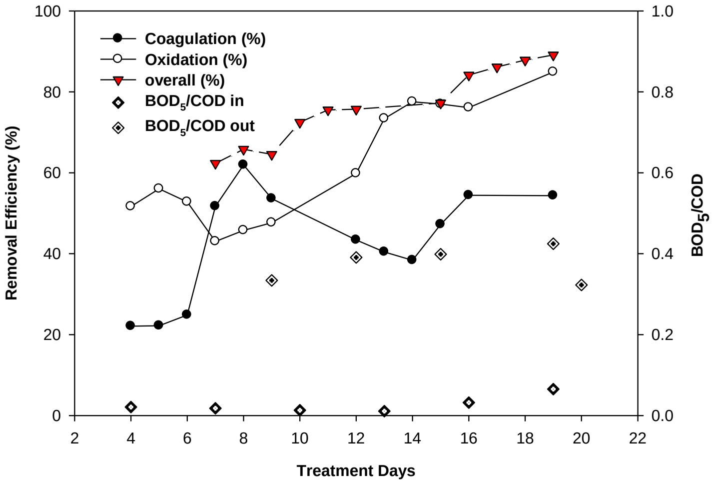

*Figure IV.5.8- Efficiency profiles for the different treatment stages of the Industrial Plant and the Biodegradability before and after the treatment*

Since this is a continuous process, one cannot say that the achieved final result is the sum of the effectiveness of each stage. This is because the volume of each tank corresponds on average at 2 days of flow operation, having the all facility from D1 to D2 the possibility to store a volume of about 6 days of treatment. With this, the mixture of wastewater with different removal efficiencies and organic loads, promotes a treated water with different COD values. However, even after some decreases in the partial efficiencies, that obliged as reported the modification in the reagents doses, the overall efficiency is always increasing reaching at the last day of treatment a remarkable 90% of COD removal.

As regards the possibility to apply a biological treatment, it can be noted that the raw effluent lacked any likelihood of success. As already mentioned, the chemical oxygen demand was waning throughout time, demonstrating that there was biological treatment at the storage lagoon, promoted through the action of microorganisms that consume a large part of the biodegradable fraction (the higher obtained value of the $BOD_5$/COD was 0.065), with a substantial amount of non-biodegradable organic matter. It is in this context that is worthy to emphasize the usefulness and effectiveness of the applied integrated process, that besides enabling organic material mineralization towards a final low COD value (200 $mgO_2.L^{-1}$), ensures that 40% of this value is biodegradable ($BOD_5$/COD = 0.4).

Figure IV.5.9 shows samples resulting from the different stages described before, within the respective sequence treatments where the visual results on each of them reflect the system efficacy, in particular on the 19th day of operation.

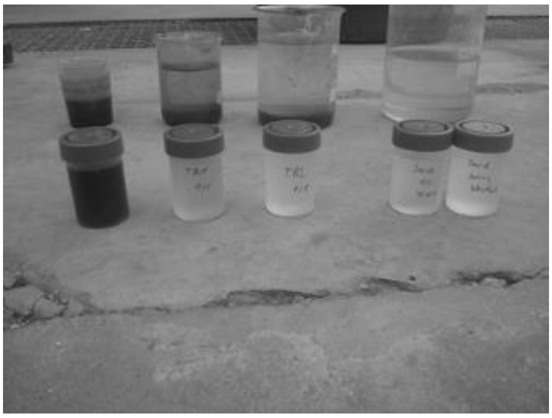

***Figure IV.5.9- Samples of all existent streams in the 19th day***

As can be easily perceived, the outlet water had a higher organic loading than the water provided from the oxidation stage, nonetheless well below the target value, demonstrating high overall process efficiency, with a clear final water complying with the legislation for discharge in municipal collector.

#### *IV.5.3.2.5 Biological treatment*

Normally, olive oil manufacturing facilities are usually small plants with a seasonal wastewater stream, and the Fenton process would be sufficient to manage efficiently with the produced effluents. However, this kind of system significantly increases the cost of treatment, so that it should be integrated with a low cost biological treatment, also demanding low intervention, or even to achieve a level of clearance able to provide water amenable to reuse, or depending of the specific requests, to be able to be discharged into the surrounding hydrologic resources. The efficiency of the Fenton process as a pre-treatment step of wastewater was proved, increasing the biodegradability until a value that enables the biological treatment, with a $BOD_5/COD=0.35-0.4$.

To assess the availability of the possible integration, the treated OMW wastewater withdrawn from the final collector was fed into the SBR for a tertiary treatment. Figure IV.5.10 shows the COD variation in the SBR effluent and removal efficiency.

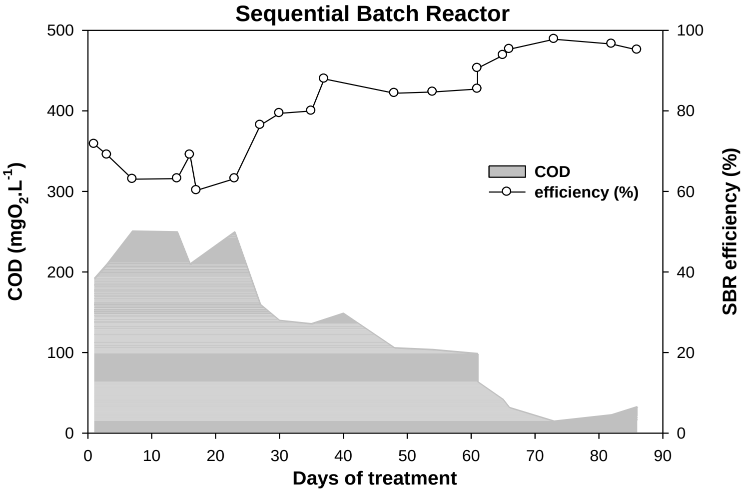

***Figure IV.5.10- COD concentration in effluent and efficiency of SBR during the operating periods.***

There were some fluctuations in the effluent COD and respective efficiency, which can be divided into 3 parts: until day 27, an adaption time is observed showing an efficiency in the range of 60 and 76%, allowing to get a treated water with COD ranged between 160 and 210 $mgO_2.l^{-1}$; from this day until day 60 where the system was fully adapted with an efficiency almost constant (80-85%), a COD in the order of 100-140 $mgO_2.\ L^{-1}$ was achieved, enabling the discharges into water courses according to the Portuguese law; finally, from de 60th day until the end of the experiment, a high COD removal of 95±2% and a resultant water with COD's below 40 $mgO_2.L^{-1}$, ensure its re-use in the industrial facilities. The stated results confirmed that the Fenton oxidation is one of the most effective treatments, being considered as a viable pre-treatment for the destruction of hardly biodegradable compounds which inhibit the use of biological processes (Guieysse and Norvill, 2014).

## Cost evaluation

### IV.5.4.1 Laboratorial

The major restrictions to exchange or to implement a new process are the operating costs, which have to be assessed before the scale up design to present the treatment system to the future user/consumer. As in this case the installation is already in place, it will only be necessary to ensure the feasibility of the proposed method with the existing resources and equipment, solely with the exchange of materials and reagents without any investment costs.

For this purpose the coagulant dose, the iron sulfate amount, the $H_2O_2$ quantity and the requested NaOH to finish the oxidative reaction as well as the sulfuric acid to the pH change before discharge were determined.

For each liter of wastewater, it was necessary 3 mL of coagulant to enable the solids removal and standardize the wastewater as well as promoting the decrease of the pH to 3.4. As discussed before the required catalyst concentration was 1.5 g and the most favorable hydrogen peroxide was 15 mL. Finally, 1.1 L of NaOH was needed to terminate the reaction and 0.45 L of $H_2SO_4$ to reduce the pH to 8 to provide an appropriated wastewater to be discharged or to be conducted for biological treatment.

### IV.5.4.2 Industrial

The operation costs for the proposed treatment scheme are reported in Table IV.5. 2. The present values are representative from all used chemicals to treat 450 cubic meters of effluent, being the displayed prices correspondent to average values obtained throughout the treatment period. The costs are fixed per m3 (€.m-3) and per kilogram of removed COD (€.kg CODremoved-1) and represent the average value obtained with the consumed reagents (during the treatment) referent to the total volume treated coming from the pond. The associated costs with the sludge treatment and disposal were not the different scales considered in the values of Table IV.5.2.

*Table IV.5.2- Costs for treatment*

| | **Costs** | | | | | | **Degradation** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **$Fe_2(SO_4)_3$** | **$FeSO_4$** | **$H_2SO_4$** | **NaOH** | **$H_2O_2$** | **Flocculant** | *** Enterprise supplier's prices<br>**unmeasurable value<br>***average** | | |
| **€.kg$^{-1}$ *** | 0.25 | 0.2 | 0.1 | 0.80 | 0.45 | 5 | KgCOD /m$^3$ | €/ m$^3$ | €/ KgCOD$_{removed}$ |
| **Laboratorial (€).m$^{-3}$** | 0.75 | 0.3 | 0.1 | 0.2 | 6.75 | ** | 5.46 | 7.87 | 1.44 |
| **Industrial (€).450 m$^{-3}$** | 250 | 50 | 50 | 80 | 540 | 7.50 | 1.99*** | 2.17*** | 1.09*** |

As it possible to observe for the presented treatment, each cubic meter of effluent costs 2.17 € getting 1.09 € for each kg of COD removed. The hydrogen peroxide has a significant relevance to the total cost with more than 50% of the total reactants charge.

Comparing the two scales, laboratorial and industrial, besides the price being so different, the cost for each cubic meter could be justified by the quantity of organic load arriving to the system that diminishes over time, what in turn, has succeeded in decreasing the quantity of coagulant and reagents, thus contributing to the operating costs reduction. Moreover, the treatment cost to remove one kg of COD is much similar, proving that the execution at laboratory level allows for a rapprochement of the actual operating costs for the proposed treatment, since the effluent derives from the same place as well as the same technology and reagents are used.

In this case it is possible to conclude that the advanced oxidation process can be an environmental and economic interesting alternative for the treatment of this kind of agro industrial wastewaters and enables the application of subsequent biological systems in order to further reduce the organic charge, thus allowing a posterior discharge into the hydrological resources.

### IV.5.4 Conclusions

This work shows that a simplified process combining the Fenton oxidation coupled to a previous coagulation stage is able to depurate the OMW. Moreover it also improves the wastewater biodegradability enabling the availability of posterior application of an aerobic biological treatment. Thus a wastewater containing a large amount of pollutants and phenolic acids that cannot be easily treated by conventional physicochemical and biological processes is transformed into water able to be reused or discharged into the natural waterways without any damage to the surrounding resources.

The laboratorial and industrial scale has significant differences, particularly on the requirement reagents doses to achieve a specific goal, as a certain COD value.

At the laboratorial scale, the coagulation stage achieves COD reductions of 38% and 40% of TSS, where the pH was changed by the acidic character of the coagulant until a value (3.4) that enables the Fenton oxidation, which can lead to a COD reduction of 75%. With this two-step treatment, the overall COD removal attains 85% and allows the wastewater discharge into a municipal collector. The operating cost inherent to the process are 7.87 €.m$^{-3}$ having a particular cost of 1.44€ per kg of removed COD, through the removal of 5.4 kg of COD per m$^3$ of wastewater.

In a distinct manner, it was observed that the organic load of the effluent shows a discrepancy over the treatment time with decreasing trend, where the last cubic meters have a COD content very near to a value that would allow the direct discharge. This reveals that there is a clearance in the pond creating a decreasing COD profile observed during the treatment time, attaining a certain value where the coagulation stage is sufficient to attain an efficiency removal that could also allow the direct discharge.

The average efficiency on the WWTP for the different stages were: 43% on the coagulation and 62% on the oxidation stage, where the reactants doses were diminished because the re-stabilization effect promoted by the excess of coagulant and the scavenger effect enhanced by the excess of both reactants in the oxidation stage due to the fact that the solids and organic load decrease over depuration time. This treatment increases the wastewater biodegradability from 0.03 to 0.37 enabling the posterior application of biological treatment if necessary discharge into the water courses. The treatment has a real average cost of 1.09€ per kg of removed COD, through the removal of 1.99 kg of COD per $m^3$ of wastewater, with an average cost of 2.17€ for each treated cubic meter.

The result of the integration of the industrial treated wastewater with biological treatment performed at laboratorial scale shows that the microorganisms need an adaptation time, reaching an average efficiency of 68% until the day 23. However, at the end of the 60th day, the biomass was totally adapted, presenting a high efficiency treatment, supporting 86% of COD removal increasing from this day on until the end with a final a remarkable degradation of 95%.

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# IV.6 Ozonation and Perozonation on the Biodegradability Improvement of a Landfill Leachate

## IV.6.1 Introduction

The population growth joined with the urban development leads to extremely high domestic solid wastes production entailing suitable management technologies to protect both environment and human health. The landfilling method is one of the most common procedures for the ultimate disposal of these pollutants (Li *et al.,* 2009), minimizing the ecological impact by allowing the waste decomposition under controlled conditions, besides presenting economic advantages (Renou *et al.,* 2008). The main issue regarding such techniques is related with the formation of large amounts of an aqueous effluent (known as leachate) due to the water content of the wastes, the rainwater that percolates through the waste bed and the aqueous remains produced during the pollutants biological oxidation (Tizaoui *et al.,* 2007).

The landfill leachates present complex composition, encompassing high organic loads as well as inorganic substances and heavy metals (Gotvajn *et al.,* 2009), depending, among other factors, of the landfill age (Goi *et al.,* 2009). This wastewater constitutes, thus, a potential threat for the quality of groundwater and its management requires special attention. It is well known that the leachate characteristics change over time, and the treatment of these streams in conventional depuration plants is hardly accomplished due to the awkward features as the high content of pollutants and low biodegradability (Tizaoui *et al.,* 2007). Nevertheless, the leachate handling must meet the quality level established for the final discharge into surroundings.

For this reason, aiming to fulfil current environmental legislation, a treatment system must be developed, which has also to be robust enough to accomplish sharp variations on the inlet effluent composition Li *et al.,* 2009). Conventionally, landfill leachate is treated by biological processes; however, the implementation of bio-systems may be inadequate due to the effluents' toxic characteristic and low BOD/COD ratio generally resulting in low efficacies (De Morais and Zamora, 2005; Goi *et al.,* 2009). Since these traditional technologies are not effective for the removal of refractory compounds and the physico-chemical processes are non-destructive, advanced oxidation processes (AOPs) arise as alternative methodologies (Wu *et al.,* 2004).

Chemical oxidation by advanced processes has as purpose to reach complete mineralization (into water and carbon dioxide) (Alvarez *et al.,* 2000), or, when economically more advantageous, enhance the biodegradability of biorecalcitrant organic pollutants up to a value that will allow a posterior biological treatment (Martins *et al.,* 2010; Cortez *et al.,* 2010).

AOPs encompass ozonation which is a treatment based on the high oxidant power of ozone, that can be used to decompose large organic molecules into smaller and less complex ones occurring at normal pressure and temperature being, hence, industrially interesting (Chaturapruek *et al.,* 2005; Cortez *et al.,* 2010). This process can be enhanced by promoting the formation of highly reactive agents, such hydroxyl radical ($HO^\bullet$), from ozone decomposition. The use of ozone at alkaline conditions ($O_3/OH^-$) or in combination with strong oxidants such as $H_2O_2$ ($O_3/H_2O_2$) favours the production of these species (Gunten, 2003; Chandrasekara *et al.*, 2013) that have an oxidation potential higher than the one attributed to molecular ozone. These processes can be, thus, attractive to treat complex streams such as leachate (Tizaoui *et al.*, 2007). The chain radical reactions are non-selective organic compounds until total mineralization. Contrarily, ozone molecule only undertakes specific reactions with other molecules encompassing high electronic density sites leading to low molecular weight by-products generally no further reactive. Therefore, ozonation is usually more efficient when the conditions support $HO^\bullet$ production (Kasprzyk-Hordern *et al.*, 2003; Pera-Titus *et al.,* 2004). Nevertheless, if reactions are incomplete, the AOPs can also promote the formation of refractory and more toxic by-products than the original pollutants. The economic factor is another restriction due to the high operational costs when high strength wastewaters are involved. A significant economic drawback derives from reactants consumption (e.g. $H_2O_2$) and the electrical power required to produce ozone in situ. The major factor that can affect ozonation efficiency in the oxidation of refractory contaminants is the presence of carbonate and hydrogencarbonate ions in wastewaters composition which can compete with the substrate for $HO^\bullet$ radicals. Besides, the excess of $H_2O_2$ on the Perozonation experiments, may also present a scavenging effect on the generated radical hydroxyls, reducing thus the process efficiency (Chandrasekara *et al.*, 2013).

In this context, the use of ozone has been studied for the oxidation of various effluents, with promising results in the degradation of landfill leachates (Wu *et al.*, 2004; Chaturapruek *et al.*, 2005; Ntampou *et al.*, 2006; Tizaoui *et al.*, 2007; Goi *et al.*, 2009) involving considerable depletions of chemical oxygen demand and colour, with also the advantage of biodegradability increase.

Within this context, the main goal of this work was to obtain a suitable technology to depurate a landfill leachate aiming to enhance its biodegradability meeting the legal limits for the discharge of this liquid effluent to the sewage to be further treated in a municipal wastewater treatment plant generally based on activated sludge, providing reliable results that can increase the industrial application of AOPs through the integration with a biological oxidative system. The data gathered here led to the design and building of an industrial installation based on AOPs to deal with this specific effluent with the intention of an immediate industrial application. Aiming to give answer to a real environmental problem, experiments were conducted to compare the efficacy using ozone-based advanced oxidation processes involving $O_3$ and $O_3/H_2O_2$.

## IV.6.2 Materials and methods

### *IV.6.2.1 Landfill Leachate Characteristics*

The leachate samples were collected from a municipal landfill in the centre region of Spain. The raw stream is pre-treated in situ by reverse osmosis, resulting in two types of effluents, the concentrate and the permeate. The concentrated course is useless and has to be discharged or so prepared and subsequently treated (Renou *et al.*, 2008), while the last one still does not accomplish the characteristics permitting their discharge to the sewage due to the high organic content represented as chemical oxygen demand, COD, so that this will be the effluent under study. The physicochemical characteristics of the permeate leachate were then analysed and listed in Table IV.6.1. It should be noticed that as previously referred the low biodegradability detected inhibits the direct application of biological methodologies.

