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Eva Florbela Domingues Gomes

SLUDGE-FREE FENTON INTEGRATED METHODOLOGY FOR AGRO-INDUSTRIAL WASTEWATERS TREATMENT

PhD thesis in Chemical Engineering, supervised by Professor Rui Carlos Cardoso Martins and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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“They look for gold in water, not realizing that water is the gold.”

- **unknown author**

AGRADECIMENTOS

O meu profundo agradecimento ao meu orientador Professor Doutor Rui Martins por todo o apoio, por toda a disponibilidade e por todas as condições para realizar a minha tese de doutoramento. Quando me faltou ânimo soube usar as palavras certas para me motivar, quando tive dúvidas conseguiu-me dar certezas e quando errei soube corrigir com gentileza. Muito obrigada pela orientação e pela amizade.

Aos meus colegas de trabalho, João Gomes, Eryk Fernandes, Telma Vaz, João Lincho, Maria João Silva obrigada pela colaboração, pelo apoio, pelas gargalhadas, pelos convívios.

Aos restantes investigadores do grupo GERST pelo bom ambiente e pela partilha de conhecimento, em particular os professores Licínio Ferreira, Margarida Quina e Rosa Quinta-Ferreira.

Aos restantes membros do DEQ, professores e investigadores, alunos, funcionários que fizeram parte do meu percurso.

Agradeço à FCT (Fundação para a Ciência e Tecnologia, Portugal) pelo financiamento da minha bolsa de doutoramento (SFRH/ BD/144096/2019). Ao projeto POCI-01-0247-FEDER-033193 (SERENA—Development of a sludge free Fenton-integrated treatment methodology for olive mill wastewaters: a water recovery) financiado pela União Europeia para o Desenvolviemnto Regional (FEDER) no enquadramento COMPETE2020.

Ao meu marido, João Gomes, por toda a dedicação, companheirismo, motivação e discussão. Desculpa! Sobrevivemos 😊Obrigada por estares presente quando eu estive ausente, obrigada pela paciência e obrigada por seres um excelente profissional, amigo, marido e pai.

Aos meus maravilhosos filhos, Tomás e Miguel, que vieram tornar este trabalho ainda mais, nem sei bem como dizer, desafiante???! Se é certo que em muitos dias me tiraram a força física também é certo que cada vez que olho para vocês encontro motivos para continuar, para vos mostrar que nunca é tarde, que não devem nunca abandonar um projeto só porque não seguem um determinado padrão. Existe espaço para os “diferentes”, mas atenção, o caminho é mais difícil!

Aos meus pais, que me apoiaram e ajudaram como podiam e sabiam.

Aos meus avós de quem tenho muitas saudades e com quem gostaria de partilhar este momento, onde quer que estejam obrigada por tudo.

À minha avó Maria que depois de muitas intempéries se recusa a quebrar e que tem sempre uma história para contar.

Por fim dedico, todo o trabalho, toda a alegria e todo o sacrifício, à memória do meu querido avô Avelino Pires, o meu melhor passado; e ao meu marido e filhos, o meu melhor presente.

RESUMO

Os efluentes agroindustriais constituem um problema ambiental devido à sua elevada carga orgânica o que requer o desenvolvimento de tratamentos adequados. Neste contexto, esta tese de doutoramento teve como objetivo desenvolver as tecnologias de Fenton isentas de lamas e comparar a sua eficiência com processos avançados de oxidação à base de sulfato (S-AOPs) para remover o carácter poluente de dois agro-efluentes, lagares de azeite e águas residuais de suinicultura.

O tratamento das águas residuais dos lagares de azeite é um problema que ainda não tem uma solução eficaz. Para minimizar este inconveniente, houve uma melhoria no processo de produção do azeite, passando da extração trifásica para bifásica nos lagares, e integrando esta última com a indústria de extração de azeite com n-hexano. Esta melhoria não resolve totalmente o problema das águas residuais dos lagares por si só, apenas liberta os lagares da carga ambiental e concentra o problema na indústria de extração de azeite. Neste estudo foi proposto o tratamento de um efluente real de uma indústria de extração de azeite, utilizando o processo de Fenton integrado com o processo de coagulação. Com as melhores condições de operação (adição faseada de um total de 40 mg/L de coagulante) com posterior reação de Fenton (4 g/L de peróxido de hidrogénio, 2 g/L de ferro (II), pH 3 e ao fim de 60 min de reação) foi possível atingir cerca de 45% de remoção de CQO (carência química de oxigénio). Isto permitiu aumentar a biodegradabilidade do efluente, para uma proporção superior a 40%, para posterior aplicação de tratamento biológico de forma a tratar definitivamente o efluente.

A formação de lamas de ferro é a maior desvantagem do processo Fenton e a permuta iónica (IE), usando a resina Amberlite@HPR1100, permitiu por um lado, remover o excesso de ferro em solução, bem como a redução do CQO do efluente real da indústria de extração de azeite, após o processo Fenton. Os resultados mostraram 75% de capacidade máxima de adsorção de ferro na resina Amberlite@HPR1100, para uma concentração de alimentação de 2 gFe^{3+}/L, e uma eficiência de remoção de CQO de 30% partindo de um valor inicial compreendido entre 17.5-22.5 gO_2/L. A utilização de catalisadores sólidos, resíduos industriais e materiais naturalmente presentes na natureza, é também uma forma interessante de evitar a formação de lamas e promover a economia circular. Com a utilização de catalisadores de baixo custo conseguiu-se, ao final de 60 min e para uma concentração de 1 g/L de catalisador, uma remoção do teor de fenólicos de 100% para red mud (RM), enquanto que no caso dos catalisadores VRA (rocha vulcânica dos Açores) e do VRC (rocha vulcânica das Canárias) este valor é de 72,0% e 74,6%, respetivamente para um OMW (olive mill wastewater) sintético.

Os S-AOPs foram avaliados como uma alternativa de depuração ao processo Fenton. O OMW sintético foi submetido a S-AOPs homogéneos e heterogéneos utilizando sulfato de ferro e catalisadores sólidos (RM e Fe-Ce-O) como fonte de ferro. O melhor desempenho foi obtido pelo Fe-Ce-O, com carga ótima de 1600 mg/L e uma concentração de persulfato de 600 mg/L a pH 5. Nestas condições foram obtidas remoções de 27%, 55% e 5% de CQO, compostos fenólicos e TOC, respetivamente.

Diferentes AOPs (processos avançados de oxidação) foram também avaliados para minimizar o impacto ambiental do efluente real da indústria de extração de azeite. Em termos de remoção de CQO, a combinação de Fenton e ozono em simultâneo, permitiu a maior redução (58,5%), embora a combinação de Fenton seguida de ozono a pH 3 tenha levado a uma remoção semelhante, cerca de 54%. No que diz respeito à mineralização, o processo de Fenton sozinho foi o mais eficiente, permitindo a remoção de 53% de TOC.

A produção de carne suína gera efluentes com alta carga poluente, sendo que o uso intensivo de produtos farmacêuticos está a enriquecer esses mesmos efluentes com esses compostos. Os tratamentos tradicionais que envolvem a depuração biológica são eficazes na remoção da carga orgânica das águas residuais da suinicultura. No entanto, o tempo e o espaço necessários, juntamente com a baixa eficiência na redução de contaminantes recalcitrantes, como compostos farmacêuticos, levam à necessidade de estudar tecnologias alternativas. Os AOPs são processos muito eficientes e requerem um curto período de tempo de tratamento quando comparados aos processos tradicionais biológicos. O processo de Fenton combinado com a coagulação e biofiltração, utilizando a espécie invasora *Corbicula fluminea*, foi avaliado como uma alternativa de tratamento para o efluente de suinicultura. A biofiltração seguida pelo processo de Fenton removeu 91% do CQO. O processo de Fenton após o processo de coagulação, permitiu uma degradação de CQO de 86%. A inibição da luminescência da bactéria *Aliivibrio fischeri*, foi reduzida cerca de 30% com a integração dos processos de tratamento. A coagulação e a biofiltração após o processo de Fenton também demonstraram ser uma boa opção para remover o ferro dissolvido no efluente tratado.

Palavras-chave: Processo de Fenton; Processos sem lamas; Efluentes agro-industriais; Processos baseados em sulfato; Recuperação de água.