***Table IV.6.1- Chemical composition of the permeate effluent and the errors associated to each parameter***

| pH | **COD (mg $O_2.L^{-1}$)** | **$BOD_5$(mg $O_2.L^{-1}$)** | **$BOD_5$/ COD** | **Toxicity [(a)] (%)** | **Biodegradability [(a)] (%)** |
|---|---|---|---|---|---|
| **7.1** | **1880** | **90** | **0.05** | **0** | **2** |
| | **± 8 %** | **± 20 %** | | **± 8 %** | **± 8 %** |

**[(a)] assessed by respirometric methods**

### *IV.6.2.2 Experimental set-up*

All the experiments were evaluated bearing in mind operational cost restrictions ensuring that all procedures can be performed without high investments. Probably higher oxidant ($O_3$ or $H_2O_2$) doses would lead to more significant depletions. Nevertheless, that would increase the operating costs of the global treatment making it not possible to commercialize.

The ozonation experiments were held in a stirred reactor operating in a semi-continuous mode. The liquid was charged at the beginning of the experiment and ozone was continuously introduced trough two porous diffusers placed in the liquid bulk. Ozone was generated from a pure oxygen stream (500 mL.min$^{-1}$) in an ozone generator BMT 804N (BMT, Berlin, Germany) and the gas ozone concentration was measured using a BMT963 vent ozone analyzer (BMT, Berlin, Germany) (Martins and Quinta-Ferreira, 2009).

The oxidation experiments proceeded as follows: 500 mL of the effluent were added to the reactor, brought to the desired temperature and the experiment started when the ozonated oxygen begun to run. The stirring speed was maintained at 750 rpm to ensure negligible external mass transfer resistances during the experiments guarantying chemical regime (Martins *et al.*, 2008). The ozone gas leaving the reactor quickly reached a stable value being possible to assume, thus, that the aqueous solution was saturated in ozone during the process.

### *IV.6.2.3 Analytical Methods*

During the experimental period, samples were withdrawn in certain intervals of time to analyze Chemical Oxygen Demand (COD), Biochemcial Oxygen Demand ($BOD_5$) and color and also access their toxicity and biodegradability by respirometry and luminescence techniques. The characterization analyses of the initial and treated leachate including $BOD_5$ and COD were performed according to Standard Methods (Greenberg *et al.*, 1985), in a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer for COD while a WTW Inolab 740 was used to measure the dissolved oxygen for $BOD_5$. Color was determined by spectroscopy using a T60 (PG instruments) spectrophotometer. pH was attained by a Crison micropH 2000. Color data are reported as the absorbance of the samples in the wavelength of the visible region with the maximum absorption ($\lambda = 380\text{-}750$ nm) which is considered as a quantitative estimation of the color of the solution. Color depletion was followed by UV-Vis spectrophotometry with a T60 UV/Vis spectrophotometer.

Respirometric techniques were used to infer about the effluent biodegradability and toxicity over activated sludge. Respirometry allows measuring the biological oxygen consumption rate under well-defined experimental conditions. It allows determining biodegradability, toxicity and inhibitory effects with a real sample of microorganisms.

The respirometric assay is used to determine the Oxygen Uptake Rate (OUR). The OUR involves an estimation of the biomass oxygen consumption rate when assimilating organic matter giving the amount of oxygen consumed per time unit, and it was assessed by a WTW Inolab 740 apparatus.

The measurements are carried out by controlling the oxygen input and output in a liquid-static-static (LSS) respirometer at 25±0.2°C. The variation of dissolved oxygen (DO) is plotted versus time and the OUR is then calculated

$$\frac{\mathbf{d(V_l \times DO)}}{\mathbf{dt}} = -\mathbf{OUR} \times \mathbf{V_l} \qquad \textbf{(IV.6.1)}$$

Where $V_l$, is the volume of the liquid phase expressed in $dm^3$, and DO is the concentration of dissolved oxygen expressed in mg $DO.dm^{-3}$, with OUR expressed in mg DO $dm^{-3}s^{-1}$.

Biomass was collected from a winery wastewater treatment plant (3000-4000 $mg.L^{-1}$ of volatile suspended solids). The bacteria oxygen uptake rate (OUR), which corresponds to the slope of the regression line of the oxygen decay along time, was measured when a totally biodegradable compound was fed (acetic acid, $OUR_{acetic\ acid\ I}$) and in the presence of the effluent ($OUR_{sample}$), leading to the sample biodegradability calculated according to Equation IV.6.2 (Martins *et al.*, 2010).

$$\%\ \boldsymbol{biodegrabability} = \left[\mathbf{1} - \left(\frac{\mathbf{OUR_{acetic\ acid\ I}} - \mathbf{OUR_{sample}}}{\mathbf{OUR_{acetic\ acid\ II}}}\right)\right] \times \mathbf{100} \qquad \textbf{(IV.6.2)}$$

After the sludge being in contact with the effluent, acetic acid was fed a second time ($OUR_{acetic\ acid\ II}$) and the sample toxicity was assessed by Equation IV.6.3.

$$\%\ \boldsymbol{toxicity} = \left[\left(\frac{\mathbf{OUR_{acetic\ acid\ I}} - \mathbf{OUR_{acetic\ acid\ II}}}{\mathbf{OUR_{acetic\ acid\ I}}}\right)\right] \times \mathbf{100} \qquad \textbf{(IV.6.3)}$$

## IV.6.3 Results and Discussion

### *IV.6.3.1 Single Ozonation (pH and [O$_3$] selection)*

In Figure IV.6.1 it is possible to observe Chemical Oxygen Demand (COD) depletion, for various pH values, while in b) color profiles, at c) the $BOD_5$/COD ratio along the treatment time and d) the biodegradability assessed by respirometric methods are show.

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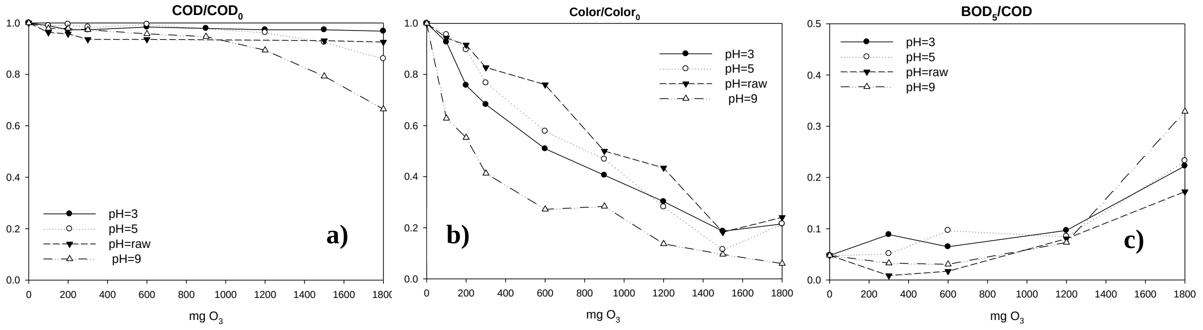


d)

| TEST | pH=3 | pH=5 | pH=raw | pH=9 |
|---|---|---|---|---|
| Respirometric Biodegradability | 28 (%) | 31 (%) | 15 (%) | 21 (%) |

***Figure IV.6.1- Effect of pH on the single ozonation of the permeate leachate (1L) as function of transferred ozone: a) normalized COD; b) color reduction; c) BOD$_5$/COD ratio and d) respirometric biodegradability after the treatment. Inlet gas ozone concentration = 10 mg O$_3$.min$^{-1}$***

By examining Figure IV.6.1 c) it can be seen that single ozonation led to an increase in the $BOD_5$/COD, which would favour the biological treatment even if only a moderate COD removal (a)) occurred. Moreover, it can be concluded that the oxidation process is strongly dependent on the initial pH (Martins and Quinta-Ferreira, 2011).

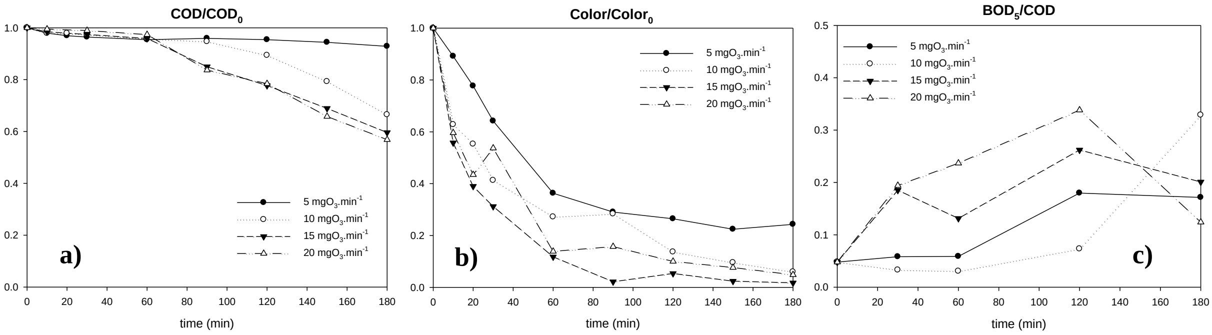
In fact, ozone oxidation follows two major pathways: at acidic pH, the ozone molecule is able to perform electrophilic attack over the pollutants while for alkaline conditions the decomposition of ozone and generation of hydroxyl radical ($HO^{\bullet}$) is promoted leading to chain radicalar degradation reactions (Gunten, 2003; Moussavi *et al.,* 2009). For pH intermediary values there is the combination of both pathways, and their efficiency can vary according to the characteristics of the effluent (Pera-Titus *et al.,* 2004; Gogate and Pandit, 2004). It is observed in our case that COD depletion was not dependent on pH until at least 10% of COD removal was achieved. However, the use of high pH values improved the efficiency of the process, with best results for COD depletion at pH=9 (34% decrease) while a very slight COD abatement is obtained after 1800 mg.$O_3$ addition at pH=3, during 180 min of reaction.

Figure IV.6.1 b) depicts the effect of ozone treatment on the color of the leachate. At pH 3 and 9, the color removal efficiencies were 79% and 95% respectively, while the intermediates pH reached approximately the same efficiency, 80%. However, it is important to refer that until the dosage of 1200 mg.$O_3$ of oxidation the test at pH 3 attained the second better color removal (higher than for intermediate pH's) probably due to the fact that the initial chromophore groups in the molecules are very vulnerable to direct molecular ozone attack (Wang *et al.*, 2004) and therefore, the color was reduced effectively at acidic conditions. Nevertheless, for higher oxidation periods the radical pathway at higher pH's prevails with superior color decay probably due to the oxidation of compounds that are refractory to ozonation.

In what regards $BOD_5$/COD ratio (Figure IV.6.1 c)) an increase from 0.05 to 0.33 was attained for pH=9. For the remaining assays, although there was an increase along time, all $BOD_5$/COD were lower than 0.33.

Respirometric techniques were still used to determine the wastewater biodegradability at the end of the experiment after 180 min reaction and its toxicological impact over activated sludge. It is observed in Figure IV.6.1 d) a biodegradability improvement after the application of the chemical oxidation process when compared with the initial effluent, effectively demonstrating that pH 5 is the one that most favors the subsequent biological treatment, reaching 30%. It should be noted that the biodegradability measured by the respirometric method gives smaller values than those attained by $BOD_5$/COD, since that methodology measures only the instantly biodegradable organic matter, while the determination of $BOD_5$ needs 5 days which means that bacteria may have some time for adaptation to the pollutants.

Moreover, the treated wastewater toxicity attained by respirometry remains 0 as the one observed for the initial mixture that was also null, indicating that the oxidation process does not produce intermediate toxic products and that the effluent can be discharged without causing negative impact over activated sludge in the biological reactor.



**d)**

| TEST | 5 mg O$_{3.}$ min$^{-1}$ | 10 mg O$_{3.}$ min$^{-1}$ | 15 mg O$_{3.}$ min$^{-1}$ | 20 mg O$_{3.}$ min$^{-1}$ |
|---|---|---|---|---|
| **Respirometric Biodegradability** | 19 (%) | 21 (%) | 14 (%) | 14 (%) |

***Figure IV.6.2- Effect of the ozone concentration on the single ozonation of the permeate leachate (1L) behaviour as function of time: a) normalized COD; b) color reduction; c) BOD$_5$/COD ratio and d) respirometric biodegradability after the treatment at pH=9***

Figure IV.6.2 a) shows the influence of the ozone inlet concentration over the ozonation efficiency and a maximum of only 10% of COD removal was reached at 60 minutes of reaction. After 3h of oxidation, while 5 mgO$_{3.}$min$^{-1}$ led to a final COD abatement of solely 7%, higher loads enhanced COD depletion, with 33%, 40% and 43% decrease when using ozone gas inlet of 10 mgO$_{3.}$min$^{-1}$, 15 mgO$_{3.}$min$^{-1}$ and 20 mgO$_{3.}$min$^{-1}$ respectively, meaning that after 180 min of reaction only a slight enhancement on COD removal in the order of ~10% was obtained at higher ozone dosages. As can be seen, two steps can be identified during the oxidation process (Gotvajn *et al.*, 2009). Initially (up to ~60min), organic molecules are transformed into smaller intermediates without significant COD changes where, however, a BOD$_5$/COD ratio improvement is observed (Figure IV.6.2 c)). In the second step COD depletion is accelerated in all experiments for ozone doses superior to 5 mgO$_{3.}$min$^{-1}$.

In Figure IV.6.2 b) the effect of the ozone load over the color of the treated leachate is also indicated. For doses of 5 and 20 mgO$_{3.}$min$^{-1}$, the color removal efficacies were 75% and 95%, respectively. The best color removal, 95%, was attained with 15 mgO$_{3.}$min$^{-1}$. It is then possible to conclude that with the increase on ozone concentration an enhancement of color elimination is observed. Since color is principally originated from the unsaturated bonds and higher quantities of specific functional groups, ozone and HO$^{\bullet}$ promote their attack, showing that higher ozone dosages, endorse initial oxidation reactions and subsequently produce less reactive species, (Chandrasekara *et al.*, 2013); however, for concentrations above 10 mgO$_{3.}$min$^{-1}$, differences are too slight with no significant improvement. The obtained efficiencies are in agreement with the values reported by Goi and collaborators (2009) that attained a COD removal of 41% and a (BOD$_7$)/COD improvement using pH 11 and ozone concentration of 42 mg.L$^{-1}$. Besides, Tizaoui *et al.*, (2007) also reached a considerable color depletion (87%); however, the applied conditions (pH = 8.7 and $[O_3] = 80\ g.m^{-3}$) only led to moderate COD (27%) depletion and $BOD_5/COD$ enhancement up to 0.2.

Figure IV.6.2 (c) presents the $BOD_5/COD$ ratio improvement from 0.05 to 0.33 for 40 $gO_3.Nm^{-3}$, against 0.13 attained at the higher dose, was observed. Moreover, the COD efficiency increase resulted, contrarily, in a lower biodegradable final effluent for ozone inlet concentrations above 10 $mgO_3.min^{-1}$. This is due to the different operating conditions involving either lower production of intermediary bio-refractory species during the oxidation procedure, or higher abatement of possibly biologically degradable pollutants. In fact, once the majority of the degradable organics were oxidized, they do not promote the formation of more biodegradable products (Gotvajn *et al.,* 2009), observed through the $BOD_5/COD$ ratio decline. It seems then that the use of high ozone loads is not favourable because effluents biodegradability decreases with concentrations above 10 $mgO_3.min^{-1}$.

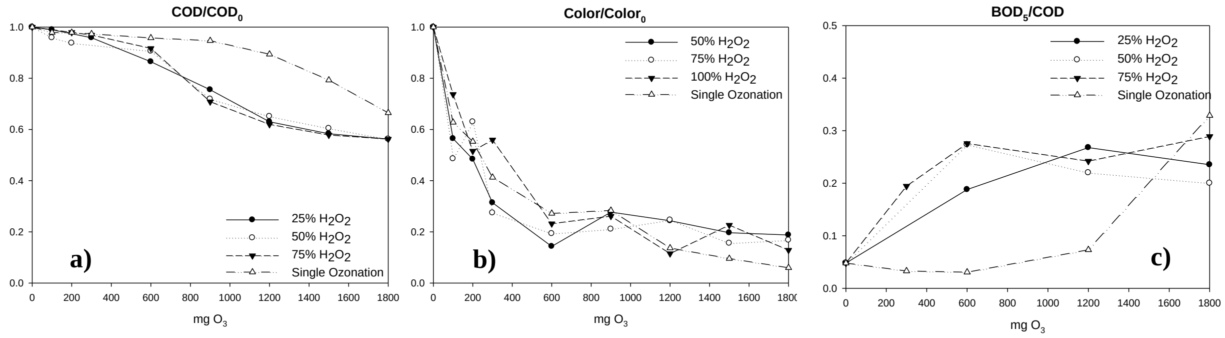
Regarding the measured biodegradability by respirometric tests (d), one observes similar results when compared with the ones attained for the $BOD_5/COD$ ratio where, for concentrations higher than 10 $mgO_3.min^{-1}$, a decrease in the effluents' biodegradability was detected, possibly due to the previously mentioned ozone scavenger effect. Moreover, due to the high cost of ozone production, the higher dosages are not industrially feasible by the great energy consumption, so it was concluded that the dosage of 10 $mgO_3.min^{-1}$ was the most suitable for industrial applications.

#### *IV.6.3.2 $O_3/H_2O_2$ ($[H_2O_2]$ and pH selection)*

The hydrogen peroxide dosage was estimated based in the stoichiometric relation (Eckenfelder, 1985) for the total COD abatement by this oxidant (Equation IV.6.4).

$$\boldsymbol{H_2O_2\left(\frac{mg}{L}\right) = 2.13 \times COD\,(\frac{mg}{L})} \qquad \textbf{(IV.6.4)}$$

In this case, it would be theoretically required a hydrogen peroxide concentration of 4 g per liter. The experimental results for the degradation during perozonation regarding COD and color depletion are shown in Figure IV.6.3. The $H_2O_2$ dosages were correspondent to 50%, 75% and 100% of that stoichiometric value.



**d)**

| TEST | 50% $H_2O_2$ | 75% $H_2O_2$ | 100% $H_2O_2$ | Single Ozonation |
|---|---|---|---|---|
| Respirometric Biodegradability | 14 (%) | 16 (%) | 27 (%) | 14 (%) |

***Figure IV.6.3- Effect of the stoichiometric $H_2O_2$ dosage on the perozonation of the permeate leachate (1L) as function of transferred ozone: a) normalized COD b) color reduction; c) $BOD_5$/COD ratio and (d) respirometric biodegradability after the treatment. pH=9, and inlet gas ozone concentration = 10 mg $O_3$.min$^{-1}$***

The performance of this process was assessed at the pH previously selected (pH=9). When only hydrogen peroxide without ozone was used (not present in the Figure), insignificant reductions in color and COD were observed.

As illustrated in Figure IV.6.3 a), 43% of COD was removed within 1800 mg.$O_3$ for all the distinct amounts of hydrogen peroxide applied, reaching a final concentration of 1080 mg$O_2$.L$^{-1}$, that permits a discharge to a municipal collector, with no noteworthy differences in the profiles for the different $H_2O_2$ dosages, and this involved more 9% abatement when compared with single ozonation, showing thus an overall increase in efficiency of 28%. Nonetheless, the presented data show that an increase in hydrogen peroxide concentration will not always increase COD removal rates. In fact, increasing hydrogen peroxide dose may change its role from being initiator for the production of hydroxyl radicals to inhibitor of such radical reactions. As a consequence, COD removal rates do not diminish in this case but no improvement is observed either as referred (Goi *et al.*, 2009).

For color removal profiles it is possible to see through Figure IV.6.3 b) that for different doses of hydrogen peroxide the results are very similar. Yet, there is a slight increase of color abatement with the amount of $H_2O_2$, with 87% for the higher dosage and 81% for the test with 50% of the stoichiometric value. Here the scavenging effect of hydrogen peroxide can be observed by presenting itself as an obstacle for the treatment enhancement (Tizaoui *et al.*, 2007)**,** lowering, on the contrary, the values obtained by single oxidation**.** In what refers to the final biodegradability improvement (Figure IV.6.3 d)) it is observed that the highest $H_2O_2$ dosage promotes higher biodegradability being reached 27%, against the almost 15% achieved with 50% and 75% of the stoichiometric dosage, and the 22% reached by single ozonation. Hereupon it is therefore necessary to select an optimal hydrogen peroxide dosage above which a decline or no effect of this reactant over the treatment efficiency is observed; so a hydrogen peroxide concentration of 4 g.L$^{-1}$ (100% of the stoichiometric value) remained the best for COD and color reductions, and biodegradability enhancement either measured through $BOD_5$/COD or assessed by respirometric techniques. Higher $H_2O_2$ dosages will have a greater cost for industrial application.

In what regards the evolution of $BOD_5$/COD ratio of the effluent, Figure IV.6.3 c), it is apparent that a higher concentration of co-oxidant provides an enhancement on this ratio, possibly due to the formation of intermediate products easier to be biologically degradable. In fact, for the different $H_2O_2$ concentrations the value of this ratio is very similar, 0.29 against 0.20 and 0.24 for decreasing $H_2O_2$ loads (100, 75 and 50 % respectively). However, for single ozonation a higher biodegradability is achieved at the end of the treatment, though much lower values were initially registered, which can be explained by the formation of intermediate by-products with a higher biodegradable character. The obtained outcomes are similar to the results reported by Tizaoui et al. (2007), that, at pH=8.7, with [$O_3$] = 80 g.m$^{-3}$ and 2 g.L$^{-1}$of $H_2O_2$, achieved a COD and Color removal of 48% and 94%, respectively. Additionally, biodegradability improved by reaching a $BOD_5$/COD = 0.7.

In order to compare the two techniques (single ozonation and perozonation) the results obtained for single ozonation (pH = 9 and 10 mg$O_3$.min$^{-1}$) and perozonation (4 g.L$^{-1}$ of $H_2O_2$ and same pH and ozone concentration) are depicted in Table IV.6.2.

*Table IV.6.2- Comparison of efficiencies of COD, color depletion, $BOD_5$/COD ratio, biodegradability and toxicity by perozonation ($O_3$+$H_2O_2$ with [$H_2O_2$]=4.g.L$^{-1}$) and single ozonation ($O_3$) after 180 min of reaction (pH=9, 10 mg$O_3$.min$^{-1}$)*

| | $O_3$ | $O_3$+$H_2O_2$ | Gain/loss (%) |
|---|---|---|---|
| **COD/COD$_0$** | 0.66 | 0.56 | **+ 23** |
| **Color/Color$_0$** | 0.06 | 0.13 | **- 9** |
| **$BOD_5$/ COD** | 0.33 | 0.29 | **- 12** |
| **Toxicity $^{(a)}$ (%)** | 0 | 0 | **=** |
| **Biodegradability $^{(a)}$ (%)** | 21 | 27 | **+ 22** |

(a)assessed by respirometric techniques

The gain / loss in what regards co-oxidant absence is also shown. In fact, for the performed operational conditions (pH =9 and [$O_3$] = 10 mg$O_3$.min$^{-1}$), 2.86 mg of $O_3$ are required to remove each mg of COD for the single ozonation procedure. However at the perozone experiment, 2.25 mg of $O_3$ per mg of COD depleted were required to reach a final COD value of 1080 mg$O_2$.L$^{-1}$. Throughout these results it is possible to see that the perozonation process does not potentiate the total clearance of the effluent. Indeed, in this case, the hydrogen peroxide addition only improves the removal of COD in 23% being, however, less efficient in removing color (-9%), besides originating a treated effluent with a lower $BOD_5$/COD ratio (-12%). But, on the other side a better instantaneous biodegradability is reached. For both systems the treated wastewater toxicity remains null, as initially.

### IV.6.4 Process Cost Evaluation

In order to evaluate the reliability of the application of these treatment processes for such effluent a study of the operating costs was carried out for each of the tested methodologies.

The ozone/oxygen gas stream was sparged with a constant flow rate of 0.5 $dm^3.min^{-1}$ and the average production of ozone was around 1.2 $g.h^{-1}$.The volume of wastewater treated in each assay was 1 $dm^3$. The pH was maintained at a set point close to 9± 0.1. For each liter of effluent 2.2 mL of 3 M NaOH solution were used in order to raise and control the pH during the oxidation and, at the end of the process, a variable amount of $H_2SO_4$ was added to reduce the pH to 7 so that the treated wastewater could be sent for biological treatment.

For the cost assessment the energy for the ozone synthesis and/or the cost of reagents were considered and for comparison of each kind of treatment the decrease in chemical oxygen demand (COD) was accounted for as well (Krichevskaya *et al.,* 2011). The ozone consumption was taken as the total ozone that was produced, the synthesis of which requires 20 kWh. $kg^{-1}$ $O_3$ (Twort *et al.,* 2000). The cost of electric energy was considered 0.1276 €.$KWh^{-1}$, the price market in Portugal for industrial applications. The fee of the hydrogen peroxide (50% w/w) was 0.35 € .$L^{-1}$ while, from Portuguese industrial sources, the costs of NaOH (50%) and $H_2SO_4$ were assumed as 0.366 €.$L^{-1}$ and 2.09 €.$L^{-1}$ per ton of each reactant.

The operations costs for the wastewater treatment based on these data are shown in Table IV.6. 3. The basic costs are fixed per $m^3$ (€/$m^3$) and per kilogram of removed COD (€/kg $COD_{removed}$) and are referent to the operational costs of the bench scale installation used in this work. The results provide the extrapolation from the actual cost to the treatment cost per $m^3$ of effluent.

***Table IV.6.3- Treatment costs of ozonation and perozonation for permeate leachate wastewater***

| | Costs €/$m^3$ | | | | Degradation | | |
|---|---|---|---|---|---|---|---|
| | $O_3$ | $H_2SO_4$ | NaOH | $H_2O_2$ | Kg COD /$m^3$ | €/ $m^3$ | €/ Kg COD |
| **Ozonation** | 6.89 | 1.57 | 0.43 | ------- | 0.63 | 8.89 | 14.11 |
| **Perozonation** | 6.89 | 1.41 | 0.43 | 1.40 | 0.84 | 10.43 | 12.06 |

The ozone production has the same cost for the two processes; however, with the addition of $H_2O_2$, perozonation would be more expensive. Thus although the addition of hydrogen peroxide endears the overall process in 23% on the COD removed when compared with the single ozonation efficiency, reducing the effective cost in the relationship of € per kg of removed COD (14.11 € for single ozonation vs 12.06 € for perozonation), showing that besides the treatment price per cubic meter of wastewater, the real effectiveness of treatment on the COD removal suppresses the increment of the cost.

The process shows to be expensive when compared with the overall operating cost (2.44 €.m$^{-3}$) of an integrated (SBR) Sequential Batch Reactor- PFS (polyferric sulfate coagulation) - Fenton oxidation system (Li *et al.*, 2009) ; however it is more economic than the system presented by Cortez and collaborators (2011) where costs with ozone based processes of 48.66 and 35.33 €.g$^{-1}$ of COD removed are referred for $O_3$/pH =11 and $O_3$/400 mg $H_2O_2$ L$^{-1}$, respectively. Besides, the same authors applied Fenton oxidation as a treatment for the same effluent achieving an operating cost of 10.93 €.g$^{-1}$ of COD removed.

Finally, single ozonation achieves a COD removal equal to the legal threshold value for sewage discharge (1250 mg$O_2$.L$^{-1}$), limiting its applicability because no error margin is available for its extrapolation to the plant, requiring then a biological treatment in order to ensure the needed organic load removal, whenever process efficiency fluctuations may occur. Perozonation reveals that is more efficient on COD deletion (1080 mg$O_2$.L$^{-1}$), besides reducing the cost per kg of COD removed, providing the possibility of disposal into a municipal sewage.

### IV.6.5 Conclusions

The study showed that single ozonation and ozone combined with hydrogen peroxide are efficient methods to treat this leachate. Biodegradability indicated by $BOD_5$/COD and respirometric tests can be significantly enhanced when ozone is applied.

Single ozonation at pH 9 endorses reductions of 34% COD and 94% color and augments biodegradability ($BOD_5$/COD = 0.33; 21% by respirometry), showing that this technology could be effectively a prior treatment for biological systems.

COD reductions up to 44%, $BOD_5$/COD = 0.27, respirometric biodegradability of 29% and colour removal of 87% were achieved after treatment with $O_3/H_2O_2$ system at pH 9 and a $H_2O_2$ concentration of 4 g.L$^{-1}$, permitting the direct discharge to a sewage collector. For this reason, hydrogen peroxide proved to enhance the treatment process when combined with ozone despite the increase in the overall operating costs, disclosing, nevertheless, to be more profitable in the cost per kg of removed COD.

Therefore, the results attained in this work reveal that ozone-based AOPs are promising alternatives providing the biodegradability improvement allowing a posterior biological oxidation at a lower cost; moreover Perozonation shows that was possible to reach an effective and unique stage of treatment, achieving the COD value that promotes a treated wastewater able to be discharged into a municipal collector However, to certify and confirm the feasibility of the treatment as an effective solution, it is necessary to perform the treatment methodology at an enlarged time scale, so that the effluent variability could be assessed in order to have a real sense of its applicability at industrial scale.

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# IV.7 Utilization of Ozone Based Techniques for Industrial Effluents Depuration and Reuse

## IV.7.1 Introduction

Industrial processes are potential sources of pollution entailing specific wastewater treatment as one important cost of manufacturing production and, attending to the decrease of water resources, its reutilization is essential for process reliability. In fact, actual environmental legislation is growing stricter imposing to the companies to focus their efforts towards wastewater depuration and water recycling which can be used in toilet flushing, garden watering, street washing and fire protection (Rivas *et al.,* 2009).

The agro and industrial effluents may have an adverse effect on environment due to the strong content of organic compounds involving, generally, high values of COD (Chemical Oxygen Demand), TSS (total suspended solids), BOD (Biochemical Oxygen Demand) and toxicity which, if directly discharged into natural water courses can provoke disastrous ecological results (Beltrán *et al.,* 1999).

In recent years, advanced oxidation processes (AOPs), in which highly reactive radicals (particularly $HO^{\bullet}$) are generated, have been increasingly applied for the degradation of various classes of compounds. Among them ozonation treatment is an effective technology for removing organic matter from drinking water and industrial wastewaters (Matilainen and Sillanpää, 2010; Klavarioti *et al.,* 2009).

In the ozonation process there are two possible pathways to be considered: the reactions with molecular ozone (direct pathway), and the reactions with hydroxyl radicals produced by ozone decomposition (radical pathway) (Liotta *et al.,* 2009; Pirgalioglu *et al.,* 2009). Both mechanisms are able to oxidize prevailing one or the other depending mainly on the medium pH, and also on the wastewater composition and ozone dosage (Beltrán *et al.,* 1999; Ma *et al.,* 2005).

In recent years, the application of new advanced oxidation techniques, such as catalytic ozonation in homogeneous or heterogeneous phase, $H_2O_2/O_3$, UV/ $H_2O_2/O_3$ and $H_2O_2/O_3/Fe^{2+}$ (Matilainen and Sillanpää, 2010) allowed to achieve almost complete mineralization of some organics (Rivas *et al.,* 2009; Martins and Quinta-Ferreira, 2009). An effective way to increase the production of hydroxyl radical is through the addition of hydrogen peroxide once this combined system can initiate the decomposition cycle of ozone, resulting in the formation of those desired radicals. In aqueous medium the hydrogen peroxide is partially dissociated in ionic species ($HO_2^-$), which will react with ozone, originating chain reactions (Gunten, 2003; Gogate and Pandit, 2004) where both radicals, hydroxyl and hydroperoxide, participate and degrade more effectively the pollutants. Several works relate the $O_3/H_2O_2$ system to treat pesticides were this process led to the formation of $HO^{\bullet}$ , which improved the degradation of all investigated compounds when compared to single ozonation (Ying-Hui *et al.,* 2006; Chelme-Ayala *et al.,* 2011) as also was applied to treat a milk whey wastewater (Martins and Quinta-Ferreira, 2013).

Beyond those referred applications, several references in the literature report the use of this methodology on the treatment of effluents from the food industry as is the case of the depuration of Baker’s yeast wastewaters with a COD decrease of 43% and a color reduction of 91% (Altinbas *et al.,* 2003). Beltran and his collaborators (Beltrán *et al.,* 1999) reached 80% of COD conversion in 2 h and a BOD/COD ratio improvement when olive wastewaters where subjected to ozone and hydrogen peroxide oxidation. In another hand, Campos and coworkers (Campos *et al.*, 2009) observed 6.8% of TSS removal during the treatment of seafood wastestreams with 0.02 g $O_3.g^{-1}$ TSS. Also in a similar reactor, industrial cork effluent was degraded by ozone and $O_3/H_2O_2$ with a higher removal efficiency for the last system (Lan *et al.*, 2008).

Some studies still incorporate UV radiation in $O_3/H_2O_2$ system. For example, Kestioglu *et al.,* (2005) treated an olive mill effluent obtaining a removal over 99% for both COD and total phenol content, while Zayas *et al.,* (2007), reached 87% of the COD degradation of a coffee wastewater within 35 min. The same enhancement was observed by Lucas *et al.* (2010), when $O_3/UV/H_2O_2$ system allowed a significant COD and TOC removal improvement when compared with single ozonation.

The initiation stage is shown by reaction (IV.7.1) and the global reaction (IV.7.2) is presented:

$$O_3 + HO_2^{-} \rightarrow HO_2^{\bullet} + O_3^{\bullet} \qquad \textbf{(IV.7.1)}$$

$$2\ O_2 + H_2O_2 \rightarrow 3\ O_2 + 2\ HO^{\bullet} \qquad \textbf{(IV.7.2)}$$

Direct oxidation by molecular ozone is usually slower when compared with the case where $HO^{\bullet}$ are formed. In fact, $O_3$ selectively reacts with higher electronic density sites leading to sutured organic compounds; usually no further react with this molecule, originating an incomplete oxidation of polluting compounds. However, the direct route is important if radical scavengers are present in the wastewater composition which can reduce hydroxyl radicals reactions (Gunten, 2003, Chandrasekara *et al.,* 2009).

Ozone has been applied to a wide range of wastewaters because many contaminants are oxidizable within the advantages of rapid reaction rates, leaving few harmful by products in treated water, and producing oxygen as a reaction end-product. The sterilization of water supplies and/or discharges has been the traditional use of ozone (Rivas *et al.*, 2009; Chandrasekara *et al.*, 2009).

In this context, two distinct wastewaters were treated: one coming from a mill for vegetables washing (VW) and another one arriving from a chemical production plant (CP).

Within this context, the main goal of the present paper is to investigate ozone-based treatments in order to achieve TSS, COD and TOC reductions to fulfill environmental regulations permitting the treated waters to be reintroduced in the process.

## IV.7.2 Materials and Methods

### *IV.7.2.1 Experimental*

Single and hydrogen peroxide aided ozonation were carried out in a semi-batch mode being the liquid pollutants charged at the beginning of the experiment and the gas continuously fed. The reactor consisted in a glass vessel (1 L of capacity) provided with magnetic stirring and two top inlets for bubbling the gas feed, by means of two gas diffusers placed in the liquid bulk. In every experiment, the reactor was filled with 300 mL of wastewater. Ozone was produced from a pure oxygen stream (99.999% Praxair, Portugal) in an ozone generator (802N BMT, Berlin, Germany) with a gas flow rate of 500 $cm^3.min^{-1}$ with an ozone inlet concentration of 40 $g.m^{-3}$, measured in a 963BMT ozone analyzer, Berlin, Germany. The perozone experiments were carried out with the calculated amount of $H_2O_2$ being introduced into the reactor just before inputting the gas stream. The stirring speed was maintained at 750 rpm, and a gas flow of 0.5 $L.min^{-1}$ was maintain to provide the external mass transfer resistances negligible during the experiments (Martins and Quinta-Ferreira, 2009), and guarantee the chemical regime (Greenberg *et al.*, 1985). Since this is a gas-liquid system, the kinetic regime (diffusional or chemical) is major issue regarding its efficiency (Lan *et al.*, 2008).