ABSTRACT

Agro-industrial wastewaters constitute an environmental problem due to their high pollutant load that entails the development of suitable treatments. Within this context, this PhD thesis aimed to develop sludge-free Fenton’s technologies and compare their efficiency with sulfate based advanced oxidation processes (S-AOPs) to remove the pollutant character two agro-effluents (olive mill and swine wastewaters).

The treatment of olive mill wastewater (OMW) is a problem that still does not have an effective solution. To minimize this drawback, there has been an improvement in the olive oil production process, moving from three-phase to two-phase extraction in olive mills, and integrating the later with the olive oil extraction industry with n-hexane. This improvement does not totally solve the olive mill wastewater problem on its own, it only releases the olive mills from the environmental burden and concentrates the problem in the olive oil extraction industry. In this study it was proposed a treatment of a real effluent from an olive oil extraction industry, using the Fenton’s process integrated with coagulation. With the best conditions for coagulation (double phased addition of a total of 40 mg/L of coagulant) integrated with the Fenton reaction (4 g/L of hydrogen peroxide, 2 g/L of iron (II) at pH 3 with 60 min of reaction) was possible to achieve about 45 % of COD (chemical oxygen demand) removal. This allowed to increase the effluents biodegradability, to a ratio higher than 40 %, for further biological treatment application to definitively treat the effluent.

Iron sludge formation is the biggest disadvantage of Fenton′s process and Ion exchange (IE), with Amberlite@HPR1100, comes as a complement to the Fenton process, allowing, on the one hand, to remove the iron excess in solution, as well as reducing the COD of the real OOEIW (olive oil extraction industry wastewater) from the Fenton process. The results showed 75% maximum iron adsorption capacity onto Amberlite@HPR1100 resin, for a feed concentration of 2 gFe^{3+} /L, and an efficiency for COD removal of 30% for an initial COD 17.5-22.5 gO_2/L. The use of solid catalysts, industrial waste and materials naturally present in nature, is also an interesting way to avoid sludge formation and to promote the circular economy. With regard to the utilization of low-cost catalysts, it was concluded that at the end of 60 min and for a concentration of 1 g/L of catalyst, the removal of phenolic content reaches 100% for red mud (RM), while in the case of VRA (volcanic rock Azores) and VRC (volcanic rock Canarias) this value is 72.0% and 74.6%, respectively for a synthetic OMW.

S-AOPs are evaluated as a depuration alternative. Synthetic OMW was submitted to homogeneous and heterogeneous S-AOPs using iron sulfate and solid catalysts (RM and Fe-Ce-O) as the source of iron. The best performance was achieved by Fe-Ce-O, with an optimal load of 1600 mg/L and persulfate concentration of 600 mg/L at pH 5. At these conditions, 27%, 55% and 5% of COD, phenolic compounds and TOC removal were obtained, respectively.

Different AOPs was evaluated to minimize real oil extraction effluent environmental impact. In terms of COD removal, the combination of Fenton and Ozone reaction simultaneously, allowed the highest reduction (58.5%) although the combination of Fenton followed by ozone at pH 3 lead to a similar removal, about 54%. In what regards mineralization, Fenton peroxidation alone was the most efficient process leading to 53% of TOC (total organic compounds) removal.

Pig production involves the generation of wastewater containing a high pollutant load. Besides, the intensive use of pharmaceutical products is leading to the effluents rich on these compounds. The traditional treatments involving biological depuration are effective on the removal of the organic load of swine wastewater. However, the time and space required along with the low efficiency on abating persistent contaminants such as pharmaceutical compounds lead to the need of pursuing alternative technologies. AOPs are very efficient and require a short period of treatment time when compared to traditional processes without the production of biological sludge. Fenton's process combined with coagulation and biofiltration using the invasive species *Corbicula fluminea* was evaluated as an alternative treatment of swine effluent. Biofiltration followed by Fenton's process removed 91 % of COD. Whereas, Fenton´s process after coagulation COD degradation reaches 86 %. Regarding to luminescence inhibition of *Aliivibrio fischeri*, the treatment processes integration can decrease it to about 30 %. Coagulation and biofiltration after Fenton's process is also a good option to remove dissolved iron from treated effluent.

Keywords: Fenton's process; Sludge-free processes; agro-wastewater; sulfate-based processes; Water Recovery.

List of Contents

I. General Introduction

I. Introduction

Our planet is covered by 70% of water, which gives the idea of water being an inexhaustible source. However, only 3% of the world´s water is freshwater - drinking water, bath water, irrigation water—and two-thirds of that are not available in frozen glaciers or otherwise is unavailable for use (WWF - World Wildlife Fund). Studies reveal that two thirds of the global population have difficulty to get water at least 1 month per year, and 0.5 billion people in the world suffer this issue all year round (Mekonnen and Hoekstra, 2016). Many of the water systems, rivers, lakes and aquifers, that keep ecosystems thriving and feed a growing human population are drying up or becoming too polluted to use. Consequently, more than half the world's wetlands have disappeared. Agriculture is the most water-consuming activity, largely due to inefficiencies in irrigation. The climate change also has an influence on water patterns, reflected in some places in scarcity and drought and in others in floods. (D'Odorico et al., 2018; Rosa et al., 2018).

Water scarcity and drought is a real and significant problem in the entire world, affecting social and economic activities, and the environment (Liu et al., 2017; Dell'Angelo et al., 2018). As a result, it is necessary to know the difference between these two concepts to identify the cause, potential impacts, and mitigation measures.

Water recycling is one of the keys aiming to increase water availability and to a smooth adaptation to climate change. Moreover, water recycling follows the circular economy concept that is widely advocated in developed countries (Ghernaout, 2018; Sgroi et al., 2018; Morote et al., 2019). Water reuse still faces some implementation barriers in several areas of the world, including the EU (Voulvoulis, 2018), due to often strict regulations, socio-economic issues, lack of awareness of the potential benefits and economic constraints arising from the need to adapt the chain of value and acceptance of the product by the consumer (Sgroi et al., 2018; Tzanakakis et al., 2020).

Currently, there is a vast knowledge of technologies indicated for the wastewater treatments that are providing high-quality treated effluents meeting the legal requirements, even for unregulated emerging pollutants and agents (pharmaceuticals, antibiotic resistance) and decreasing significantly (or even eliminating) risks for public health and the environment (Adegoke et al., 2018; Zerva et al., 2018; Pazda et al., 2019). Water recycling brings many important benefits such as controlling pollution, preserving the spread of antibiotic resistant genes, and emerging pollutants, maintaining biodiversity and improving the adaptation and resilience of urban and rural communities to climate change. As is already done in some countries, namely in Spain, it is necessary to include recycled water in water management plans. Such plans must include all the information on treatment processes and associated costs, quality and quantity of reused water and where it can be used (e.g. irrigation or recreational activities) for the communities benefit (Iglesias et al., 2010).

Agro-industrial wastewaters are effluents that generate great concern because they are produced in large volumes, are of seasonal variability and are characterized by high pollutant load with multiple organic and inorganic contaminants of environmental concern. There are many processes that are efficient in responding to this problem. However, it is necessary to continuously study new processes and/or optimize existing ones in order to improve efficiencies, lower costs and comply with legal discharge limits in sewer systems and/or in natural waters (Amor et al., 2019).

Wastewater treatment can be performed by conventional technologies, including physical, biological and chemical methods or advanced technologies like membrane separation processes, reverse osmosis, ultrafiltration, and advanced oxidation processes or even a combination of them. The choice of the treatment approach should consider the type and nature of the agro-industrial wastewater (Oller et al., 2011). The aromatic compounds are frequently present in agro-industrial wastewaters. These contaminants of high molecular weight are recalcitrant in nature and resistant to biodegradation, thus the choice of a suitable wastewater treatment must ensure the removal of these cumbersome pollutants from the discharging effluents.

The production of olive oil implies a high consumption of water and consequently generates a high amount of wastewater (OMW). It is estimated that for every ton of olives processed, the amount of OMW produced is 1.2-1.8 m^3, resulting in more than 30 thousand m^3 of OMW produced annually in the Mediterranean basin alone (Haddad et al., 2017). Considering pollution effect, 1 m^3 of OMW has the impact of 200 m^3 of domestic sewage (El-Abbassi et al., 2012). Usually, OMW is composed by 83%–96% water, 3.5%–15% organic constituents and 0.5%–2% mineral compounds, by weight (Kıpçak and Akgün, 2013). The dark colour of OMW is atributed to the presence of polyalcohol, polyphenols, volatile acids, nitrogen compounds, pectin, oil and tannin in is composition (Erkonak et al., 2008). OMW also has low biodegradability and some studies argue that it is due to the presence of phenolics (aromatic compounds) that are very toxic and ecologically harmful, causing imbalances in bacterial activity, plants and aquatic organisms (Mekki et al., 2013; Abu-Lafi et al., 2017). From another point of view, some authors refer to the potential of phenolic compounds as antioxidants, antiallergic, anti-inflammatory, anticancer and antihypertensive, and can be recovered, valued and reducing the environmental footprint (Caproso et al., 2017; Martins et al., 2021).