At regular interval times, samples were steadily withdrawn to measure the concentration of COD and TOC. In tests were hydrogen peroxide has been applied, after the samples collection, the reaction was stopped by the addition of a certain amount of NaOH, enough to raise pH to 12, allowing the decomposition of $H_2O_2$ into water and oxygen. For TOC measurement, samples were filtered with 0.45 µm disposable filters for further analysis, as opposed to COD determination where sample solids also contribute.

### *IV.7.2.2 Analytical Methods*

Total Organic Carbon (TOC) was assessed with a *Shimadzu 5000A Analyser,* which operates based on the combustion/non-dispersive infrared gasanalysis method. Chemical Oxygen Demand was obtained by the method stipulated in *Standard Methods 5220 D: closed reflux,* colorimetric method (Campos *et al.,* 2009). The samples were digested during 2h at 148 ºC in a WTW CR3000 thermoreactor (Weilheim, Germany) and the COD value measured in a WTW MPM3000 photometer. The Folin-Ciocalteau method was used to determine total soluble phenolics (TPh) as described elsewhere (Martins and Quinta-Ferreira, 2009).

The Total Suspended Solids (TSS) was acquired by Standard Methods "*2540D: Total Suspended Solids Dried at 103 - 105 °C* (Eaton *et al.,* 1995). To check repeatability, some experiments were randomly run in duplicate and the samples withdrawn were analyzed in triplicate to minimize the experimental error. The deviations between runs were always lower than 2% and 5% for TOC and COD results, respectively.

## IV.7.3 Results and Discussion

### *IV.7.3.1 Characterization of the Effluents*

Two wastewaters were collected from industries located in Portugal and their physico-chemical characterization is summarized in Table IV.7.1.

***Table IV.7.1- Characterization of the effluents.***

| | **Vegetable Wash (VW)** | **Chemical Production (CP)** |
|---|---|---|
| **pH** | 7.5 | 6.8 |
| **COD (mgO$_2$. L$^{-1}$)** | 155 | 1100 |
| **TOC (mgC. L$^{-1}$)** | 122 | 273 |
| **TPh (mg..L$^{-1}$)** | 1.1 | 0 |
| **TSS (mg.L$^{-1}$)** | 960 | 100 |

The vegetable wash effluent came from a carrot processing company and consists in a stream encompassing low organic content as it can be observed by the relatively low COD and TOC values (155 mgO$_2$.L$^{-1}$ and 122 mgC.L$^{-1}$) and the measured only 1.1 mg.L$^{-1}$ of Total Phenolic Content. Nevertheless, the effluent was subjected to a prior railing; however still had a high load in suspended solids (960 mg.L$^{-1}$). A COD value of 1100 mgO$_2$.L$^{-1}$ is imparted to the chemical processing (CP) wastewater as well as 273 mgC.L$^{-1}$ in TOC and 100 mg.L$^{-1}$ in TSS as well the absence of TPh.

Therefore, we decided not to follow this parameter along experiments once the legal limit for polluted streams discharge is 2 mg.L$^{-1}$, well above our values.

#### *IV.7.3.2 Single Ozonation: Effect of pH*

All the tests were performed at initial pH with no control during the oxidation reaction.

##### *IV.7.3.2.1 Vegetable Wash Effluent*

The effect of pH over single ozonation efficiency was studied in the range of 3 to 9. Normalized COD and TOC reductions during the oxidation procedure of Vegetable Wash (VW) wastewater plotted against the experimental time over a period of 120 min are represented in Figure IV.7.1 when different pH values were applied.

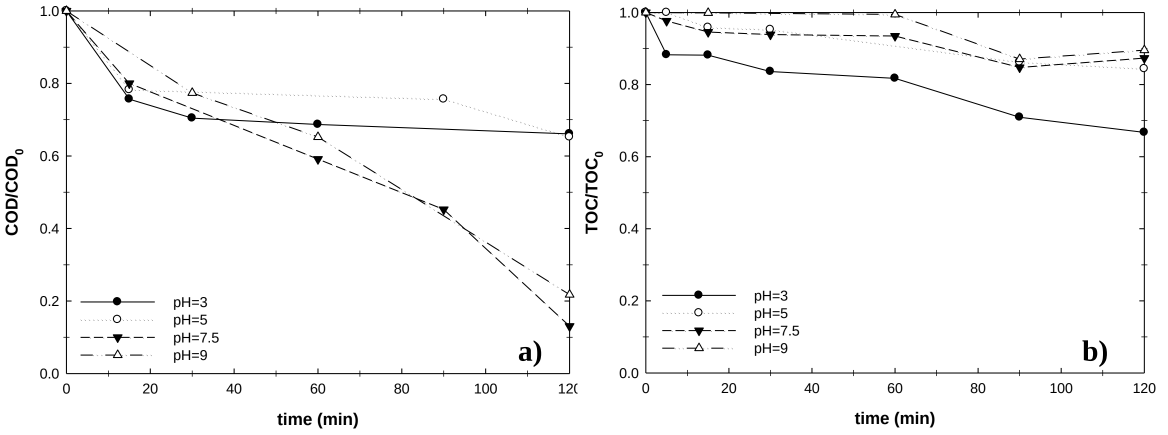

***Figure IV.7.1- Normalized concentrations of COD a) and TOC b) at single ozonation for VW as a function of time for different pH values at Normal Temperature and Pressure (NTP). [O$_3$] = 40 g.Nm$^{-3}$***

It can be ascertained that the percentage COD removal increased with ozonation time and pH affects the way that ozone reacts with organic molecules. As seen, the pH effect on COD reduction by ozonation (Figure IV.7.1 a)) is pronounced for reaction times lower than 20 min for all experiments and for tests carried out at higher pH values this decrease is strengthened for further oxidation times, which demonstrates the importance and effectiveness of the radical mechanism in the degradation of pollutants. The highest removal was measured for the raw effluent pH (7.5), where more than 40% of COD was degraded within 60 min of reaction being achieved a final abatement of 87% (after 120 min) reaching the concentration of 15 mgO$_2$.L$^{-1}$. For lower pH values (3 and 5) degradation mainly occurred within 10 min (24 and 20%, respectively); nevertheless, for extended oxidation times low improvement was detected with only 32% of COD removal being attained after 120 min for both operational conditions.

The reactions of ozone with hydroxide (IV.7.3) and hydroperoxide-ions (IV.7.4) initiate the ozone decomposition chain mechanism:

$O_2 + OH^{-} \rightarrow HO^{-}_2 + O_2$ **(IV.7.3)**

$O_2 + HO^{-}_2 \rightarrow HO^{\bullet}_2 + O_2^{-\bullet}$ **(IV.7.4)**

The next stage is the reaction between ozone and the superoxide radical ($\bullet O_2^{-}$), a major agent of the propagation of ozone decomposition, producing the desirable hydroxyl radicals (Reactions IV.7.5- IV.7.9):

$HO^{\bullet}_2 \leftrightarrow O_2^{-\bullet} + H^{+}$ **(IV.7.5)**

$O_2^{-\bullet} + O_2 \rightarrow O_3^{-\bullet} + O_2$ **(IV.7.6)**

$O_3^{-\bullet} + H^{+} \leftrightarrow HO^{\bullet}_3$ **(IV.7.7)**

$HO^{\bullet}_3 \rightarrow HO^{\bullet} + O_2$ **(IV.7.8)**

$HO^{\bullet} + O_3 \rightarrow HO^{\bullet}_2 + O_2$ **(IV.7.9)**

However it is observed that higher pH (pH=9) originated a diminution on COD removal efficacy, with 78% of COD abated after two hours of treatment when compared with the 88% attained for pH = 7.5. This can be attributed to the significant value of IC (aproximally 50 mgC.L$^{-1}$). IC content is due to carbonate and hydrogen carbonate ions which are well known radical scavengers competing with the pollutants for hydroxyl radicals as described in reactions IV.7.10 and IV.7.11:

$HO^{\bullet} + HCO_3^{-} \rightarrow O_3^{-\bullet} + H_2O$ **(IV.7.10)**

$HO^{\bullet} + CO_3^{2-\bullet} \rightarrow O_3^{-\bullet} + OH^{-}$ **(IV.7.11)**

TOC content of treated wastewaters was monitored during the reaction period in order to evaluate the mineralization degree and the results are shown in Figure IV.7.1 b) for different pH values. As observed, a mineralization of about 33%, with a concentration of 44.2 mgC.L$^{-1}$, is attained for pH = 3 whereas between 10 and 18% of TOC removal is obtained for all other pH values. These lower values of TOC decrease when compared with the COD abatement are probably dueto the fact that pollutants can easily suffer partial oxidation (COD removal) while total mineralization is a hander task. The difference between the TOC and COD removal efficiency demonstrates that the final compounds are recalcitrant to ozone action leading to a large amount of degradation of COD, 87%, but a low percentage of TOC removal, and the consequent overall mineralization of the pollutants in the treated effluent isthen more complex to achieve (Rivas *et al.*, 2009).

Contrarily to COD removal, TOC depletion efficacy was found to decrease with alkaline conditions. The TOC abatement behavior can also be attributed to the higher impact of the radical scavenging over the final mineralization of the by-products formed during the partial oxidation of the parent compounds (Pera-Titus *et al.*, 2004). In this context, it was possible to reach 33% TOC depletion at pH=3, 18% at pH=5 and smaller than 15% for raw pH and 9.

#### *IV.7.3.2.2 Chemical Production Wastewater*

The treatment experiments for achieving the required COD and TOC *of Chemical Production (CP) wastewater* removal over a period of 180 min are illustrated in Figure IV.7.2.

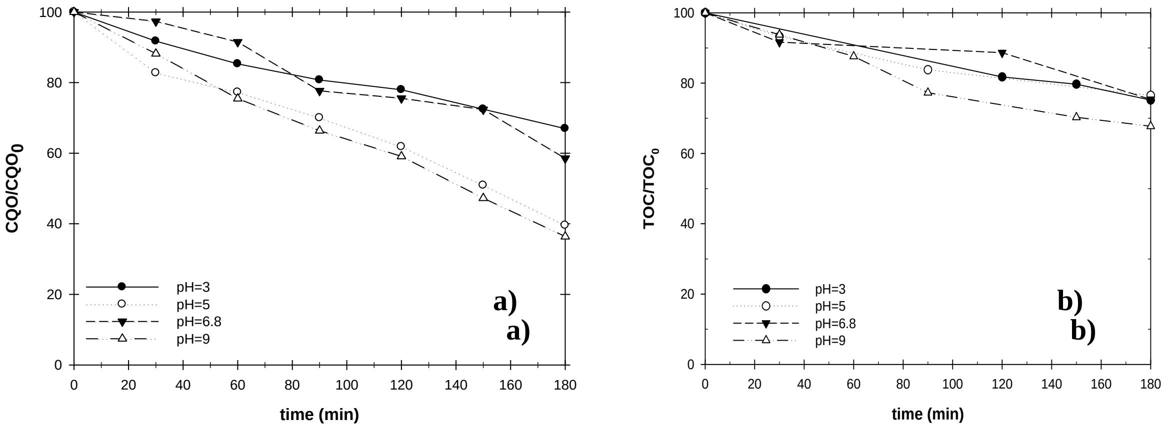

***Figure IV.7.2- Normalized concentrations of COD a) and TOC b) at single ozonation for CP as a function of time for different pH values at NTP. $[O_3] = 40\ g.Nm^{-3}$.***

Figures IV.7.2 a) and b) show the evolution of residual normalized COD and TOC with time during oxidation tests carried out at different pH values, fixed ozone dose and temperature in the depuration of the chemical industry effluent (CP). As it can be seen from Figure IV.7.2 a), the percentage of COD removal increased with an augment in the solution pH being the maximum COD depletion attained for a pH of 9 with 64% of final elimination, reaching the concentration of 400 $mgO_2.L^{-1}$. The ozone decomposition is directly affected by the solution pH as already mentioned. However, in this case, contrarily to what was attained before for the VW, at the raw pH it is observed a decrease in the oxidation performance when compared with the higher pH, with a removal of 51% similar to pH 5 in which 50% of COD degradation was reached, what proves that the direct ozone attack is a possible treatment for this wastewater, although at pH 3 only 33% of COD removal was obtained. These results reveal that the purification of the effluents can be promoted by directly or indirectly oxidation pathways, involving either direct oxidation by ozone or attack of the pollutants by radicals.

In Figure IV.7.2 b) it is clear that the efficiency of TOC removal increased for alkaline conditions with 24% depletion after 120 min at pH 3, 5 and raw while the higher mineralization values were attained at pH 9 with 32% of TOC degradation, with a final concentration of 184 mgC.L$^{-1}$.

The best results both for COD and TOC were then obtained at pH 9 with 63 and 32% of depuration respectively. Increasing TOC removal rates with the increasing pH can be attributed to the presence of hydroxyl radicals in the solution at the higher pH value since, as referred, these oxidant species have a higher reactive potential than molecular ozone leading thus to better mineralization at high pH.

Although the removals of COD and TOC vary with pH for both wastewaters, the pH values between 6 and 8 are more favorable for COD depletion of VW and CP effluents. As the raw pH's of these wastewaters were within this range these were the selected values to carry on the following experiments. This also allows a cost reduction in industrial applications, since it will not be necessary to adjust pH, saving this way in reactants. Comparing these results one can generally observe a higher COD removal for VW for higher pH's with 87% alongside to 50% of CP in alkaline conditions with pH=9.

Since pH was not controlled during the experiments it is important to known its variation along the reaction procedure. So for more acidic mediums (pH=3) pH was maintained at a similar value with no alteration, but when intermediary pH's as 5 and raw were it was verified that this parameter tended to 8 for CP effluent and to 9 for VW wastewater at the end of the reaction. The same conditions were observed at alkaline pH. The increase in wastewater pH with ozone is thought to be due to degradation of volatile fatty acids formed during the oxidation procedure (Wu *et al.,* 2004).

### *IV.7.3.3 Ozonation with Hydrogen Peroxide (Perozonation)*

Unless pH is increased, ozonation does not produce enough ($HO^{\bullet}$) radical concentrations in order to promote complete mineralization of dissolved pollutants. The recalcitrant nature towards ozone of the substances present in effluents suggests the utilization of another way to increase the production of hydroxyl radical through the addition of hydrogen peroxide to ozone (Gunten, 2003; Wu *et al.,* 2004; Poyatos *et al.*, 2004).

This combined system can initiate the decomposition cycle of ozone, resulting in the formation of the desired hydroxyl radicals. In aqueous medium the hydrogen peroxide is partially dissociated in ionic species ($HO_2^-$), which react with ozone, that when decomposed originates chain reactions (Gunten, 2003; Gogate and Pandit, 2004) promoting the effective pollutants degradation.

The implementation of this radical system makes degradation of refractory molecules possible, combining the advantage of selective molecular ozone reactions and posterior non-selective free radical attack reactions (Gogate and Pandit, 2004, Azbar *et al.,* 2004) at neutral pH medium.

The hydrogen peroxide dosage was calculated based in the stoichiometry relation (Azbar *et al.*, 2004) for conversion of an organic compound to $CO_2$ and $H_2O_2$ endorsed by the peroxide oxidation of COD and is given by the Equation IV.7.11.

$$H_2O_2\ \left(\frac{mg}{L}\right) = 2.13 \times COD\ \left(\frac{mg}{L}\right) \qquad \textbf{(IV.7.11)}$$

which can be translated into a stoichiometric equivalent concentration of 246 mg.L$^{-1}$ (7.2 mmol.L$^{-1}$) of $H_2O_2$ for the VW effluent and 2430 mg.L$^{-1}$ (71.5 mmol.L$^{-1}$) for the CP wastewater.

#### *IV.7.3.3.1 Vegetable Wash Effluent Perozonation*

Normalized COD and TOC abatements of Vegetable Wash (VW) wastewater obtained by perozone oxidation for different $H_2O_2$ loads are shown in Figure IV.7.3.

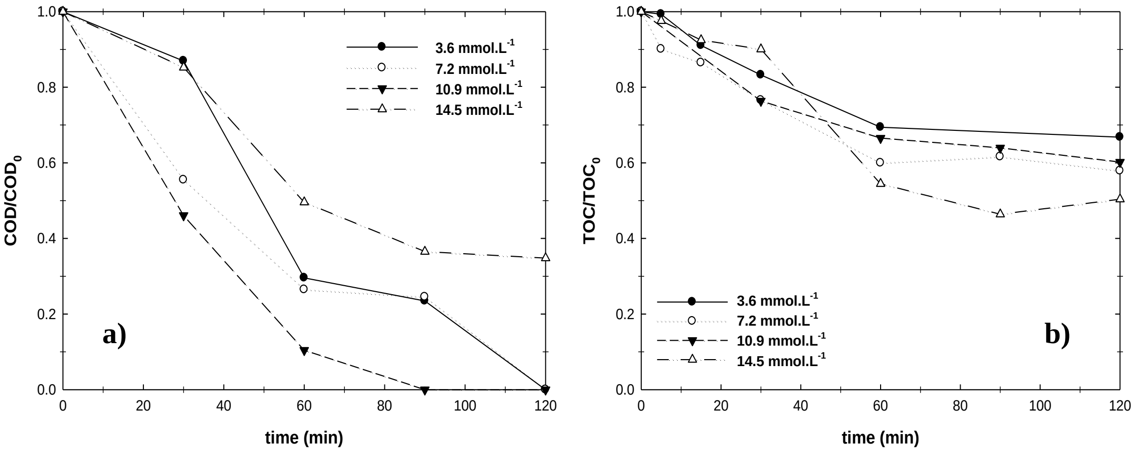

***Figure IV.7.3- Normalized concentrations of COD a) and TOC b) at perozonation for VW as a function of time for different $H_2O_2$ concentrations at raw pH, at NTP. [$O_3$] = 40 g.Nm-3***

Figures IV.7.3 a) and b) show the evolution of residual normalized COD and TOC with time during ozonation experiments carried out at different dosages of hydrogen peroxide and fixed ozone dose, temperature and raw pH. The $H_2O_2$ dosages were correspondent to 50% (3.6 mmol.L$^{-1}$), 100% (7.2 mmol.L$^{-1}$) 150% (10.9 mmol.L$^{-1}$) and 200% (14.5 mmol.L$^{-1}$) of the stoichometric value given by the referred correlation.