Considering all the information currently available about OMW, it is mandatory to treat properly this effluent, particularly in the Mediterranean region.

The growth of the world population implies an increase in the consumption of meat, namely pork, and consequently a high production of swine wastewater (SW) is observed worldwide. The major challenge with this increase in population, where food demand is suspected to increase by 70–100%, is ensuring food security in a sustainable and environmental friendly way (Prosekov and Ivanova, 2018). To increase swine production and decrease mortality, so-called intensive farming, veterinary antibiotics and steroidal hormones are used and SW results from washing the swine farm as well as swine excreta (which will contain these pharmaceuticals). This wastewater is typically rich in nitrogen (particularly ammonia nitrogen), phosphorus and organic carbon (as represented by chemical oxygen demand – COD and biological oxygen demand – BOD). The composition of SW might vary according to age of pigs, feed composition, number of pigs in the farm, pig housing methods and other environmental factors like temperature and humidity (Chynoweth et al., 1999). Untreated SW discharge can have serious consequences such as affecting water quality and causing toxicity due to ammonia and nitrogen as well as promoting eutrophication and proliferation of harmful algae containing cyanotoxins, which can cause acute intoxication in humans (Giannuzzi et al., 2011). The application of SW as manure can lead to the accumulation of heavy metals and the accumulation of available phosphorus in the crops (Zhang et al., 2017). This indicates that in case there is no effective treatment of SW, the pollutants can easily damage the ecosystems and reaching humans.

I.1. Objectives

Considering the problematic associated to the two agro-industrial wastewaters reported in the previous section, the main objective of this PhD thesis is to developed suitable treatment technologies based on Advanced Oxidation Processes for two agro-industrial effluents with different characteristics, OMW and SW aiming to reach a recoverable water for reuse. In a first approach the aim was combining different processes and overcome the great disadvantage of Fenton process, which is the formation of iron sludge. It is well documented that the Fenton process has great efficiency in the treatment of agro-industrial effluents and therefore the first approach was to integrate the coagulation process with the Fenton peroxidation to treat an OMW from the oil extraction industry. Coagulation is a very used method to decrease the organic load of wastewater that allows disturbing colloidal formations and favoring the aggregation of small particles. This is an essential step for OMW bearing in mind these effluents characteristics.

The production of iron sludge, which is the biggest disadvantage of the Fenton process, can be minimized using solid catalysts, and residues rich in iron, red mud (RM), and other materials present in nature, the volcanic rocks of azores (VRA) and volcanic rocks of Canaries (VRC) can be an option. Besides, the integration of Fenton's process with ion-exchange technologies may allow to recover the dissolved iron used as catalyst in homogeneous Fenton's. Besides, the usage of *Corbicula fluminea* as a biofiltration agent can be considered to further refine the chemical treated effluent besides removing dissolved iron from the water. *C. fluminea* is an invasive species and in this approach of using it after Fenton process can be considered as a pest management approach by giving it an environmental application.

An alternative to the Fenton process is persulfate process. This technology, in terms of operation, is very similar to Fenton reaction, but in this case the predominant oxidant radical formed is $SO_4^{\cdot-}$. The literature indicates that it can remove resistant pollutants and can operate in a wider pH range. Thus, bearing in mind the advantadges of these technologies it was also an aim of this thesis to compare both treatment approaches.

I.2. Thesis structure

The thesis is divided into four chapters, as can be seen in the Figure I.1. At the initial one, a brief introduction is given on the water problematic that will be addressed. Moreover, the objectives and scope of this work on agro-industrial wastewater treatment encompassing water disinfection and chemical decontamination are described.

In the second chapter an overview about the application of Fenton´s process for OMW treatment is presented. This allows to understand what has been done in this field and what are the future challenges. The different treatment approaches for swine wastewater treatment focusing on pharmaceuticals removal were reviewed. The performance of AOPs such as Fenton (H_2O_2 and Fe^{2+} ions), photo-Fenton, ozone (O_3), electrooxidation and photocatalysis are compared with electrocoagulation and biological systems. Finally, an approach to future challenges is discussed. The major findings regarding the application of S-AOPs for real agro-industrial wastewater depuration are discussed. Moreover, these technologies are compared as an alternative to Fenton's process, which is a widely studied advanced oxidation process and with high efficiency in the treatment of agro-industrial effluents.

The third chapter presents the various studies of technologies for agro-industrial treatment.

The final remarks with the most important conclusions of each chapter and the recommendations of future work were presented at the final chapter (IV).

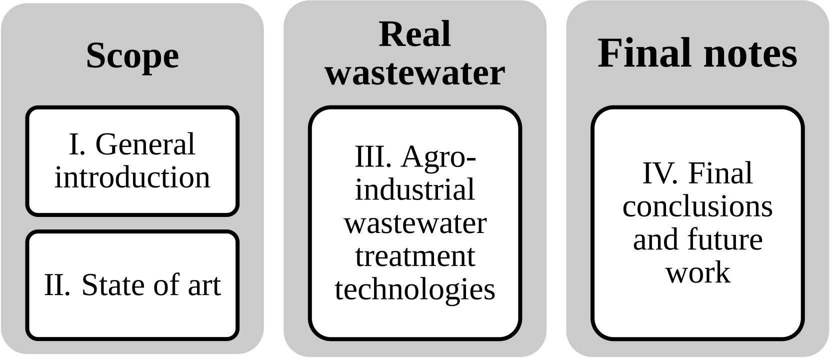

Figure I.1. Summary guidance of the thesis structure.

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II. State of the art

II. State of the art

II.1. Detoxification of Olive Mill Watewater by Fenton´s Process

This section gives a literature overview on the work dealing with Fenton´s process for the detoxification of olive mill wastewaters. It is based on the publication: Domingues, E., Gomes, J., Quina, M.J., Quinta-Ferreira, R.M., Martins, R.C. (2018) Detoxification of Olive Mill Wastewaters by Fenton´s Process. Catalysts. 8 (12), 662.

II.1.1. Overview of OMW treatment by Fenton´s Process

Water is an essential resource for life maintenance. The decline on the quantity and quality of the available freshwater due to large drought periods and contamination due to human activity is increasing social and political awareness for water protection. Thus, even more restrictive legislation must be established to safeguard a sustainable exploitation of hydric resources. This means that industry will have to accomplish even tighter limits in what regards the quality of discharged wastewater. In this context, there is the need for developing efficient water treatment systems. In fact, one of the basilar stones of the current European commission program regarding water is the development of technologic and innovative solutions able to lead to safe water for all citizens. Due to the water shortening and increasing supply demanding, liquid effluents must be envisaged as alternative sources of fresh water (Bourgin et al., 2018). In this context, researchers and stakeholders must putt on efforts so that economical viable technologies can be developed to reach safe water for both ecosystems and human health from adequate treatment of contaminated streams. Such goal will only be reached by combining processes to take advantage from their synergies.

Mediterranean Sea area countries suffer from severe drought periods and water shortening is a particularly serious problem in those countries. Moreover, agro-industries (such as olive mills) are an important part of their industrial tissue. Even if those industries are a relevant key in their economic development, the wastewaters generated are a major environmental danger. On one hand, agro-industries are high water demanding and, on the other hand, during their operation a high amount of polluted streams are created. Thus, the treatment of those effluents is a major step aiming environmental preservation and water recovery.

The Mediterranean countries are the major producers of olive oil. During olive oil extraction, up to 10 million ton of liquid effluents are generated each year (Pulido, 2016). The composition of OMW depends on several factors, such as the climate, the cultivation and the method of milling used to produce olive oil. There are several types of processes used in the production of olive oil such as traditional pressing, three-phase and two-phase decanting processes (Mert et al., 2010). Olive mill wastewaters can be characterized by a strong odour, dark colour and high organic load including sugars, tannins, polyalcohols, pectins and lipids (Dias et al., 2004; Cañizares et al., 2006). The common treatments based on biological reactors tend to be inefficient to OMW due to the presence of toxic compounds on their constitution (Guido et al., 2006; Saadi et al., 2007). Moreover, their high organic load (chemical and biochemical oxygen demand may reach up to 100 to 200 g/L) make these streams hard to manage as well as the fulfilment of the legal thresholds for their discharge to the environment (Azbar et al., 2004). Some recovery strategies were studied to take advantage of OMW characteristics. For example, Fabrizio et al. (2018) studied an integrated microalgae biomass production and olive mill wastewater biodegradation. In fact, OMW can have nutrients like phosphorus and organic carbon that help microalgae growth. Moreover, aiming at water recovery, robust and efficient treatment approaches are required. In this context, advanced oxidation processes are promising technologies to reduce the environmental impact of these effluents (Cañizares et al., 2006; Amaral-Silva et al., 2017) and to promote water recovery from effluents (Oller et al., 2011; Gomes et al., 2017). Among them ozonation (Martins et al., 2014) and Fenton´s process (Amaral-Silva et al., 2016a) show interesting potential for the treatment of olive mill wastewater (OMW).

The Fenton’s process is based on the production of hydroxyl radicals through the catalytic decomposition of hydrogen peroxide promoted by iron ions. Thus, this technology shows interesting features for full scale application since it occurs at room temperature and pressure and no sophisticated equipment is required (Bautista et al., 2008; Ochando-Pulido et al., 2017). Besides, there are no safety nor environmental issues related with hydrogen peroxide (Badawy et al., 2006). Consequently, there are several studies involving the application of this process for the treatment of water and wastewater (Burbano et al., 2005; Benzaquén et al., 2015; Amaral-Silva et al., 2016a). The main drawback of this technology is the need of removing the dissolved iron from the treated effluent (Table II.1.1). In fact, the required amount of catalyst is usually much higher than the legal threshold of iron permitted for an effluent discharge to the natural water courses. Currently after the oxidation process, the wastewater is alkalinized so that insoluble $Fe(OH)_3$ is produced and precipitates as iron sludge (Cao et al., 2009). Typically, these sludges are dried and directed to landfills which do not allow the catalyst reuse. Besides, since the sludges incorporate some organic compounds that coagulate with $Fe(OH)_3$ they may have a negative environmental impact and constitute a second source of pollution. This way wastes minimization and management are a technologic challenge. Besides, the possibility of catalyst recovery would reduce the environmental impact and the operating costs of the process.

Table II.1.1. Pros and cons of homogeneous Fenton's process.

Homogeneous Fenton's process	
Advantages	**Disadvantages**
- Easy operation - High COD removal - Biodegradability improvement - Established technology	- Sludge formation - Operation in acidic conditions (pH~3) - Requires neutralization of pH

Even though these disadvantages, there is much industrial interest on the Fenton's process due to its ability to deal with cumbersome effluents (such as those coming from olive oil extraction) which are unable to be directly managed through the traditional biological systems. In fact, Fenton's process shows high capacity for improving the biodegradability and reducing the toxicity of bio-refractory effluents (Martins et al., 2010a). In this context, scientific efforts are in force to overcome the problems associated with the iron sludge production. This involves strategies like iron recovery from the sludge to be directly reused in Fenton's reaction (Rossi et al., 2013; Bolobajev et al., 2014) or as precursor of solid catalysts (Zhang et al., 2017). Moreover, the selection of active and stable heterogeneous catalysts for Fenton's peroxidation instead of soluble iron salt is being addressed (Rodrigues et al., 2017; Zhang et al., 2017). The use of light and/or electro driven Fenton's process (González et al., 2007; Malato et al., 2007; Liu et al., 2018; Poza-Nogueiras et al., 2018;) may also reduce the amount of iron required for the reaction.

Bearing in mind the high industrial interest on the Fenton's process, the aim of the present section is to give a critical overview on the works dealing with this process for the detoxification of olive mill wastewaters. These effluents were selected as case study due to their high environmental impact particularly on the Mediterranean basin countries that also suffer from a strong water shortening. In this context, Fenton's process can be a suitable alternative for water recovery on this water demanding industry.

II.1.2. Homogeneous Fenton´s process

The classic Fenton's process operates at homogeneous conditions, where hydrogen peroxide decomposition into hydroxyl radicals is promoted by the dissolved ferrous iron according to Equation II.1. (Walling, 1975).

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\cdot} \qquad \text{II.1.}$$

However, other reactions can be involved in the global mechanism such as those described by Equations II.2 and II.3 (Neyens and Baeyens, 2003).

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-} \qquad \text{II.2}$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad \text{II.3}$$

In those reactions, Fenton's main oxidant (hydroxyl radicals) is scavenged which may reduce the process efficiency. This means that the ratio between H_2O_2/Fe^{2+} must be carefully selected for avoiding the scavenging effect. Lucas and Peres (2009) tested the effect of pH, temperature, H_2O_2/Fe^{2+} molar ratio and H_2O_2/COD weight ratio for the Fenton's peroxidation of OMW (collected in Portugal and diluted to an initial COD ~2 g/L). The best operating conditions (pH 3.5, 30 ºC, $H_2O_2/Fe^{2+} = 15$ and $H_2O_2/COD = 1.75$) led to a COD removal of 70%. Moreover, the authors were able to determine the Arrhenius constant (28.2 kJ/mol) for the system that was kinetically well described by a pseudo-first order equation.

One important feature of the Fenton's process is the capability of improving the effluent BOD_5/COD ratio which means that this chemical process can be followed by a biological system for further degradation of the effluent (Vlyssides et al., 2004). Therefore, if the legal limits for local sewage discharge are accomplished, the pre-treated OMW can be conducted to the municipal wastewater treatment plant (MWTP) for final depuration. Gomec et al. (2007) verified that Fenton's oxidation (2 g/L of H_2O_2 and Fe^{2+}) was able to improve COD removal of OMW after acid cracking and cationic polyelectrolyte coagulation. COD degradation reached 89% and the wastewater was within the legal limits (regarding COD and suspended solids) for discharge to the local sewage. However, as the authors refer, information must be collected about the effect of the chemical process over the treated effluent biodegradability and toxicity so that its impact over the biological systems of the MWTP can be thoroughly assessed. This information can also help on the optimization of the Fenton's process since this system can be expensive due to the chemical and energy requirements. Hydrogen peroxide is reported to assume up to 75% of the process global operating cost (Rivas et al., 2001). Moreover, Rivas et al. (2001) determined an average stoichiometric ratio of 3 mol of H_2O_2 per mol of COD removed. Thus, instead of seeking large organic matter removal efficiencies, one can be focused in partial oxidation of the pollutants aiming to improve biodegradability and reducing toxicity. Fenton's process has been reported to be able to moderately remove COD, while a large polyphenolic fraction is degraded leading to an effluent able to be depurated by aerobic biological systems in a high extent (Beltrán-Heredia et al., 2001). This way it can be followed by a biological treatment for example in a municipal wastewater treatment plant (MWTP). Thus, the costs associated with the effluent processing may be reduced.

It must be highlighted that Rivas et al. (2001) compiles the most important steps in Fenton's mechanism and gives the kinetic constants for each one of them. This may be important while developing mathematical models to simulate the process.

Mert et al. (2010) studied physicochemical (acid cracking), Fenton and Fenton-like processes in the pre-treatment of OMW. The chemical pre-treatment had a positive effect on biodegradability. Acid cracking led to a removal> 67% of COD and 72% of total-phenols. Fenton's process, with the optimal conditions: pH=3, [H_2O_2]=3.5 g/L and [$FeSO_4$]=3 g/L achieved up to 81% COD removal, 86% phenol removal and 350 mL/L sludge volume, whereas Fenton-like process optimal conditions (pH=3, [H_2O_2]=3 g/L and [$FeCl_3$]=2.5 g/L) were able to reach 88% COD removal, 91% phenol removal and 300 mL/L sludge volume. The authors also studied the costs of the processes in terms of required chemicals. They found that the Fenton-like process is the most economical and feasible option for the treatment of OMW before discharge into sewage for the protection of central wastewater treatment plants. Moreover, the OMW inhibitory effect over activated sludge was truly diminished after the chemical treatment. Thus, Fenton's process may be envisaged as a suitable pre-treatment before a traditional activated sludge reactor.