It can be observed from Figure IV.7.3 a) that the COD removal increased with the augment of $H_2O_2$ in the solution and total COD decrease has been accomplished within 90 minutes of oxidation for a concentration of 10.9 mmol.L$^{-1}$ but also after 120 minutes of reaction for 3.6 and 7.2 mmol.L$^{-1}$. However, for a hydrogen peroxide concentration of 14.5 mmol.L$^{-1}$ only 65% COD removal was achieved, reaching the concentration of 40 mg.O$_2$L$^{-1}$. This fact is due to the high concentration of hydrogen peroxide which is well known by its radical scavenger effect when in excess (Equation IV.7.12). This will lead to the consumption of hydroxyl radicals reducing, thus, the process efficiency as was already observed in other works (Pera-Titus *et al.*, 2004; Matilainen and Sillanpää, 2010):

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad \textbf{(IV.7.12)}$$

In Figure IV.7.3 b) the efficiency of TOC removal increased with increasing hydrogen peroxide concentration. 50% of TOC was eliminated and a final concentration of 29.5 mgC.L-1 was obtained after 120 min when 14.5 mmol.L-1 of $H_2O_2$ were applied. Similar TOC removal, 40%, was reached with 7.2 and 10.9 mmol.L-1 of hydrogen peroxide, and the smallest $H_2O_2$ concentration led only to 33% depuration. So, contrarily to the COD removals, the TOC depletions were found to increase with the H2O2 dosage. This fact could be explained by the complex effluent composition, were exists an numerous forms of organic compounds, some not quantified by closed reflux colorimetric method, as volatile straight-chain aliphatic compounds (Greenberg *et al.*, 1985) such as alcohol, sugars and alkenes, which means that, probably the initial COD value is under valorized. Those compounds can suffer mineralization (leading to TOC removal); however, since they were not accounted for the initial COD, their degradation is not identified regarding COD measurement.

#### *IV.7.3.3.2 Chemical Production Effluent Perozonation*

The experimental results for the degradation of Chemical Production (CP) wastewater during perozonation regarding COD and TOC depletion are shown in Figure IV.7.4. The $H_2O_2$ dosages were correspondent to 50% (35.7 mmol.L$^{-1}$), 100% (71.5 mmol.L$^{-1}$) and 150% (107.2 mmol.L$^{-1}$) of the stoichometric value given by the Equation IV.7.11.

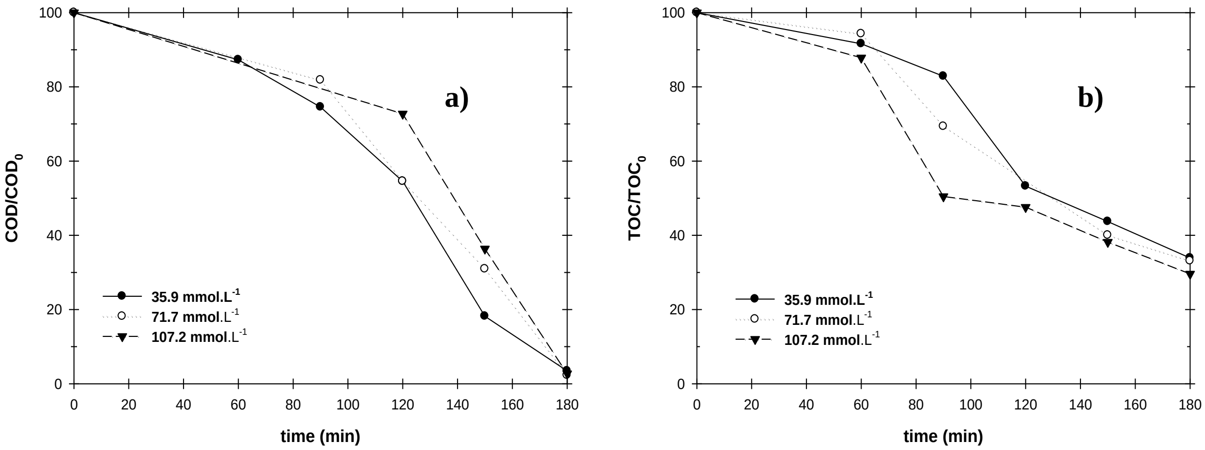

***Figure IV.7.4- Normalized concentrations of COD a) and TOC b) at perozonation for CP as a function of time for different $H_2O_2$ concentrations at raw pH, at NTP. $[O_3]$ = 40 g.Nm$^{-3}$.***

The performance of perozonation was evaluated at the raw pH selected previously (pH=6.8). As illustrated in Figure IV.7.4 a), up to 96% of COD was removed within 180 min of reaction for all the distinct amounts of hydrogen peroxide, reaching a final concentration of 38 mg$O_2$.L$^{-1}$. According to these values, the removal of COD is slightly lower when higher concentrations of hydrogen peroxide were applied. This phenomenon can be explained by the scavenger effect described above, where the excess of $H_2O_2$ acts as radical scavengers reducing the availability of those oxidant species to react with pollutants.

In agreement to what was previously observed, in Figure IV.7.4 b) is showed that the efficiency of TOC removal increased with increasing concentration of hydrogen peroxide. 70% of TOC removal was obtained after 180 minutes with 71.5 mmol.L$^{-1}$ of $H_2O_2$ with a final concentration of 67 mgC.L$^{-1}$. Nevertheless, similar TOC depletion, 65%, was achieved for the others peroxide concentrations used. It is therefore always unavoidable to investigate for an optimal hydrogen peroxide concentration above which a decline or no effect of $H_2O_2$ on treatment would be observed.

Within this context, it seems that, for the particular case of CP wastewater the optimal hydrogen peroxide concentration leading to the highest depuration values is the lowest value (35.9 mmol.L$^{-1}$), with which approximately 65% of mineralization was obtained saving this way reagents without significant loss of efficiency.

### *IV.7.3.4 Single Ozonationversus Perozone Ozonation*

Within these results, a comparison between the performance of single ozonation and perozone, on COD, TOC and TSS at the end of the oxidizing procedure for the two studied effluents, is presented in Figure IV.7.5. The experiments were run at the raw pH with an ozone concentration of 40 g.Nm$^{-3}$.

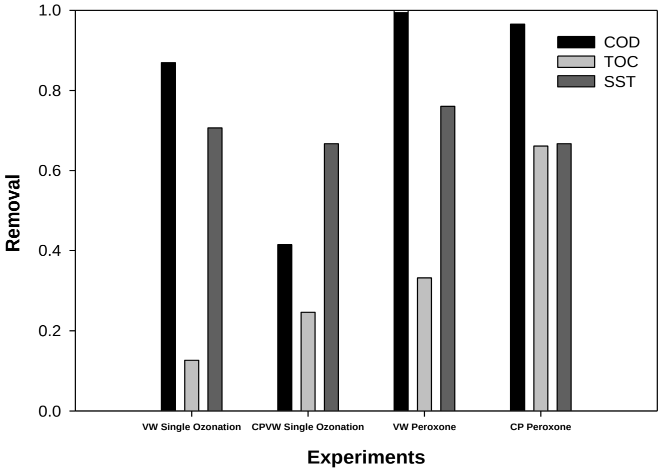

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***Figure IV.7.5- Removals of COD, TOC and SST for $O_3$ alone and $O_3/H_2O_2$-based advanced oxidation, for the VW and CP at raw pH and NTP. $[O_3]$ = 40 g.Nm$^{-3}$.***

As observed, single ozonation can be an efficient technology to eliminate the COD content of these effluents. Indeed, ozone alone ensured COD removals of about 87% and 41% for VW and CP respectively whereas the combined $O_3/H_2O_2$ system increased COD elimination up to 100% for the Vegetable Wash and 96% for the Chemical Production effluent meaning that this combination improved in 17% and 56% the COD degradation when compared with single ozonation for VW and CP, respectively.

Looking at the effect of hydrogen peroxide, Figure IV.7. 5 shows that $H_2O_2$ increased the TOC removal rate by more than the double when compared to ozone alone due to higher hydroxyl radical production in the $O_3/H_2O_2$ system. For the VW effluents an increase from 13% to 33% was observed while for the CP wastewater mineralization the enhancement was from 25% to 66% comparing single with hydrogen peroxide aided ozonation.

In what concerns the Suspended Solids, the fact of been able to reduce the concentration of suspended solids with the chemical treatment, allows the process to be carried out with no sedimentation and no significant sludge formation (You and Tsai, 2010). However there is no important improvement for the $O_3/H_2O_2$ system, attending that for CP the same removal was reached and for the VW wastewater only a slight difference of 6% was detected.

To gauge if the reaction mechanism is mainly going towards mineralization or oxidation, the Average Oxidation State (AOS) was determined an indicator of the oxidation extent of wastewaters treatment (Momani *et al.,* 2004). This parameter is defined as a ratio between COD and TOC in molar units, and is calculated as follows through equation IV.7.15:

$$AOS = 4 \times \frac{TOC-COD}{TOC} \qquad \textbf{(IV.7.15.)}$$

where TOC is in molC.$L^{-1}$ and COD in mol$O_2$.$L^{-1}$

AOS indicates how chemical substances in the effluent become more oxidized: superior COD/TOC ratios imply a higher degree of mineralization (+4) while smaller ratios means partial oxidation (-4). In Figure IV.7.6, the Average Oxidation State (AOS) is shown.

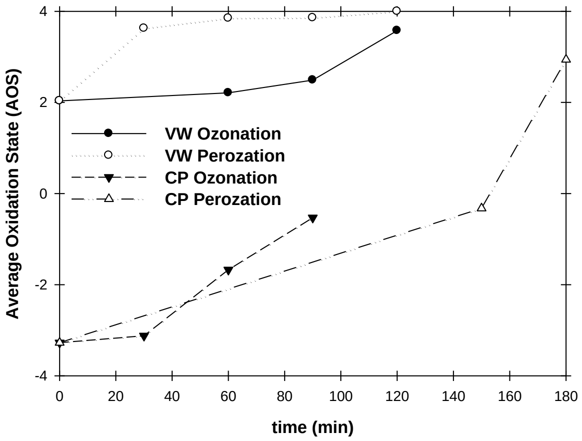

*Figure IV.7.6- AOS to the selected tests of single ozonation and perozonation of VW and CP wastewaters*

As can be seen, the two effluents, different initial oxidation states for VW (+2.0) and CP (-3.2) show that VW has a higher oxidation state. According to these results, AOS throughout the different processes increase, which means that the final products are more oxidized than the initial substances. For the VW wastewater all the oxidant systems reach an oxidation state very close to total mineralization (+4) of the treated waste water after the oxidation period. For the CP effluent single ozonation promotes a partial oxidation since low AOS values are always attained (below 0). However, the $O_3/H_2O_2$ system favours the complete oxidation of pollutants since AOS values closer to +4 were attained strengthening the role of hydroxyl radicals guiding reaction towards total mineralization.

After a thorough analysis of the results, the VW effluent after perozonation (raw pH and [$O_3$] = 40 g.$Nm^{-3}$) achieved 0 mg$O_2$.$L^{-1}$, 38 mgC.$L^{-1}$ and 23 mg.$L^{-1}$ on COD, TOC and TSS, respectively. Whereby water for human consume must meet the maximum values of 30 mg$O_2$.$L^{-1}$ and 25mg.$L^{-1}$ of COD and TSS respectively, so this treated water reaches those values and could be reintroduced in the first stage of vegetable washing. In what regards the CP effluent it were reached 38 mg $O_2$.$L^{-1}$, 62 mgC.$L^{-1}$ and 44 mg.$L^{-1}$ on COD, TOC and TSS when ozonation aided by hydrogen peroxide was applied. This stream could be used in the irrigation or in the other applications existent in the plant. It seems thus that perozonation promotes mineralization of the effluents revealing to be an attractive technology when compared with single ozonation, as also referred in literature (Rivas *et al.*, 2009).

Ozone's multiple uses for disinfection, by-products removal, along with the improvements in suspended solids make it an especially appropriate treatment process. From the results attained in this work, it was concluded that perozonation is a suitable technology for wastewater remediation leading to streams able to be reused according to Portuguese legislation; however toxicological tests would strengthen the viability of its application to wash vegetables (Zoutman *et al.*, 2011).

## IV.7.4 Conclusions

The aim of this work addressed the study of the performances of $O_3$ alone and $O_3/H_2O_2$-based advanced oxidation systems to treat an agro-industrial vegetable wash wastewater (VW) and a chemical production (CP) effluent with distinct characterization. VW had COD and TOC values of 155 and 122 mg.$L^{-1}$ respectively and 660 mg.$L^{-1}$ of TSS. CP had a moderate value of COD, 1100 mg$O_2$.$L^{-}$, 273 mgC.$L^{-1}$ of TOC content and 100 mg.$L^{-1}$ of Suspended Solids.

The study revealed that ozone combined with hydrogen peroxide is an efficient method to treat those wastewaters. The main conclusions taken from this research were:

- Single ozonation leads to COD reductions of 87% and 41%, TOC content removals of 13 and 26% and a TSS decrease of 70 and 66% for VW and CP respectively;
- Total and up to 90% of COD depletions, TOC degradations of 33 and 66% and SST reductions of 76 and 66% were achieved after the treatment with $O_3/H_2O_2$ for VW and CP respectively;
- Hydrogen peroxide proved to enhance the oxidation process when combined with ozone in almost twice the overall efficiency in TOC removal when compared to ozone alone;
- Best hydrogen peroxide concentrations of 3.6 mmol.$L^{-1}$ and 35.7 mmol.$L^{-1}$ were selected for VW and CP depuration, respectively, since for higher loads the scavenger effect reduced the treatment effectiveness.
- Comparing the methodologies used for the treatment of those effluents, we selected the perozone as the most adequate technique, which in addition to having achieved the best results for those parameters, reached the better AOS values and also had the advantage of the low cost of $H_2O_2$ compared with the cost associated with a greater amount of ozone production for reach the same efficiency.

- In our case the treated water could be reintroduced in the washing vegetables operation, and the final CP effluent could be used in the irrigation or in the other applications existent in the factory layout.

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# IV.8 Integration of advanced oxidation processes and activated sludge for the treatment of high refractory industrial wastewater

## IV.8.1 Introduction

Industrial activity generates large amounts of highly charged wastewater comprising refractory compounds, involving mainly oil, greases and surfactants from the extrusion, cutting and washing phases, respectively, from the productive process. In this paper an effluent coming from a plant that produces automotive coating pipes was analyzed. Currently, the in-situ methodology used to treat this wastewater in the industrial unit was a Reverse Osmose System (RO) coupled with only a solids separation process based on a set of sieves and filters for the removal of solids up to 100 mesh. This procedure shows several severe drawbacks as the RO membrane stabilization performance, fouling, as well as the problems associated with the disposal of the resultant RO concentrate (Bennera *et al.,* 2008). In fact, the system showed to be ineffective after three months of operation due to the variations on the composition of the effluent. The possible recurrence of the problem, constrains the decision to replacement the membranes, which constitutes a very high operating cost.

Also, more financially appellative processes as the biological treatments are ineffective in practice due to the low biodegradability and composition changes of the effluent that do not permit microorganisms acclimation. However, when this conventional methodology is combined with chemical or physical systems, the reduction of the refractory pollutants and the consequent biodegradability improvement may provide conditions so that a further bio-treatment may be applied (Ribeiro *et al.,* 2015).

In this sense, Advanced Oxidation Processes (AOPs) emerge as suitable alternatives, able to degrade bio-refractory pollutants through the oxidation promoted by hydroxyl radicals. This is the case of the Fenton reagent, based on the oxidant power of hydrogen peroxide catalyzed by iron ions, recognized as a feasible and efficient process using low cost reagents (Ribeiro *et al.,* 2015; Perdigón -Melón *et al.,* 2010)

Ozonation is also an interesting method operating at ambient conditions of pressure and temperature. This system allows taking advantage of the oxidant power of molecular ozone that is able to degrade compounds comprising high electronic density groups. Besides, at alkaline medium or using hydrogen peroxide as a co-oxidant the formation of hydroxyl radicals is enhanced leading, generally, to higher efficiencies (Martins *et al.,* 2012; Amaral-Silva *et al.,* 2012)

One of the advantages of these processes, besides the possible mineralization of the pollutants, is the fact that they can also enhance the mixture biodegradability due to the bio-refractory contaminants oxidation (Martins *et al.,* 2010). This will allow the application of a posterior biological treatment. However, the AOPs can also lead to products more toxic than the original compounds if reactions are incomplete. The economic factor is another restriction due to the high operational costs when high strength wastewaters are involved. A significant economic drawback derives from reactants consumption (e.g. $H_2O_2$), production of iron sludge waste for Fenton Process, in-situ ozone production power requirements for the ozone based processes, besides the high investment costs on adequate equipment and materials (Poyatos *et al.,* 2009; Oller *et al.,* 2011).

The main objective of the present work addressed the setting up of an appropriated technology to depurate an industrial wastewater from the coating automotive tubes industry reaching a final treated stream legally able to be discharged into the hydrological resources.

The main objective of the present work addressed the setting up of an appropriated technology to depurate an industrial wastewater from the coating automotive tubes industry reaching a final treated stream legally able to be discharged into the hydrological resources.

## IV.8.2 Material and Methods

### *IV.8.2.1 Wastewater characterization*

The wastewater samples were collected from the industrial outlet stream of the factory. The effluent was characterized by a light-brown color. Table IV.8.1 summarizes the main physic-chemical characteristics of the wastewater. As it can be observed, it shows a moderate amount of suspended solids promoting turbidity. Moreover, relatively high COD and low $BOD_5$ levels are found, which leads to a $BOD_5$/COD ratio of about 0.11 revealing its low biodegradability. These characteristics seem to inhibit the direct application of biological processes.

***Table IV.8.1- Wastewater Characterization***

| ***COD*** ***($mgO_2.L^{-1}$)*** | **TSS** **($mg.L^{-1}$)** | **$BOD_5$** **($mg.O_2.L^{-1}$)** | **pH** | ***$BOD_5$/ COD*** |
|---|---|---|---|---|
| *10500±1240* | 2300±1500 | 1140±230 | 7.8±1.2 | *0.11* |

During the experimental period, samples were taken at certain intervals of time. The efficiency of the processes was analyzed through Chemical Oxygen Demand (COD) that was measured by the closed reflux, colorimetric method specified in Standard Methods 5220 D, (Greenebrg *et al.,* 1985) performed in a COD thermo-reactor HANNA HI 839800 and a HANNA HI

83224 photometer. Ammonia nitrogen (N-NH4), nitrite nitrogen ($N-NO_2$), nitrate nitrogen ($N-NO_3$), and phosphates ($P-PO_4$) were also analyzed with an HANNA HI 83224 photometer.

The oxygen consumption of a microorganism consortium obtained from garden soil during 5 days of contact with the samples, leading to the $BOD_5$, was determined using an automatic sensor HANNA HI 4421, and the pH was determined using a HANNA HI 4522. The Total Suspended Solids (TSS) were determined by Standard Methods: “2540 D: Dried at 103 - 105 °C”**.** (Greenebrg *et al.*, 1985)

### *IV.8.2.2 Analytical Techniques*

During the experimental period, samples were taken at certain intervals of time. The efficiency of the processes was analyzed through Chemical Oxygen Demand (COD) that was measured by the closed reflux, colorimetric method specified in Standard Methods 5220 D (Greenebrg *et al.,* 1985) performed in a COD thermo-reactor HANNA HI 839800 and a HANNA HI 83224 photometer. Total Nitrogen (TN) and Total Phosphates (TP) were also analyzed with an HANNA HI 83224 photometer. The COD analysis was performed with HANNA kits. Three available vials ranges were used, HI93754A for Low Range ($0\text{-}150 \pm 4\ mgO_2.L^{-1}$), HI93754 B for Medium Range ($0\text{-}1500 \pm 22\ mgO_2.L^{-1}$) and HI93754A for High Range ($0\text{-}15000 \pm 220\ mgO_2.L^{-1}$).

In what regards to Total Nitrogen analysis was accomplished with HI94767 A ($0\text{-}25 \pm 0.5\ mgN.L^{-1}$) and HI94767 B ($10\text{-}150 \pm 3\ mgN.L^{-1}$) whilst Total Phosphorous concentration was determinate by the HI 94763B ($0\text{-}\ 1.15 \pm 0.02\ mgP.L^{-1}$) and HI 94763C reactants ($0\text{-}32.6 \pm 1\ mgP.L^{-1}$).

Microscopic analysis were performed with a MOTIC BA 120 microscopy. The pH was determined using a HANNA HI 4522. Total Suspended Solids (TSS) were determined by Standard Methods: “2540 D: Dried at 103 - 105 °C” (Greenebrg *et al.,* 1985)**.** The oxygen consumption of a microorganism consortium obtained from garden soil during 5 days of contact with the samples, leading to the $BOD_5$, was determined using an automatic sensor HANNA HI 4421. The methodology used with this inoculum allows to verify whether the wastewater is biologically assimilated by any consortium of microorganisms, permitting to compare the several tests as well as ensuring the worst possible scenario, quantifying the biodegradability, without any previous microorganisms adaptation.

### *IV.8.2.3 Experimental set-up*

#### *IV.8.2.3.1 Coagulation*

Several coagulants, with different characteristics, were tested in order to treat this wastewater. Aluminum polychloride (Kemira Pax-18) and ferric sulfate ($Fe_2SO_4$), as well as an organic coagulant, with the reference ADVP19, were used. Coagulation experiments were performed in a conventional jar-test apparatus (Velp) equipped with 6 beakers of 1-L volume. Due to economic factors, the pH cannot be changed to values extremely acid or alkali, avoiding, for instance, new tanks construction with other materials. Moreover, this will diminish the costs associated with acid and soda for pH correction. Similarly, coagulant consumption, due to economic restrictions, may not exceed a maximum of 2 liters per $m^3$. The best operative pH (among 2 and 8) was assessed through the addition of 1 $g.L^{-1}$ of each coagulant. Besides, the most efficient chemicals doses to COD and TSS removal (between 0.1 and 2 $g.L^{-1}$) were determined for the previously selected pH (at ambient temperature). Each chemical was added to 500 mL of effluent in the mentioned conditions. The procedure consisted in three successive steps: a stage with a quickly mixing for five minutes (120 rpm) followed by 15 min stirring (15 rpm) in order to endorse the coagulation stage. Finally, after settling for 30 min, the supernatant was withdrawn and used for chemical analysis.

#### *IV.8.2.3.2 Fenton's process*

Fenton's oxidation was handled in batch regime using 1.5 L stirred glass reactors. The tests were performed using ferrous iron sulphate ($FeSO_4.7H_2O$, Industrial grade, with 19.7% (w/w) of iron content and hydrogen peroxide ($H_2O_2$, 49.5 % w/w) at ambient temperature. Generally, 1000 mL of wastewater with the pH corrected to 3.7 were introduced into the reactor and stirred. Different ratios between iron and hydrogen peroxide were tested, from 2:1 to 10:1 (w/w) (Durán-Moreno *et al.,* 2010) in order to verify the applicability of the process in a wider range, being the required $Fe^{2+}$ dosage added, dependent on the selected $[H_2O_2]$: $[Fe^{2+}]$ ratio. The reaction started when 25 % of the volume of the $H_2O_2$ stoichiometrically necessary to totally oxidize the initial COD value (Lucas and Peres, 2010), which corresponds to 5.58 $g.L^{-1}$, was added in two aliquots, at the beginning and at the fourth hour of reaction. It was select this value due to the economic factors, since the costs with $H_2O_2$ dosage is referred as one of Fenton Process application limitations (Poyatos *et al.,* 2009), while the amount of iron could be optimized according that restriction since this is a cheaper reactant.

The oxidation terminates at the end of 420 minutes of operation when NaOH was added until reaching pH of 11 to precipitate the iron in solution that would remove a fraction of the organic matter, promoted by the consequent coagulation step[11], and quench the remaining $H_2O_2$. Posteriorly, after 15 minutes of agitation that promotes the iron flocks formation and the total residual hydrogen peroxide depletion (Martins *et al.,* 2010), a certain dose of cationic flocculant was added in order to improve the flock formation and consequent settling.

#### *IV.8.2.3.3 Ozonation*

Ozonation experiments were carried out in a reactor operating in a semi-batch mode. 1000 mL of effluent were initially charged in a magnetically stirrer glass reactor while ozone was continuously introduced through a diffuser placed in the liquid bulk. The stirring speed was kept at 750 rpm to guarantee insignificant external mass transfer resistances during the experiments ensuring chemical regime (Amaral-Silva *et al.,* 2012). Ozone was generated from pure oxygen in an ozone generator C-Lasky C-L010DS (AirTree), with a concentration of 2 $g.h^{-1}$. Samples were periodically withdrawn for further analysis. In the perozone, the hydrogen peroxide was added at the raw effluent before feeding the ozonated gas stream. On the controlled pH tests, pH was corrected at pre-determinate time intervals through addition of NaOH (50%) and $H_2SO_4$ (37%), (Industrial grade). In what concerns the $O_3$/COD (w/w) a dose of 3.81 g of ozone per gram of initial COD was used, due to the fact that the equipment used for ozone generation only produces a fixed concentration.

#### *IV.8.2.3.4 Biological Treatment*

The resultant treated wastewater was posteriorly refined by an aerobic biological system performed at laboratory scale and executed in two small-scale Sequential Batch Reactors (SBRs) with an active volume of 400 mL. The aeration was provided by ceramic diffusers placed in the bottom of the reactors and connected to an aquarium compressor, promoting the air diffusion with the aim of providing the necessary oxygen concentration to endorse aerobic conditions ($[O_2] > 2$ $mgO_2.L^{-1}$).This was assured with periodically dissolved oxygen (OD) measurements in the SBR by using the dissolved oxygen sensor HANNA HI 4421. The compressor was linked to a clock that switches on and off this equipment, in order to divide the reaction phase into periods with and without aeration, and also set the settling and discharge phases.

Both treatments were composed by four distinct sequential phases: reaction phase of 20 hours, programmed to aerate in intervals of 30 minutes; settling phase 2 h; discharge phase 1 h; and filling phase 1h. The reactors were operated with a hydraulic retention time (HRT) of 20 days and the SBR was inoculated with 400 mL of sludge, from a biological reactor of a winery wastewater treatment plant, with 1500-2000 $mg.L^{-1}$ of Mixed Liquor Volatile Suspended Solids (MLVSS) and 150 $mgO_2.L^{-1}$ of COD in the supernatant. The low organic load existing in the reactors during the startup allows the microbiota adaptation to the wastewater under study.

In one of the reactors, a selected microbial consortium by bioaugmentation ("BioSBR") was supplied. The bioaugmentation process was carried with a selected microbial consortium (EU50) provided by the Biosystems Company. According to the supplier specifications this consortium is specific to treat water and soil contaminated with fine chemicals, petrochemicals and detergents and, to improve biological treatment, 45 g of the EU50 consortium should be added per $m^3$ of effluent. Therefore, during 10 days the referred quantities were used. Then the addition was made in every 4 weeks. The biological reactor without bio augmentation as named "SBR".

Every day, samples were taken from the supernatant to analyze the COD values. Moreover, microscopy was used for the observation of the microbial species allowing their identification. The evolution of the protozoan community was assessed by the calculation of the Sludge Biotic Index (SBI) according to the method described by Madoni (2004). The SBI is calculated considering the protozoan community dominant in the activated sludge, and the performance of the biological reactor is classified according to this value in four classes: Class I (SBI 8 - 10) - biological reactor has well colonized and stable sludge, optimal microbial activity and high removal efficiency; Class II (SBI 6 - 7) - biological reactor has well colonized and stable sludge, almost optimal microbial activity and good removal efficiency; Class III (SBI 4 - 5) - biological reactor presents an insufficient biological activity and mediocre efficiency removal; Class IV (SBI 0 - 3) - biological reactor with low biological activity and little efficiency removal.

## IV.8.3 Results and discussion

### *IV.8.3.1 Coagulation*

Initially, a coagulation study was performed in order to remove the solids and pre-treat the water for posterior oxidation. Several jar test experiments were performed to establish the most effective coagulation operational conditions. Initially, the runs were performed with the intention of defining the most effective pH for a proposed coagulant dose of $1 kg.m^{-3}$. Thus, pH was changed from 3 to 8. These tests revealed that the optimal pH was 8, 4 and 7 for Pax-18, $Fe_2SO_4$ and ADVP19, respectively in what regards to TSS and COD depletion.

To optimize the coagulant load, different doses ranging from 0.1 until 2 $kg.m^{-3}$ were tested for the best pH attained for each coagulant. The data collected revealed that the optimal concentration of each coagulant was 0.75 $kg.m^{-3}$, 1 $kg.m^{-3}$ and 0.2 $kg.m^{-3}$, for Pax-18, $Fe_2SO_4$ and ADVP19, respectively, achieving at this conditions the best analyzed parameters removal rates as present in Figure IV.8.1, where it is possible to compare the Chemical Oxygen Demand (COD) and Total

Suspended Solids (TSS) depletion, as well as the achieved biodegradability for the referred optimized operational conditions for each tested coagulant.

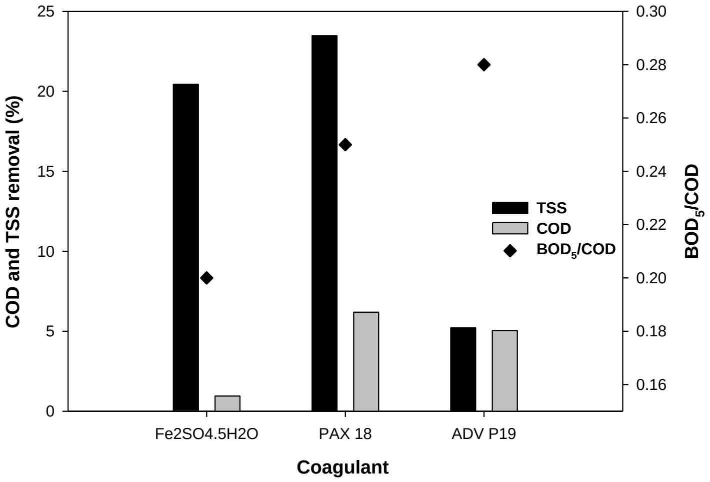

*Figure IV.8.1- COD, TSS removals and $BOD_5/COD$ attained for the different optimized coagulation trial*

It is possible to observe that the most effective coagulant was the PAX 18 (pH =8; 0.75 $kg.m^{-3}$) with more than 23.5% of suspended solids and 6.2% of COD removal. This reduction led to an effluent with 9850 $mgO_2.L^{-1}$ and 1760 $mg.L^{-1}$ of COD and TSS respectively. Besides, the ferric coagulation (pH =4 and 1 $kg.m^{-3}$) only reaches a depletion up to 1% and 20.4% of those parameters (COD and TSS, respectively). The worst solids removal was promoted by the organic coagulant (pH =7 and 0.2 $kg.m^{-3}$) with the abatement of solely 5.2% of TSS. The fact that the solids removal percentage was so different from the COD results led to the conclusion that the solids are mainly inorganic and do not contribute to the global COD.

The data collected show that coagulation is insufficient to attain an efficient depuration of this effluent, and that besides the solids content removal, a great amount of pollutants are dissolved. Thus an oxidation step is required for their elimination. Nevertheless, a biodegradability enhancement was verified for all the used coagulants, however all the tests reached a value lower of 0.3, which is considered as the minimum for being subjected to a biological treatment.

### IV.8.3.2 Fenton's oxidation

In what respects to Fenton's oxidation, Figure IV.8.2 shows the COD removed for the experiments performed at different $Fe^{2+}$: $H_2O_2$ (w/w) ratios after 12 hours of reaction.

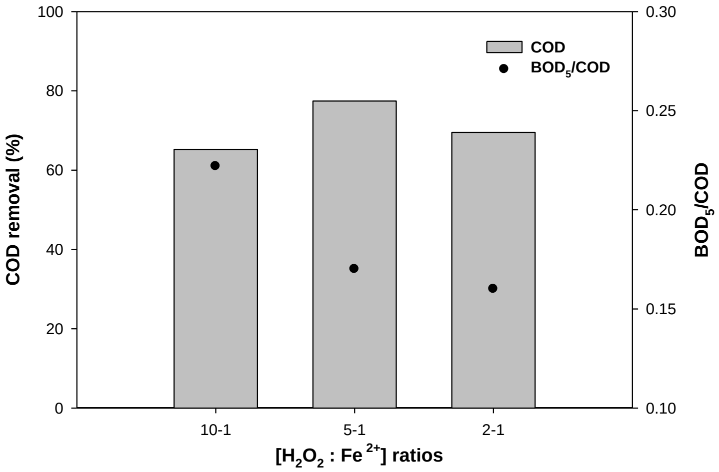

*Figure IV.8.2- COD and $BOD_5$/COD ratios for the Fenton experiments*

Attending that the hydrogen peroxide content is always the same, the effect of iron concentration on COD removal and biodegradability evolution can be assessed by the results depicted in Figure IV.8.2. It is possible to observe that the increase in the iron load dose led to a better COD removal until the 5:1 test (77.5%) reaching a COD of 2370 $mgO_2.L^{-1}$. On the other hand, higher doses (10:1 test) inhibit the treatment efficiency due to the scavenger effect promoted by the excess of iron (Martins *et al.,* 2010), with a final organic content degradation of 65.2%. For the lowest iron amount, 69.5 % of COD was eliminated, attaining a final value of 3200 $mgO_2.L^{-1}$.

It is still possible to visualize that higher iron concentration reduces the wastewater biodegradability. This behavior can be explained either by the oxidation and consequent removal of the biodegradable organic matter fraction in solution (reduction of $BOD_5$) or by the toxicity to the bacteria related with the iron added to the solution.

As these tests were performed with the purpose of an industrial application, the trials were carried out aiming to achieve a COD value below 1250 $mgO_2.L^{-1}$, which corresponds to the maximum allowable legal value for discharge in the municipal sewage. Fenton's process was unable to satisfy this premise. Probably, increasing the $H_2O_2$ and consequent iron load, could further improve the efficiency; however the operational costs with hydrogen peroxide and the sub products formed as the iron sludge treatment are prohibitive for the industrial acceptance of this process (Poyatos *et al.,* 2009).

### *IV.8.3.3 Ozonation*

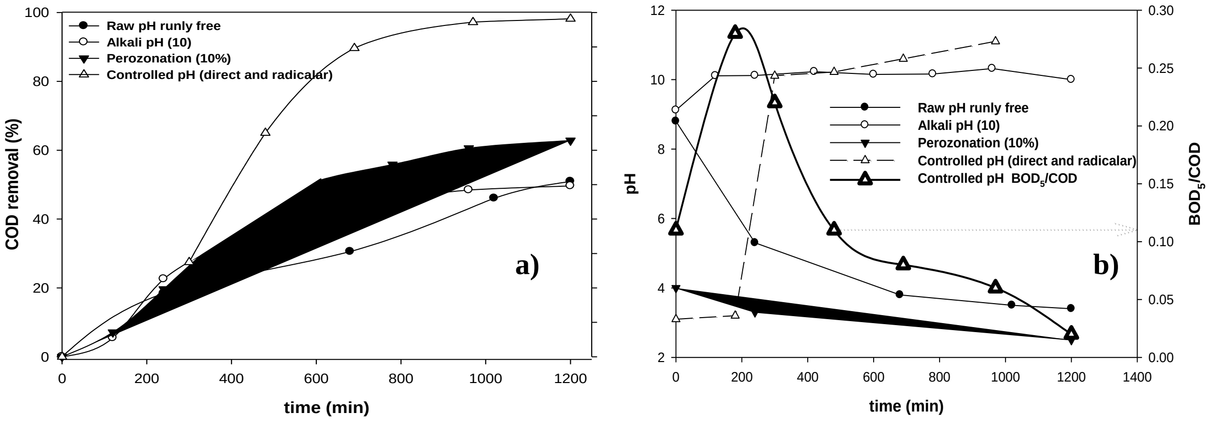

*Figure IV.8.3- pH and BOD$_5$/COD a), COD b) ratio for the ozonation experiments [O$_3$] = 2 g.h$^{-1}$*

Subsequently to the Fenton experiments where the wastewater debugging until a discharge value or either the biodegradability improvement until a value that allows biological treatment was not attained, possibly due to the presence of refractory pollutants to the chemical oxidation, the potentiality of ozone, with its diversity of depurative mechanisms (direct and radical oxidation), was tested as a solution to this problem.