Fenton's process can also improve methane production yield during OMW anaerobic digestion (AD). Indeed, the high organic load of OMW makes it an interesting substrate for biogas production using anaerobic digestion. However, its high toxicity may constitute a drawback. Maamir et al. (2017) verified that submitting OMW to Fenton's pre-treatment ([H_2O_2]/[Fe^{2+}] = 1000 (mol/mol), [Fe^{2+}] = 1.5 mM, 120 min and pH 3) improved methane yield up to 24%. Moreover, the highest methane yield after 30 days of AD (63%) was obtained when Fenton's pretreated OMW was used without previously precipitate iron. This was attributed to the delignification of the effluent during the Fenton's process. However, the biogas production was reduced when compared with the case where the untreated effluent was applied. This was associated with the production of toxic by-products during oxidation. Thus, following the effluents toxicity during chemical oxidation is crucial if the aim is the combination with a further biological processing afterwards.

Nieto et al. (2001) treated an OMW coming from a two-phase olive-oil process industry as well as the wastewaters from olives and olive-oil washing, with a homogenous Fenton-like reaction (Fe^{3+}/H_2O_2). This process shows an efficiency of more than 90% in the degradation of organic matter and phenolic compounds with a ratio of catalyst to hydrogen peroxide between 0.02 and 0.04 and pH 3. The pH 3 was achieved just with the addition of the catalyst when the ratio $[FeCl_3]/[H_2O_2]>0.01$. The authors were able to obtain the apparent activation energy (Ea) for the Arrhenius equation (8.7 kJ/mol). At the end of the treatment the remaining water was ready to be used for irrigation.

Esteves et al. (2017) proved the stability of the Fenton's process in continuous conditions using a continuous stirred tank reactor (CSTR) for the degradation of a phenolic mixture (vanillic, caffeic, gallic, 3,4-dihydroxyphenylacetic and coumaric acids and tyrosol) mimicking the phenolic content of OMW. For a residence time of 120 min, $[Fe^{2+}]$ = 100 ppm, $[H_2O_2]$ = 2.0 g/L and T = 30 ºC TOC and phenolic content removals of 47.5% and 96.9% were obtained. Moreover, a high toxicity removal as well as biodegradability enhancement was observed which would allow the further treatment of the wastewater by conventional biological systems. It should be referred that the feed pH of 5 was autocorrected to 3.2 (which is within the optimal range for Fenton's process) when the reactants were mixed with the wastewater. This will reduce the costs associated with the pH correction before the oxidation.

In order to overcome the drawback associated with iron sludge production, Reis et al. (2017) analysed the combination between the Fenton's process and ion exchange to recover iron. The Fenton's process was able to remove up to 81% of COD of OMW in 60min using pH 3.5, $[Fe^{2+}]$ = 50 mg/L and $[Fe^{2+}]/[H_2O_2]$ = 0.002 (w/w). Lewatit TP207 resin removed 90% of iron from the Fenton's treated stream. Moreover, its efficiency was independent on the load of organic matter in the wastewater. Besides, even for large amounts of dissolved iron it was possible to adapt ion exchange operating conditions (e.g. increasing the quantity of resin) to maintain the desired efficiency of iron removal. Thus, this sequential treatment seems to be an interesting approach to avoid the formation of iron sludge after Fenton's treatment. Also, Víctor-Ortega et al. (2016) concluded that a Dowex Marathon C cation exchange resin is able to recover iron from a Fenton's treated OMW. However, in this case sludge production was not avoided since ion exchange was only applied to remove the dissolved iron remaining after sludge precipitation. The ion exchange column was able to recover 100% of the iron even after 10 complete cycles. The treated OMW shows quality for being used as irrigation water according to Food and Agriculture organization (FAO) considering the resulting salinity.

The performance of nanofiltration-NF (using DK series membrane) and low-pressure reverse osmosis-RO (AK series membrane) was evaluated to recover the iron from OMW after Fenton's treatment. Up to 99.1% and 100% of iron recover was obtained using NF and RO, respectively (Ochando-Pulido et al., 2016). The concentrate could be redirected to Fenton's reactor minimizing the catalyst waste. Moreover, the permeate was able to be reused for irrigation. With NF it was possible to obtain a lower membrane fouling index which means that longer membrane lifetimes are expected as well as lower filtration areas.

Even though these interesting results, recovered iron recycling as Fenton's catalyst must be still evaluated. This is an important point, for example Qiang et al. (2003) and Li et al. (2007) tested the possibility of directly reusing the iron sludge coming from Fenton's process as catalyst for this treatment. However, even if high COD removal was obtained, the treated effluent conductivity increased very much due to the high amount of acid used for iron dissolving. Martins et al. (2010b) verified that the final sludge could be reused without being previously dissolve even if by a limited number of times. Table II.1.2 summarizes some studies reporting homogeneous Fenton process in the treatment of OMW.

Table II.1.2. Treatment of OMW with homogenous Fenton process.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
OMW collected in Portugal and diluted to initial COD ~ 2 g/L	Fenton	pH=3.5 T=30 ºC H_2O_2/Fe^{2+}=15 H_2O_2/COD=1.75	COD removal of 70%	Lucas et al., 2009
OMW after cracking and cationic polyelectrolite coagulation.	Fenton	2 g/L of H_2O_2 and Fe^{2+}	COD removal of 89%	Gomec et al., 2007
OMW	Fenton	pH=3 [H_2O_2]=3.5 g/L [$FeSO_4$]=3 g/L	81% COD removal 86% phenol removal 350 mL/L sludge volume	Mert et al., 2010
OMW	Fenton-like	pH=3 [H_2O_2]=3 g/L [$FeSO_4$]=2.5 g/L	88% COD removal 91% phenol removal 300 mL/L sludge volume	Mert et al. 2010
OMW	Fenton	pH=3 [H_2O_2]/[Fe^{2+}]=1000 mol/mol [Fe^{2+}]=1.5 mM t=120 min	improve methane yield up to 24%	Maamir et al., 2017
OMW coming from a two-phase olive-oil process industry as well as the wastewaters from olives and olive-oil washing	Fenton-like	pH=3 ratio of catalyst to hydrogen between 0.02 and 0.04	90% in the degradation of organic compounds and phenolic compounds *Ea*=8.7 kJ/mol	Nieto et al., 2001
Phenolic mixture (vanillic, caffeic, gallic, 3,4-dihydroxyphenylecetic, coumeric acids and tyrosol)	Fenton	t=120 min [Fe^{2+}]=100 ppm [H_2O_2]=2.0 g/L T=30 ºC	TOC removal 47.5% phenolic content removals of 96.9%	Esteves et al., 2017
OMW	Fenton	t=60 min pH=3.5 [Fe^{2+}]=50 mg/L [Fe^{2+}]/[H_2O_2]=0.002 (w/w)	81% of CODremoval	Reis et al., 2017

II.1.3. Heterogeneous Fenton´s process

The use of suitable solid catalysts can overcome the sludge generation shortcoming of the Fenton's process. Moreover, this would allow catalyst recovery and reuse which would reduce the operating costs. Besides, another drawback of homogeneous Fenton is related with iron solubility. In this context, acid conditions are generally required to ensure iron solubilisation.

Moreover, after treatment neutralization of the medium is necessary to promote iron separation. Whereas in heterogeneous Fenton pH change may not be required so savings can be obtained by this procedure. In the heterogeneous Fenton's process, iron or other metal(s) are supported so that ions are not dissolved in the liquid bulk. Several types of solid catalysts were tested for OMW depuration through this process. Rossi et al. (2014) tested the efficiency of Fe/Cu oxides prepared by coprecipitation according to the procedure described by Imamura et al. (1985) for the degradation of a phenolic mixture usually present in OMW. Among the tested catalysts the Fe-Cu-O with a molar proportion of 50/50 was the most efficient on the removal of organic matter. However, low biodegradability improvement was observed which may be a drawback to the process. Contrarily, Martins et al. (2010c) and Rossi et al. (2012) concluded that the Fe-Ce-O 70/30 heterogeneous catalyst was able to improve phenolic mixture biodegradability while reducing toxicity during Fenton's process. In fact, a chemical process should be envisaged as a pre-treatment to improve the biodegradability of an effluent so that a further treatment step involving biological degradation may be efficiently applied. This way, the treatment cost can be reduced.

Kallel et al. (2009), studied the applicability of advanced Fenton process, hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, as a pre-treatment of OMW. They consider the following factors: hydrogen peroxide and zero-valent iron dosages, initial pH and initial COD. The best conditions achieved were acid pH (2.0-4.0), 5% H_2O_2, Fe^0 = 20 g / L. Under these conditions, after 3 h, the colour of the OMW had disappeared and the amount of phenolic compounds decreased by 50% compared with the initial load. The advanced Fenton process has shown to have several advantages namely high efficiency, the fact that specific equipment is not necessary and cheaper systems can be built by comparing the use of metallic iron with iron salts. In fact, the use of zero valent iron enhances the catalyst regeneration since Fe^{3+} can be reduced to Fe^{2+} at the Fe^0 surface which will improve the process efficiency avoiding the waste of H_2O_2. Moreover, it would also allow the use of iron wastes such as irons shavings coming from metal processing industry as a low-cost catalyst for this process (Martins et al., 2013).

The laboratory catalyst Fe-Ce-O 70/30 showed interesting results in heterogeneous Fenton peroxidation of weathered OMW coming from an evaporation pond (Martins et al., 2010d). Although COD removal was not so high (25%) the following operating conditions were selected: pH 4, $[H_2O_2]$ = 115 mM and 1.5 g/L of catalyst. In fact, at those conditions the final effluent was biodegradable (BOD_5/COD = 0.54) and with low toxicity which enables a further biological depuration. Moreover, the catalyst showed stability regarding metal leaching since the concentration of iron dissolved in the effluent after treatment was below 0.12 mg/L.

Aiming the remediation of a mixture of six phenolic compounds (4-hydroxy-3,5-dimethoxybenzoic, 4-hydroxi-3-methoxybenzoic, 3,4,5-trimethoxybenzoic, 3,4-dimethoxybenzoic, 3,4-dihydrobenzoic and 4-hydroxybenzoic), usually present in real OMW, Martins and Quinta-Ferreira (2011a) compared the efficiency of homogenous Fenton´s process and the heterogeneous process over the solid Fe-Ce-O 70/30. For the homogenous Fenton´s process the most favourable conditions of reaction were 0.9 g/L of Fe^{2+} and $[H_2O_2]$=310 mM, whereas for the heterogenous Fenton´s process the best conditions were 1 g/L of Fe-Ce-O 30/70 and $[H_2O_2]$=244 mM. Both processes were carried out at pH 3 as suggested by Neyens and Bayens (2003). Analysing the results in terms of total phenolic content (TPh) removal, the results pointed out that both processes are efficient although for the homogeneous process the first 15 min of reaction were enough for total TPh degradation, while for the heterogenous process 120 min were required. Regarding TOC and COD, the homogenous Fenton process achieves a much greater reduction in the first 15 min, 46% and 60% respectively, compared to 31% and 48% attained by the heterogeneous system. At the end of the reaction, the performance of both processes is very similar concerning to TOC removal, obtaining an approximate reduction of 57%. The homogeneous process has a better performance in COD removal corresponding to 60% compared to 49% for heterogenous Fenton. Although the homogeneous Fenton process is quite efficient in COD removal, the Fe-Ce-O heterogeneous catalyst requires a lower hydrogen peroxide load besides rendering the final effluent more suitable for bioprocessing. Table II.1.3 summarizes results of studies focused on the application of the heterogeneous Fenton’s process in the treatment of OMW.

Table II.1.3. Treatment of OMW with Heterogenous Fenton process.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
OMW	Heterogenous Fenton: H_2O_2 and zero-valent iron	pH=2 - 4 5% of H_2O_2 Fe^0=20 g/L t=3 h	Total color removal. 50% of phenolic content removal	Kallel et al., 2009
Weathered OMW	Heterogenous Fenton: H_2O_2 and Fe-Ce-O	pH=4 $[H_2O_2]$=115 mM [Fe-Ce-O]=1.5 g/L	25% of COD removal Final effluent biodegradable (BOD_5/COD)=0.54 and low toxicity	Martins et al., 2010d
OMW	Heterogenous Fenton: H_2O_2 and Fe-Ce-O	pH=3 $[H_2O_2]$=224 mM [Fe-Ce-O]=1 g/L	31% of TOC removed 48% of COD removed Total TPh degradation after 120 min	Martins et al., 2011a

II.1.4. Photo-Fenton process

The use of light may enhance Fenton's process efficiency (Table II.1.4). During the Fenton's reaction, Fe^{3+} ions are accumulating which reduces the process efficiency since Fe^{2+} ions are more effective on the catalytic decomposition of hydrogen peroxide into hydroxyl radicals. However, the presence of light, photo reduction of ferric ions may occur (eq.II.4) and the regenerated ferrous ions may continue the hydroxyl radical's production cycle (Babuponnusami and Muthukumar, 2014). Moreover, at some conditions, the direct photolysis of hydrogen peroxide may lead to $HO^{\bullet}$ according to Equations II.4 and II.5.

$$\mathrm{Fe(OH)^{2+}} + h\nu \rightarrow \mathrm{Fe^{2+}} + \mathrm{HO^{\cdot}} \qquad \text{II.4}$$

$$\mathrm{H_2O_2} + h\nu \rightarrow 2\mathrm{HO^{\cdot}} \qquad \text{II.5}$$

Table II.1.4. Treatment of OMW using photo-Fenton process.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
OMW	Photo-Fenton: different medium pressure commercial UV-lamps	pH=3 $[H_2O_2]$>8 g/L $FeCl_3$ solution 3 g/l t=5-30 min T=20 ºC	90% of COD, total organic carbon, total phenolic compounds and turbidity removals	García et al., 2017
OMW (tyrosol, vanillic acid, caffeic acid, coumaric acid and ferulic acid)	Photo-Fenton: FeS_2 and $CuFeS_2$; UV LED (maximum emission wavelength of 395 nm)		$CuFeS_2$led to total phenolic compounds depletion; 98% of TOC removal. pH autocorrection (~3). High toxicity towards *A. fischeri* due to Fe and Cu leaching.	Ltaïef et al., 2018
OMW	Solar photo-Fenton after coagulation/flocculation		95% of COD removal Removed OMW phytotoxicity High dilution required.	Ioannou-Ttofa et al., 2017

Garcia and Hodaifa (2017) treated OMW by photo-Fenton reaction in a batch reactor and using $FeCl_3$ solution (3 g/L) as catalyst precursor at 20 ºC and pH 3. They studied different H_2O_2 concentrations as well as different medium pressure mercury commercial UV-lamps. With a concentration of H_2O_2> 8 g/L and a short reaction time (5-30 min) allowed 90% of COD degradation as well as removal of total organic carbon, total phenolic compounds and turbidity. All tested UV-lamps presented virtually similar removal percentages. After the treatment, the obtained water can be used for different purposes according to the achieved parametric values: for olives irrigation (pH = 6-9, COD < 1 gO_2/L) or for discharge into urban effluent treatment plants (pH = 6-9, final COD 0.5 gO_2/L). It should be noticed that these limit values are according to Spanish Standards.

The use of chelating agents such as oxalate, citrate and EDTA may widen the operational pH range of the Fenton's process since no iron precipitation occurs this way. The use of 60 mg/L of oxalate promote solar photo-Fenton of a mixture of phenolic compounds found in OMW (protocatechuic, gallic and p-coumaric acids) leading to total removal of the initial compounds in 5 min and up to 94% of mineralization in 194 min (Monteagudo et al., 2011). This efficiency increase is related to the photo-sensitivity of ferrioxalate complexes that can absorb radiation up to 550 nm enlarging this way the useful spectrum of solar radiation. A stoichiometric ratio between consumed hydrogen peroxide and TOC removed within 1 and 3 was always determined. Moreover, the analysis of the role of the oxidant species revealed that besides $HO^{\bullet}$ and $O_2^{\bullet -}$, also singlet oxygen may play important paper in mineralization.

Also, some compounds already present in wastewaters such as phenolic compounds may be used as iron chelating agents. OMW is rich on those substances and therefore can be used as a chelating agents source avoiding the use of additional chemicals. Davididou et al. (2018) verified that highly diluted OMW, even if with lower efficiency than typical chelates like EDDS (Ethylenediamine-N, N-disuccinic acid) was a suitable alternative for chelating iron during the photo-Fenton oxidation of saccharin.