In Figure IV.8.3 a) one can observe the COD depletion and the BOD$_5$/COD value achieved along the ozonation trials. It should be noticed that for the different experiments the same ozone inlet load (2 g.h$^{-1}$) was applied.Several tests were performed to analyze the impact of pH (that was fixed or changed along the treatment). Moreover, the impact of the application of hydrogen peroxide was assessed.

In Figure IV.8.3 b) it is possible to observe the pH variation during the experiments, and the BOD$_5$/COD profile for the trial with the best removal rate. It can be concluded from these results that the oxidation process is strongly dependent on the medium pH. In fact, ozone oxidation follows two major pathways: at acidic pH the ozone molecule is able to perform a direct electrophilic attack on the pollutants (which is limited to high electronic density groups); while the alkaline pH promotes the decomposition of ozone and the generation of hydroxyl radicals (HO$^\bullet$) that will unselectively attack the pollutants (Zayas *et al.*, 2007).

For all the experiments, a similar COD degradation efficiency is observed for the first 200 min of reaction whichever the conditions. This behavior must be related with the degradation of the compounds comprising high electronic density sites (such as aromatic rings) that are very reactive. That decomposition leads to the formation of low molecular weight carboxylic acids which explains the pH lowering during the experiment where pH was left run freely. These by-products are more refractory and molecular ozone is unable to further degrade them. In fact, for the case where pH was left run freely a final COD abatement of barely 51% was obtained after 1200 min of reaction.

The use of alkaline medium (pH 10) slightly improved the process efficiency with 49% of COD degradation being achieved after 600 min when compared with the 30% attained for the case where pH was left run freely at the same experimental time. However, after this, a plateau with non-significant organic matter abatement is observed and a final efficacy similar to the one attained when pH run freely is achieved. This should be related with the presence of some radical scavengers in the wastewater composition such as carbonates that inhibit the hydroxyl radicals action over pollutants**.** (Amaral-Silva *et al.,* 2012).

In this context, in order to take advantage of ozonation dual mechanism (direct and radicalar), an experiment where pH was maintained at 3 during 400 min and afterwards changed to 10 was performed. While for the first 400 min of reaction the COD degradation profile is very similar to the one attained for the last two experimental conditions, after this time (when pH is changed to 10) a significant improvement is observed. A final 98% of COD depletion is reached at the end of the treatment which leads to a COD = 220 mg$O_2$.$L^{-1}$.

In the first phase of the treatment (pH 3) molecular ozone is able to directly attack the initial pollutants comprising high electronic density sites. Moreover, at those acidic conditions the carbonates are converted into carbon dioxide and stripped from the water. This means that the radical scavengers present in the wastewater are removed, allowing that the hydroxyl radicals produced in the alkaline phase (pH 10) further degrade the remaining organic matter. The presence of such scavengers in solution should explain the low efficiency of the case where pH is maintained at 10 since the beginning of the oxidation process.

The utilization of hydrogen peroxide as co-oxidant was still analyzed (pH 4 and a hydrogen peroxide concentration corresponding to 10% of the stoichiometric dose) (Lucas and Peres, 2009). These operating conditions improved COD removal when compared with the case where pH was freely adjusted leading to a maximum of 23% of degradation after 1200 min. Still, this result is far from the efficiency attained when a two stage pH approach was applied.

Bearing now in mind the biodegradability of the treated effluent, the following conclusions can be achieved from the $BOD_5$/COD final values also shown in Fig. 3 a): controlled pH (0.02) < pH running freely (0.17) ≈ perozonation (0.18) < pH 10 (0.22). The low biodegradability observed when a two stage pH procedure is applied must be related with the low final COD obtained what points out that the residual COD (only 2% of the initial value) is attributed to compounds not able to be biologically degraded, meaning that a further activated sludge treatment would not be appropriate.

Figure IV.8.3 b) shows the temporal evolution of $BOD_5$/COD along the experiment that led to the best COD removal (two stage pH). As it can be observed, a biodegradability improvement is attained for the first 200 min of oxidation ($BOD_5$/COD = 0.28). This is probably related with the removal of the bio-refractory initial pollutants (too much complex for being bio-processed) leading to the production of low molecular weight compounds. However, the further mineralization of the wastewater leads to a depletion of the organic matter available for microorganisms, promoting a decrease on the $BOD_5$/COD ratio.

## IV.8.4 Reactants cost evaluation

The reactants consumption volumes for the controlled pH test are presented in Table IV.8.2 as well as the final COD achieved, as well as the achieved COD removal. The industrial price for NaOH (50%) and $H_2SO_4$ is 0.45 €.$L^{-1}$ and 0.35 €.$L^{-1}$, respectively. Ozone production requires 20 kWh. $kg^{-1}$ $O_3$. The cost of electric energy was considered to be 0.1276 €.$KWh^{-1}$, the market price in Portugal for industrial applications.

***Table IV.8.2- Reactants consumption for pH control and COD removal for each stage of the controlled pH test per cubic meter of wastewater.***

| Controlled pH | initial pH | Oxidation time | Oxidation cumulative time(min) | final pH | $H_2SO_4$ ($L.m^{-3}$) | NaOH ($L.m^{-3}$) | % COD removal |
|---|---|---|---|---|---|---|---|
| -- | 9.12 | 0 | 0 | -- | -- | -- | 0 |
| **$O_3$ (3)** | 3.1 | 300 | 300 | 2.56 | 3.5 | -- | 27.5 |
| **$O_3$ (10)** | 10.6 | 180 | 480 | 8.2 |  | 2.8 | 65.0 |
| **$O_3$ (10)** | 10.7 | 210 | 690 | 9.6 |  | 3.6 | 89.6 |
| **$O_3$ (10)** | 10.7 | 280 | 970 | 10.1 |  | 2.8 | 97.2 |
| **$O_3$ (10)** | 11.1 | 230 | 1200 | 10.7 | -- | -- | 98.2 |
| **Neutralization** | 10.9 | -- |  | 8 | 4 | -- |  |
| **Total** |  | 1200 |  |  | **7.5** | **9.2** |  |

It is concluded that the proposed treatment system has an associated cost in order to reduce the COD content from 10500 to 220 $mgO_2.L^{-1}$. The NaOH, $H_2SO_4$ and $O_3$ consumption, leads to a cost of 33.04 € per cubic meter of treated effluent. For the installation where it is expected to produce about $10m^3$ / day of wastewater this would lead to an operating cost of reagents in the order of 330.04 €/day, which results in an annual cost of 76239.24 €/year (for 21 days of work per month and 11 months per year).

## IV.8.5 Biological oxidation

Due to the high operational costs referred before, a treatment option as the biological urges as a possible option (Durán-Moreno *et al.,* 2010; Oller *et al.*, 2011). In this context, the possibility of integrating an activated sludge system with ozonation was assessed. So, ozonation was stopped on the oxidation time corresponding to the best $BOD_5$/COD ratio (0.28, 200 min of operation) and the pre-treated wastewater was able to be biologically oxidized. The objective was to find a stable treatment solution which complements the chemical process leading to a final effluent with a COD below 1250 $mgO_2.L^{-1}$ allowing its disposal in the municipal sewage. Thus, the introduction of a Sequential Batch Reactor after the chemical treatment was analyzed. In this study, the influence of the bio augmentation (BioSBR) was also tackled and compared with the traditional SBR systems, considered as the biological reactor without bio augmentation (SBR).

The biological reactors under study were fed with effluent coming from the AOP process whose composition is described in IV.8.3.

*Table IV.8.3- Characterization of the Ozonation Treated Effluent (OTE)*

| Sample Characterization | COD | $BOD_5$ | Total Nitrogen | Total Phosphorous | $BOD_5$/COD | pH |
|---|---|---|---|---|---|---|
| **Value** | 5470 $mgO_2.L^{-1}$ | 1430 $mgO_2.L^{-1}$ | 16 mg $N.L^{-1}$ | 27 mg $P.L^{-1}$ | 0.3 | 8.6 |

Daily, the pH of the OTE was corrected to 7.5 before entering into the SBRs and the concentration of dissolved oxygen was maintained above 2 $mgO_2.L^{-1}$ by adjusting the air compressor.

Figure IV.8.4 shows the evolution of the COD concentration of the effluent that was treated by the “SBR” and “BioSBR” reactors and the removal efficiency (RE) of each one as well.

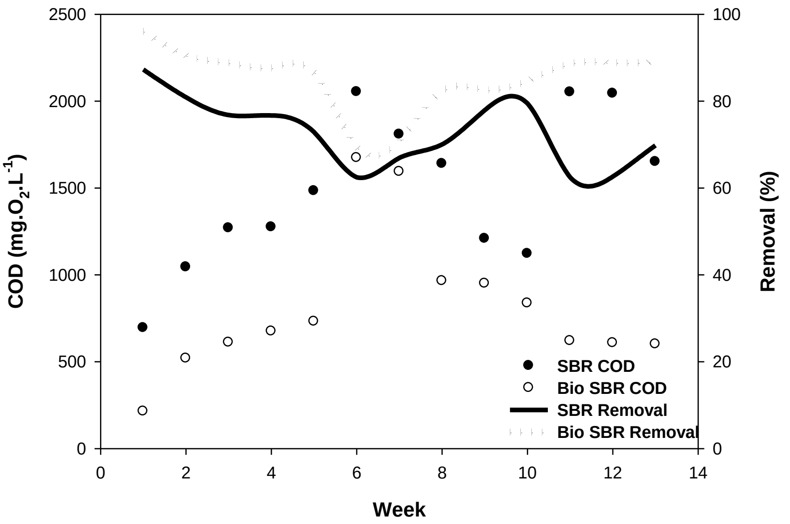

***Figure IV.8.4- Evolution of COD concentration of the treated effluent (represented by points) and removal efficiency (represented by lines) of the reactors under study ("SBR" reactor and "BioSBR" reactor)***

Analyzing Figure IV.8.4 it is observed that, during the 13th week of monitoring, the "SBR" reactor reached, on average, 1487 ± 163 mgO$_2$.L$^{-1}$ of COD and a removal efficiency of 73 ± 3 %. Until the 6th week the COD concentration of the treated effluent increased from 695 to 2052 mgO$_2$.L$^{-1}$ as a consequence of the increase of the organic load, due to the fact that the biomass was not previously adapted to this wastewater. The biomass was in a container and the supernatant COD was 150 mgO$_2$.L$^{-1}$. With the additions of increasing loads of OTE, the dilution effect vanished along the operation time, and COD increases. Indeed, the dilution factor is very important in this kind of treatment because it allows the adaptation of resistant microorganisms to the toxicity of the chemical effluent through the homeoviscous adaptation, this is, the modeling the fluidity of the bilayer from the cytoplasmic membrane in order to confer resistance to toxic compound (Twort *et al.*, 2000). After the 6th week the COD concentration decreased until 1121 mgO$_2$.L$^{-1}$ (week 10). However, in the 11th week an increase of organic load in the treated effluent (2051 mgO$_2$.L$^{-1}$) is observed. At the end of the experiment this reactor showed a tendency to decrease the COD concentration (1651 mgO$_2$.L$^{-1}$).

The "BioSBR" reactor had on average 815 ± 90 mgO$_2$.L$^{-1}$of COD varying from 214 to 1673 mgO$_2$.L$^{-1}$, and a global removal efficiency of 85 ± 2%. Like the "SBR" reactor, the COD concentration increased until the 6th week from 214 to 1673 mgO$_2$.L$^{-1}$, COD decreased gradually from 1593 to 620 mgO$_2$.L$^{-1}$ (7th to 11th week) and stabilized at around 600 mgO$_2$.L$^{-1}$ until the end of the trial. These results indicate that the bio augmentation is beneficial for the stabilization of the removal efficiency of organic compounds.

The protozoan community is used as bio indicator of the biological treatment efficiency through the quantification of the Sludge Biotic Index developed by Madoni (2003). The Figure IV.8.5 and IV.8.6 describe the evolution of Ciliated Protozoa (Swimming, Crawling and Sessile) and Sludge Biotic Index (SBI) (Madoni, 2003) in the reactor with and without bio augmentation.

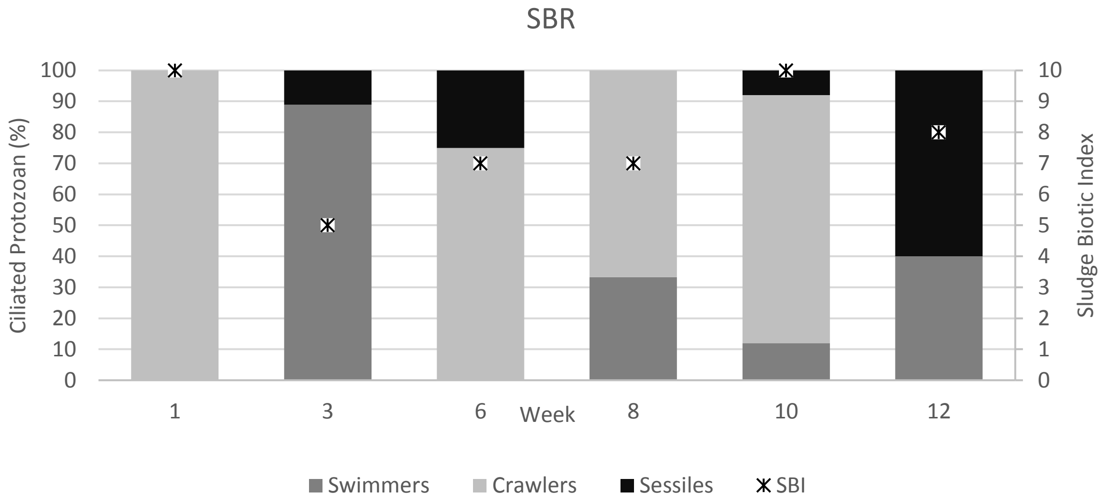

*Figure IV.8.25- Evolution of ciliated protozoa in the "SBR" reactor.*

Analyzing these results is observed that in the first week of treatment both reactors had only crawlers in the activated sludge and presented a SBI of 10 which indicates that the reactors have a well colonized and stable sludge, optimal microbial activity and high removal efficiency according to Figure IV.8.5 (Class I). This is due to the fact that the reactors were inoculated with activated sludge collected from the same bioreactor.

In Figure IV.8.5 shows that in the 3th week the community of crawlers disappeared and the swimmers appear in higher quantity (89%) than the sessiles (only *Vorticella* at this point), and the SBI decreased to 5. This indicates that the biological reactor presents insufficient biological activity and mediocre efficiency removal (Class III), which is normal in this phase due to the microorganism adaptation to the effluent organic load. In the 6th week one can observe an increase of the SBI to 7 (class II), because of the development of crawlers; this indicates that the microorganisms became more adapted to the effluent and now the reactor shows well colonized and stable sludge, almost optimal microbial activity and good removal efficiency. In the 8th week the SBI remained in 7, even though the community of crawlers dominated over swimmers. In the 10th week the community of sessiles reappear and the SBI increased to 10 (Class I). In the final analysis, the SBI decreased to 8 due the augmentation of swimmers; however, this community is still in Class I, this is, the reactor is well colonized and stable sludge, optimal microbial activity and high removal efficiency are achieved.

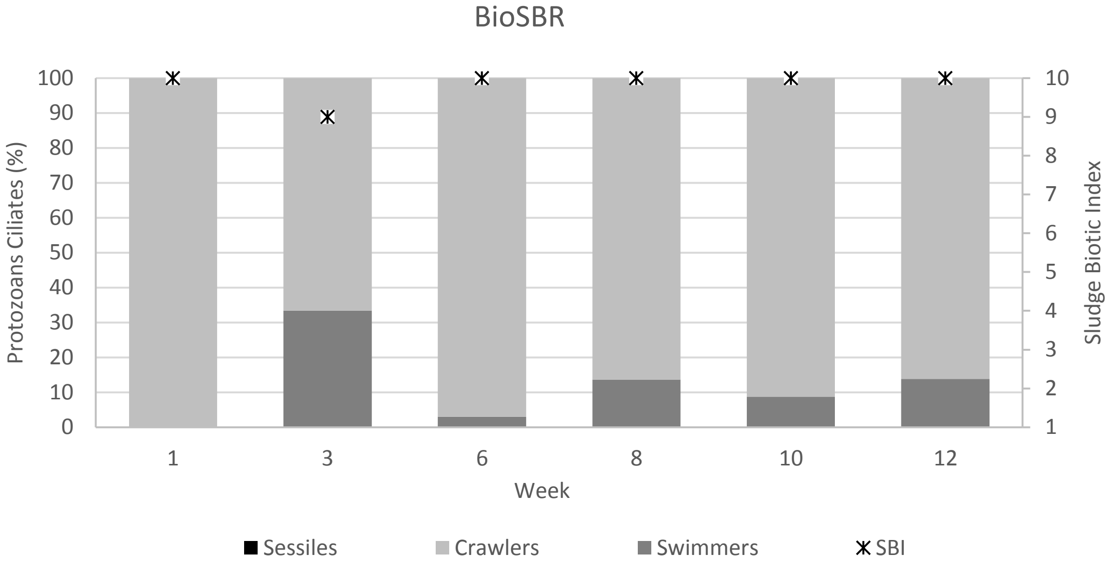

***Figure IV.8.6- Evolution of ciliated protozoa in the "BioSBR" reactor***

From Figure IV.8.6 can see that in the 3$^{th}$ week the community of crawlers decreased from 100% to 67% and the swimmers appear in high quantity (33%). The SBI decreased to 9 but the microbiological community is still classified as Class I, which means that the reactor is well colonized with stable sludge, optimal microbial activity and high removal efficiency. Until the end of the experiment the community of crawlers dominated over the swimmers and the SBI increased to 10 and maintained in there, revealing that the reactor stabilized with optimal microbial activity and high removal efficiency (Class I). This seems to indicate that the BioSBR is an interesting approach as a complement for ozonation.

Although the OTE presents a biodegradability of 0.28, using the $BOD_5$ determination method, the results of SBR treatment indicate that the biodegradable organic load in the effluent under study is higher probably due to the microorganisms adaptation during the monitoring time, which consequently improved the removal efficiency of the biological oxidation.

## IV.8.6 Conclusions

In this work several treatment techniques were applied to clean up a high refractory industrial effluent.

Physical-chemical procedures as coagulation showed to be ineffective with a maximum removal of 23.5 and 6.2 % of TSS and COD, respectively.

Fenton oxidation was also unable to treat this wastewater (leading to a final COD value of 2370 $mgO_2.L^{-1}$ which is not allowable for discharge into the local municipal sewage) due to the presence of radical scavengers in the wastewater composition that limit the oxidation. The biodegradability improvement is thus insufficient to enable the application of a biological treatment

A methodology that was able to provide an effluent with the required low level of organic matter was ozonation with different stages induced by pH variation, attaining 98.2 % COD degradation with a final COD value of 220 $mgO_2.L^{-1}$. The main conclusions drawn from these investigations of ozonation and biological processes were:

- Direct ozonation presents low efficiency on the depuration of this wastewater;
- $H_2O_2$ addition on the ozonation at acidic pH improved the oxidative process efficiency; however, radical scavenger compounds as carbonates inhibit the method, limiting the oxidation extension;
- Alkaline oxidation improves the process; but the presence of radical scavengers in the wastewater composition seems to restrain the reaction.
- The utilization of multi-stage pH leads to significant efficiency improvement. It seems that the initial acidic conditions are able to remove radical scavengers, which will enhance hydroxyl radicals action during the alkaline stage. These operating conditions led to a treated wastewater within the limits for discharge into the hydrological resources.
- The use of ozone for biodegradability enhancement and the introduction of a sequential batch reactor afterwards showed interesting results and the bio augmentation is beneficial for the stabilization of the reactor microbial flora. Under those conditions a treated effluent with less than 1000 $mg.L^{-1}$ of COD was obtained, which can be sent to the municipal sewage plant.

The results obtained showed that ozone based treatment with different pH stages provides a treated water able to be discharge at the hydrological resources, but also the potential of combining AOPS with biological systems leading to an enhanced and more attractive cost/benefit application.

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# V. CONCLUSIONS AND FORTHCOMING WORK

In this section of the thesis, a general overview of the main results is presented, along with the most relevant conclusions. Finally, suggestions for future work are recommended.

## V.1 General Overview and Concluding Remarks

Under the frame of emerging cleaner production technologies, suitable treatment methods for industrial wastewaters urge to be developed. The biological treatments are the most widely used depurative technologies. Nevertheless, these systems encompass several drawbacks when applied to effluents containing non-biodegradable, bio recalcitrant and/or toxic pollutants. Moreover, those technologies are extremely sensitive when changes in the effluent matrix happen. The strategy of coupling chemical (by application of the Fenton process or ozone based technologies) and biological systems is a good alternative to minimize these fluctuations or as an alternative when biological treatment *per si* is ineffective.

Advanced oxidation methods (AOPs) are considered to enhance existing treatment technologies, being complementary or even replace them. These processes chemically modify the structure of the pollutants, by transforming them into less toxic and biodegradable intermediates, allowing then a biological procedure, to complete the degradation of the pollutant load in a shorter time and in a less expensive way. Chemical and biological treatments must be always monotorized to ensure that the chemical pretreatment induces beneficial effect on the biocompatibility of the treated wastewater.

Therefore, we can conclude that the two oxidative processes depicted throughout this thesis are different, and therefore inferred different conclusions about their application.

Fenton Oxidation was applied seeking for a suitable treatment for three distinct wastewaters.

Winery wastewater was submitted to an integrated coagulation-Fenton-like system that enables a synergetic effect of both treatments. The coagulation step leads to COD and TSS reductions of 25 % and 40.7 %, maintaining an iron content as well as an acidic pH that enables the oxidative stage. The oxidation step, where 10 % of the stoichiometric oxidant dosage was applied, leads to a COD reduction of 42% and a $BOD_5$/COD improvement of 60%, with a final content of 59 ppm of iron. At the end of this two stage process also 89% and 80% of Total Phosphorous and Nitrogen were removed. The combined process endorses a COD removal of 56.6% and enhanced the wastewater biodegradability ($BOD_5$/COD = 0.4), showing that it could be efficiently used as prior treatment to a subsequent biological systems. Thus, with the application of a posterior biological treatment, it was possible attaining 95% of efficiency removal after complete adaptation of the biological system. The obtained treated water characteristics were within the legal required limits, permitting the direct discharge into the hydrological resources or even for reuse purposes. The operating costs inherent to the coagulation-oxidative process were of 0.27 € per kg of removed COD. The $Fe_2(SO_4)_3$ amount, represents 40% of the total costs, and the sum of NaOH and $H_2SO_4$ dosages costs are very similar to those of the oxidant, reaching 26%.

The performance of laboratorial Fenton's peroxidation over the elderberry juice production wastewater treatment leads to an effluent within the legal limits, allowing its discharge throughout the hydric resources, since the final COD, $BOD_5$ and TSS values accomplished the legal limits for those parameters to be discharged into the hydrological courses (150 $mgO_2.L^{-1}$, 40 $mgO_2.L^{-1}$ and 60 $mg.L^{-1}$, equivalent to removals of 78%, 90% and 63%, respectively). Moreover, a $BOD_5$/COD improvement of 600% was reached. This treatment system entailed an operating cost of 4.384 $€.m^{-3}$.

The process was extremely dependent on the $[H_2O_2]$: $[Fe^{2+}]$ ratio (5:1), but the major significant improvement is determined by the reactants concentration. The best results were attained with the operational conditions of initial pH=3, $[H_2O_2]$: $[Fe^{2+}]$ =20:5 mM. A unique pre-acidification stage before the oxidative process revealed to be a better approach than correcting pH during the process. For lower $[H_2O_2]$: $[Fe^{2+}]$ chemical coagulation prevails, and to a $[Fe^{2+}]$ =20 mM, the TDS concentration drops when compared with 10 mM, showing that iron dosage is strictly related with the coagulation stage, and in this sense it is necessary to optimize this dosage in order to take advantage of the synergistic effects of both phases (oxidation and coagulation) in the Fenton process.

It was possible to achieve significant removal efficiencies when OMW was subjected to coagulation/flocculation. In fact, this process led to a high phenol and COD removal (82 and 84% respectively) as well as a $BOD_5$/COD improvement (0.20 against the initial 0.05). Moreover, the further combination with Fenton process revealed larger COD and total phenol content abatement (90% and 92%) and a biodegradability enhancement to 0.52 in relation with the raw wastewater thus enabling the availability of a posterior application of an aerobic biological treatment. On the other hand, the addition of minor amounts of hydrogen peroxide over the time reaction significantly favors the Fenton's oxidation. The precipitation step also removes organic compounds, indicating that in addition to precipitate ferrous sludge, it acts as a polishing stage in what regards to COD removal.

In another work with a different olive mill wastewater the coagulation stage achieves COD reductions of 38% and 40% of TSS. The global process (involving coagulation and Fenton's process) allows attaining an overall COD removal of 85% which permits the wastewater discharge into the municipal collector. This system entailed a cost of 1.44€ per kg of removed COD. Thereafter these conditions were extrapolated to a real WWTP where, the evolution of the efficiency of each stage of treatment was significant. The coagulation was able to remove 30% of COD in the first day and 50% in the last one, while the Fenton´s oxidation efficiency ranged from 40 until a 90% in the last day, with [$[H_2O_2]$: $[Fe^{2+}]$ ratios changing between 7.5:1 and 10:1. The treatment attained an average efficiency of 43% on the coagulation and 62% on the oxidation stage increasing the wastewater biodegradability from 0.03 to 0.37 enabling the posterior application of biological treatment. The treatment has a real average cost of 1.09€ per kg of removed COD.

***Main conclusions from Fenton's process studies:***

- Fenton process is effective and its application is economic viable when it is applied to increase biodegradability and reduce toxicity of the wastewaters,
- Applying a coagulation stage favors significantly the posterior oxidation process, to reduce COD and TSS, but above all to minimize the load variations in order to stabilize the efficiency of the Fenton's process;
- $[H_2O_2]$:[COD] and $[H_2O_2]$: $[Fe^{2+}]$ ratios should be optimized to the lower value in order to instigate the partial oxidation and not mineralization and favor the coagulation stage, taking advantage of these synergetic effect and reducing the operational costs;
- The Fenton's precipitation stage promotes organic compounds removal, indicating that in addition to precipitate ferrous sludge, it acts as a polishing stage in what regards to COD removal.

Ozone based treatment shows to have potential to depurate four distinct wastewaters. The main goals were to increase the biodegradability so that a posterior biological oxidation is possible, obtaining an effluent able to direct discharge into the hydrological resources or even reutilization of the treated water.

The depuration of two different effluents, vegetable wash (VW) and chemical production (CP), was investigated by ozonation and $O_3/H_2O_2$ focusing the treated water reuse. The experiments show that hydrogen peroxide enhance the oxidation process when combined with ozone in almost twice the overall efficiency in TOC removal when compared to ozone alone. The addition of 35.7

mmol.$L^{-1}$ $H_2O_2$ increment COD depletions to 100% (0 $mgO_2$.L-1) vs 87%, TOC abstractions of 33% (38 mgC.$L^{-1}$) vs 13% after 120 min for the VW; in that concerns the CP, the use of 3.6 mmol.$L^{-1}$ ($H_2O_2$) allows to obtain removals of 96% (38 $mgO_2$.$L^{-1}$) vs 41 %, 66% (62 mgC.$L^{-1}$) vs 26% for COD and TOC respectively after 180 minutes of oxidation. In the single ozonation experiments pH shows to be the most important variable, reaching COD removals of 87% for VW for higher pH's , and 50% of CP with pH=9. The $O_3/H_2O_2$ system favors the complete oxidation of pollutants since AOS values closer to +4 were attained strengthening the role of hydroxyl radicals guiding reaction towards total mineralization. The treated water could be reintroduced in the washing vegetables operation, and the final CP effluent could be used in the irrigation or in other applications existent in the factory layout.

A landfill leachate characterized by moderate COD value, 1880 mg $O_2$.$L^{-1}$, very low biodegradability ($BOD_5$/COD = 0.05) was treated by single ozonation and ozone combined with hydrogen peroxide. Single ozonation at pH 9 endorses reductions of 34% of COD and 94% of color and augments biodegradability ($BOD_5$/COD = 0.33; 21% by respirometry), showing that this technology could be effectively used as a prior treatment for biological systems. However, the addition of 4 g.$L^{-1}$ of $H_2O_2$, enhanced the COD reduction to 44%; however, this system was less efficient in what regards color depletion (-9%), besides originating a treated effluent with a lower $BOD_5$/COD ratio (-12%) when compared with single ozonation. Nevertheless, the ozone + hydrogen peroxide system led to an effluent able to be directly discharged to a sewage collector.Moreover the addition of hydrogen peroxide reduces the treatment cost per kg of removed COD (14.11 € for single ozonation vs 12.06 € for perozonation).

A high refractory industrial effluent was studied in order to accomplish a treated water able to be discharges into the hydrological resources or, if not possible, to a municipal sewage. Several experiments with different procedures as coagulation and Fenton oxidation showed to be ineffective with a maximum removal of 23.5 and 6.2 % of TSS and COD, respectively. Different strategies of ozone based processes were attempted, showing that single ozonation presents low efficiency. , $H_2O_2$ addition at acidic/neutral pH improved the oxidative process efficiency; however, radical scavenger compounds as carbonates inhibited the method, limiting the oxidation extension. Multi-stage pH's ozonation led to an efficiency improvement. Initial acidic conditions allowed removing radical scavengers, what will enhance hydroxyl radicals action during the alkaline stage after NaOH addition, attaining 98.2 % of COD degradation with a final COD value of 220 $mgO_2$.$L^{-1}$ after 1200 min of operation. Thus, the treated water was within the limits for discharge into the municipal wastewater treatment plant. It was observed that a biodegradability improvement was attained at 200 min of oxidation ($BOD_5$/COD = 0.28), and for this reason the integration of a biological treatment was tested with bio augmentation. The final COD stabilized around 600 $mgO_2$.$L^{-1}$ until the end of the experiment, originating a treated effluent with less than 1000 $mgO_2.L^{-1}$. Thus, the treated wastewater can be conducted to the municipal sewage.

***Main* conclusions *from ozonation studies:***

- the combination of pH variations and co-oxidant additions are essential for the best use of both oxidative mechanisms (electrophilic attack and hydroxyl radicals);
- the $H_2O_2$ addition on the ozonation improves the oxidative process efficiency since it enhaces the production of hydroxyl radicals;
- initial acidic conditions promote the radical scavengers removal, which will enhance hydroxyl radicals action during oxidative mechanisms;
- ozone-based AOPs are promising alternatives providing the effluent biodegradability improvement allowing a posterior biological oxidation.

## V.2 Forthcoming Work

The results of the present work reveal the importance of Fenton's process and ozonation for the depuration of bio-refractory liquid effluents. Moreover, these chemical methodologies can be envisioned as a part of an integrated scheme allowing partial degradation of the bio-refractory fraction after or before an economical biological reactor. In addition, it was clear the need of carrying out investigation for the characterization of each wastewater in order to provide the best depuration solution for each case. The most crucial issue of the Advanced Oxidation Processes application at industrial scale is the maintenance of the real efficiency during the productive cycle and the operational costs of the entire treatment.

Thus main purpose of the proposed work is to extrapolate the laboratory investigation to the physical application. For this a scale not lower than 10,000 X higher (1L to 10 $m^3$) should be used. Only this way, reliable data regarding the real application of these technologies can be gathered.

For this main purpose the following issues are requested:

- Carry out AOPs laboratory assays with a time scale that allows to identify the processes behavior when the wastewater characteristics change;
- Chemical oxidation experiments using optimized reactant dosages should be performed with the wastewaters taken from the production site at different times, because of fluctuations in the wastewater quality;
- The integration of physical-chemical processes is required, involving particular processes such as the coagulation / flocculation and filtration, in order to minimize the solids and organic content load variations, as well as to maintain the pH for the reaction, preserving the procedural efficiency;
- Develop methods for automated control to chemicals dosage and operating conditions (pH), assessing the performance of the process according the wastewater variability;
- Optimize the AOPs in a way that the operating costs (taking only into account the reagents) do not pass the threshold of 3-4 €.$m^{-3}$, charge for which the companies showed interest in paying when compared with existing depurative techniques (reverse osmosis, nano-filtration, evaporation; coagulation / adsorption), turning these processes aside from effective, competitive;

- Study and analyze the application of biological treatments after the implementation of AOPs, with the variability of the output effluent (residual reactants, COD and $BOD_5$) to a time scale that allows to assess their *in situ* viability, instead of evaluating only the biodegradability of the laboratory assays.

Individually for each investigated AOP it is proposed:

***Fenton oxidation***

- To analyze the effect of TSS variation in the Fenton process;
- To develop methodologies in order to enhance thickening and handling of iron based sludge originated during Fenton process;
- To develop strategies to reuse the iron sludges as coagulant or as catalyst.

***Ozone based processes***

- To analyze the effect of TSS and TDS variation, to assess the efficiency of the oxidation process;
- To develop units with simple and effective methodologies of coagulation and membrane filtration as pre-treatment for ozonation;
- To develop multi-stages reactors that allow pH changes and others oxidants addition in differents sections of the same unit.

After completing this work, one can predict that with the integration of those technologies, with some complementary processes such as membranes, it is possible to achieve treatment efficiencies that allows to attain an output water with all the requirements to be reused.

The presented processes integration scheme (Figure V.2.1) involving coagulation, chemical oxidation, biological and other chemical oxidation, complemented with an ultrafiltration system after the biological treatment, and a reverse osmosis as a safety system seems to be an effective strategie for an effluent depuration with the aim to fulfil the drinking water requirements.

After completing this work, one can predict that the integration of existing presented technologies, with some complementary, precisely membrane separation, it is possible to achieve removal rates, that allows to attain an output water with all the requirements to be consumed.

The presented processes integration scheme (Figure V.2.1) involving coagulation, chemical oxidation, biological and other chemical oxidation, complemented with an ultrafiltration system after the biological treatment, and a reverse osmosis as a safety system seem to be the an effective strategies for an effluent depuration with the aim to fulfil the drinking water requirements.

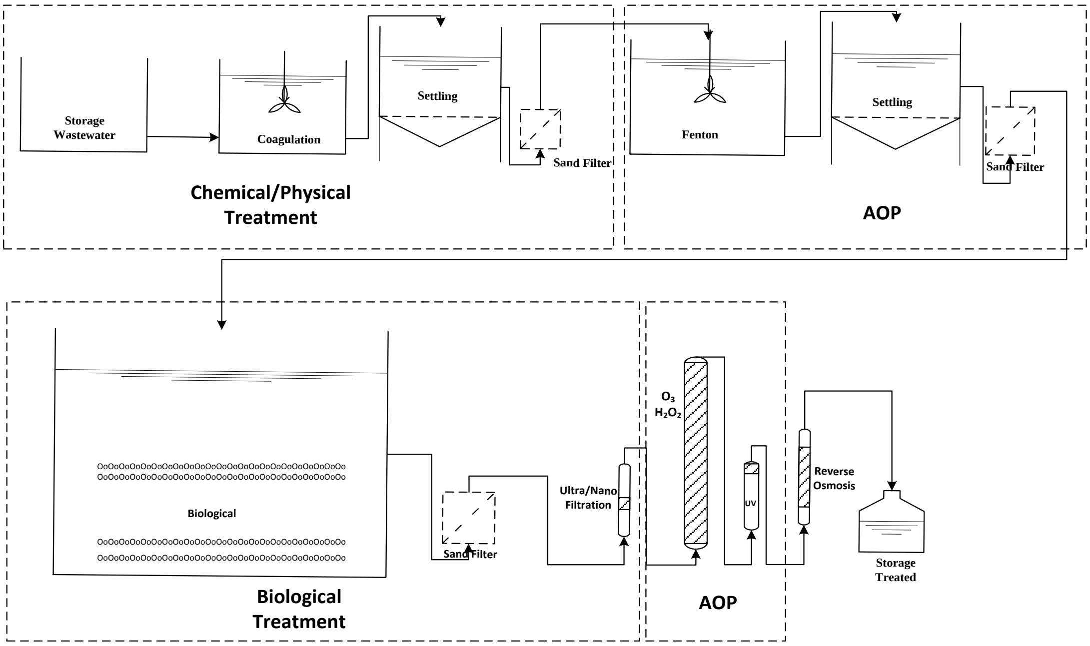

*Figure V.2.1- Treatment scheme to attain drinking water*