The use of natural materials as low-cost catalysts in Fenton's process reduces the costs with catalyst preparation (Figure II.1.1). Moreover, if those materials present photo-activity they can be used in photo-Fenton's processes. In this context, Ltaïef et al. (2018) studied the catalytic potential of mined pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) in photo-Fenton's oxidation of phenolic compounds present in OMW (tyrosol, vanillic acid, caffeic acid, coumaric acid and ferulic acid). Photo-Fenton was promoted by high intensity UV LED (maximum emission wavelength of 395 nm). The results showed that chalcopyrite was a suitable catalyst for this process since total depletion of the phenolic compounds was observed while 98% of TOC was removed. Besides, the catalysts were able to spontaneously correct the wastewater pH for the proper value required for Fenton's oxidation (~3). The drawback is the high toxicity of the resultant treated samples to *Aliivibrio fischeri* which was attributed to the Fe and Cu dissolved during the reaction.

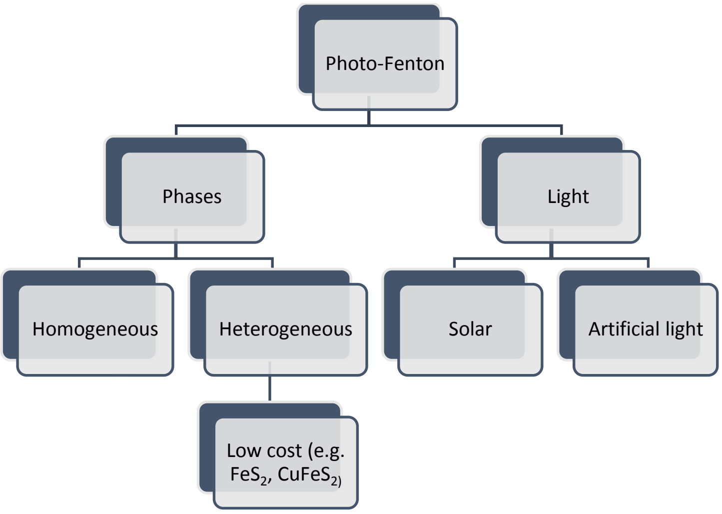


Figure II.1.1. Photo-Fenton methodology.

The efficiency of biological oxidation, photo-Fenton's process and filtration for the treatment of OMW was analysed (Ioannou-Ttofa et al., 2017). Solar photo-Fenton after coagulation/flocculation reached up to 95% of COD removal. Besides, such procedure removed OMW phytotoxicity. Since olive oil production is mainly concentrated at the Mediterranean region where sun light is plentifully available the operating costs of this treatment would be reduced. However, a shortcoming of this procedure is related with the high dilution of the initial OMW required for the application of such management strategy. According to the Strenghts, Weakenesses, Opportunities and Threats (SWOT) analysis performed, one of the main strengths/opportunities of this technology is related with the possibility of safely using the treated water for the agricultural fields irrigation which would reduce the water stress provoked by this industry. However, this implies broad analysis of the potential ecological and human health impact of such streams. As for the weaknesses, these are mainly related with the operating costs associated with the low incomes of the small olive mills. Moreover, the lack of strict legislation regarding the disposal of OMW may also constitute a threat for the wide spread of efficient wastewater treatment technologies.

II.1.5. Integrated systems

An important aspect of OMW is their high content in polyphenolic compounds. These substances are well known by their antioxidant potential (Obied et al., 2005) making them high-valuable compounds for cosmetic pharmaceutical and food industries with prices ranging 2000 €/g. In this context, OMW can be an interesting source for these substances. Thus, OMW treatment strategy may encompass a recovery step before oxidation (Table II.5). Papaphilippou et al. (2013) proposed an integrated treatment scheme involving coagulation-flocculation for the removal of solids followed by extraction with ethyl acetate for the recovery of phenolic compounds (caffeic acid, tyrosol, gallic acid and oleuropein). The remaining OMW still possessed high organic charge. Thus, the authors proposed a solar photo-Fenton step which at the optimal conditions (0.2 g/L $Fe^{2+;}$ 5 g/L H_2O_2 and pH 3) led to 73% of COD removal. However, the oxidized samples showed higher toxic character than raw OMW towards *Daphnia magna* due to the intermediates formed. This means that further depuration is required to reach a safe treated stream. Moreover, the integrated treatment system economic viability must be deeply assessed before proposing such approach (Figure II.1.2).

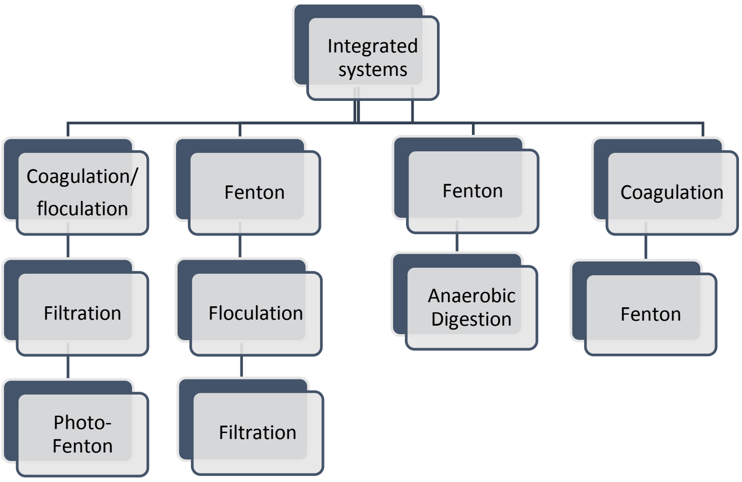


Figure II.1.2. Examples of integrated treatment systems involving Fenton's processes

Alver et al. (2015) studied the olive mill effluent treatment by integrating coagulation and Fenton oxidation. They concluded that the best operating conditions for the Fenton process were pH=3, Fe^{2+}=2.5 g/L, H_2O_2=1 g/L, Fe^{2+}/H_2O_2=2.5. Pre-coagulation had a good impact in the degradation of organic matter through the following Fenton's process step, but it was not able by itself to substantially remove COD and total phenol.

Membrane processes are usually suitable management strategies when water reuse is intended since water with high quality can be obtained. Nevertheless, the main disadvantage of such approaches is related with the membrane fouling, which will imply the membrane frequent regeneration or even substitution and the pressure required which will increase the process costs. In this ambit, Ochando-Pulido et al. (2012) studied a pre-treatment before the membrane process to decrease the fouling formation during the processing of olive mill wastewater. The purpose was to recirculate the treated effluent to the manufacture process or alternatively in the olives washing machines to close the water loop. Pre-treatment processes involved Fenton-like oxidation, flocculation-sedimentation and filtration through olive stones. The pre-treatment decreased COD and polyphenols concentration, acting also in the particle size distribution of the nanometric suspended matter which means near-zero membrane fouling. This pre-treatment also showed to be efficient for the composite osmosis reverse membrane operation, which achieved a baseline after initial flux decay due to concentration polarization.

With the objective of developing an economical solution for the treatment of OMW, El-Goahary et al. (2009) studied the integrated system of wet hydrogen peroxide catalytic oxidation (WHPCO) followed by two stages up flow anaerobic sludge blanket (UASB) reactor (10 L each). Fenton´s reaction was used like a pre-treatment with diluted wastewater (1 OMW :1 tap water). The optimum operating conditions were pH=3, COD:H_2O_2=1.0:1.1, Fe^{2+}:H_2O_2=1:50. The results showed that the use of Fenton´s as a primary treatment of OMW improved the efficiency of anaerobic digestion and could degrade an important part of toxic compounds present in OMW. In the final effluent residual concentration of p-hydroxy-benzaldehyde (0.432 mg/L) and 3.273 mg/L for cinnamic acid was detected. The authors concluded that the anaerobic systems have a high potential to tolerate the abrupt organic load and the toxic compounds present in this kind of wastewater.

Amor et al. (2017) proposed a combined treatment of olive mill wastewater by Fenton´s reagent and anaerobic biological process. For the Fenton´s process they used a fixed H_2O_2/COD ratio of 0.20, pH 3.5 and a H_2O_2/Fe^{2+} molar ratio of 15:1. This pre-treatment allows to achieve a reduction of 17.6 of chemical oxygen demand and 82.5% on total polyphenols. In the anaerobic digestion, the authors used previously adapted microorganisms immobilized in Sepiolite and performed the biological tests with variation of the substrate concentration supplied to the reactor which allowed an increase on COD removal from 52% to 74%. The combination of Fenton´s reaction with anaerobic biological process compared with single anaerobic degradation is better because an increase in the organic matter degradation is observed. In fact, the biokinetics constant is higher in the combined process (k_N=0.036 h^{-1} compared with k_N=0.017 h^{-1} for the single process). The authors concluded that the combination of the Fenton process with anerobic digestion is a good option in the treatment of OMW. Rizzo et al. (2008), investigated the combined treatment by coagulation with natural organic coagulant, chitosan and advanced oxidation processes, namely photocatalysis, Fenton and photo-Fenton, in order to improve biodegradability of OMW. In optimal conditions (pH 4.3, 400 $mg_{chitosan}$/L), coagulation removed 81% of total suspended solids. Photo-Fenton showed to be very efficient in COD and aromaticity removal, 93% after 0.5 h. Fenton process reduced 81% of COD after 1h reaction. TiO_2 photocatalysis tests did not show a significant organic matter removal in the investigated conditions. According to the results, an initial COD removal was observed at the first stages of TiO_2 photocatalysis. However, COD increases afterwards which was attributed to the formation of partial oxidized by-products that are only detectable at those conditions through COD analysis. Even after 350 min of reaction this process was not able to totally oxidize organic compounds probably due to the high pollutant load of the effluent when compared with the radiation flux as well as due to the strong color of the wastewater which reduced the catalyst irradiation. Chitosan coagulation combined with Fenton or photo-Fenton could be a good alternative, considering the good removal of organic matter and its aromatic fraction by Fenton and photo-Fenton processes and the potential reuse of the organic sludge produced by chitosan coagulation. Still, one must bear in mind the costs of chitosan that may be prohibitive for industrial application. Nevertheless, the economic viability will depend on the way the organic sludge may be reused. In fact, the use of this biomaterial instead the traditional metal-based coagulants will reduce the formed sludge potential toxicity. Thus, probably it may be used (after stabilization through anaerobic digestion and/or composting) as a soil amendment. Table II.1.5. summarizes the refered studies.

Table II.1.5. Treatment of OMW with integrated processes.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
OMW	Integrated treatment scheme involving coagulation-flocculation for the removal of solids followed by extraction with ethyl acetate for the recovery of phenolic compounds (caffeic acid, tyrosol, gallic acid and oleuropein). Thus, a solar photo-Fenton step	0.2 g/L of Fe^{2+} 5 g/L H_2O_2 pH 3	73% of COD removal High toxicity (*Daphnia magna*) due to the intermediates formed	Papaphilippou et al. (2013)
OMW	Integrating coagulation and Fenton oxidation	pH=3 Fe^{2+}=2.5 g/L H_2O_2=1 g/L Fe^{2+}/H_2O_2=2.5	Pre-coagulation had a good impact in the degradation of organic matter through the following Fenton's process step.	Alver et al., 2012
OMW	Pre-treatment process involved Fenton-like oxidation, flocculation-sedimentation and filtration through olive stones and after membrane process	----	The pretreatment decreased COD and polyphenols concentration and acts in the particle size distribution reducing membrane fouling	Ochando-Pulido et al., 2012
OMW	Integrated system of wet hydrogen peroxide catalytic oxidation (WHPCO) followed by two stage upflow anaerobic sludge blanket (UASB) reactor	1OMW :1 tap water pH=3 COD:H_2O_2=1.0:1.1 Fe^{2+}:H_2O_2=1:50	Fenton´s reaction improves the efficiency of anaerobic digestion	Goahry et al., 2009
OMW	Combined treatment by Fenton´s reagent and anaerobic biological process	H_2O_2/COD ratio of 0.20 pH 3.5 H_2O_2/Fe^{2+} molar ratio of 15:1	Pre-treatment: 17.6% of COD and 82.5% total polyphenols removal. Biodegradability was improved.	Amor et al., 2017

Table II.1.5. Treatment of OMW with integrated processes (cont.)

Effluent	Process	Optimal conditions	Results	Reference
OMW	Combined treatment by coagulation with natural organic coagulant, chitosan and advanced oxidation processes, namely photocatalysis, Fenton and photo-Fenton	----	Coagulation: removed 81% of total suspended solids Photo-Fenton: efficient in COD and aromaticity removal, (93% after 0.5 h) Fenton process reduced 81% of COD after 1 h reaction TiO_2 photocatalysis: no significant COD removal Chitosan coagulation combined with Fenton or photo-Fenton could be a good alternative.	Rizzo et al., 2008

II.1.6. Industrial Applications

There are some reports regarding the industrial application of the homogeneous Fenton's process for the remediation of OMW. Amaral-Silva et al. (2017) evaluated at bench and then at the industrial scale the integration between coagulation using iron (III) sulphate followed by Fenton's process. The coagulation step reduced the suspended solids and removed some COD while leading to enough dissolved iron to be used as catalyst in the following oxidation step. At the industrial scale such approach led to an effluent with 200 mgO_2/L in COD. Furthermore, the biodegradability enhancement obtained (BOD_5/COD increased from 0.03 to 0.42) enabled a successful activated sludge post-treatment which could further refine the effluent. An average operating cost of 2.70 €/m^3 of treated effluent was estimated.

Martins et al. (2010e) verified that the use of the Fenton's process (pH 3, $[H_2O_2]$ = 88 mmol/L and $[Fe^{2+}]$ = 60 mmol/L) enhanced the further treatment of OMW by ozonation at the industrial scale. Moreover, through respirometric tests, it was concluded that the resulting effluent was biodegradable. Besides, the legal limits for discharge in the municipal wastewater treatment plant were accomplished. This means that further biological treatment can be applied to further polish the treated water.

Hodaifa et al. (2013), studied the effect of operating conditions such as pH, space–time, H_2O_2 and Fe(III) doses, as well as $[FeCl_3]/H_2O_2]$ ratio on the efficacy of Fenton's process in a continuous reactor at pilot scale for OMW treatment. With optimum conditions (pH 3, 3 h and $[FeCl_3]/[H_2O_2]$ between 0.026 and 0.058 w/w upon Fe(III) concentrations ranging from 0.35 to 0.40 g/L and ambient temperature) the Fenton´s process reached 97% of organic matter degradation and 99% of phenolic compounds removal. The obtained effluent can be used as irrigation water or discharged directly into the municipal wastewater system for further tertiary treatment.

II.1.7. Concluding remarks

Fenton’s process shows interesting features that make it industrially desirable whenever the traditional biological systems fail to accomplish the parameters imposed for wastewater treatment. This happens when the effluent to be treated presents low biodegradability or a strong seasonality which is the case of OMW. Fenton’s process is able to operate at room conditions of pressure and temperature and does not involve dangerous reactants nor sophisticated equipment. Several works have been reported regarding its application for the abatement of the pollutant in OMW. However, the fulfilment of the treated water standards for reuse may imply harsh operating conditions involving high loads of reactants. This may limit its application since the operating costs could be prohibitive. Nevertheless, Fenton’s process may be envisaged as a pre-treatment preceding a biologic system. In fact, usually the by-products formed during the chemical reaction tend to be more biologically amenable than the initial pollutants. Thus, the effluents’ biodegradability increases while its toxicity reduces, which enables further bioprocessing. Still, the major drawback associated with this process is related with the iron sludge produced at the end of the treatment that will require management since it constitutes a second environmental problem. Moreover, this traditional approach does not allow the catalyst recovery. In this ambit, the use of light to enhance the process can be an option since it allows the reduction of the amount of catalyst required. Moreover, the development of heterogeneous catalysts is an interesting alternative since their recovery and reuse would be easier. However, the major drawback is associated with their stability regarding the leaching of the metals. Recently the integration of Fenton’s process with ion-exchange resins showed promising results aiming homogeneous catalyst recovery and reuse.

Even if the drawbacks related with this technology are not fully overcome, its industrial interest is remarkable since some full-scale applications are already implemented. Namely in what regards the treatment of olive mill wastewaters, this technology (in homogeneous phase) is able to fulfil the legal parameters established for wastewater treatment in the regions where those plants are installed.

Moreover, the olive oil mill production is changing which is reflected in the wastes produced. Now two-phase systems are being preferred since are less water demanding. However, a large amount of solid wastes with high toxic character (Pinho et al., 2017) are produced. Besides, from this wet waste a high organic concentrated leachate is produced. In this context, Fenton’s process can be optimized to deal with these new challenges in what regards both liquid and solid contaminants (Quina et al., 2015).

II.2. Adavanced Oxidation Processes perspective regarding swine wastewater treatment

The advanced oxidation processes on the removal of contaminants from swine wastewater is now overviewed. This section is based in the publication: Domingues, E., Fernandes, E., Gomes, J., Martins, R.C. (2021) Advanced oxidation processes perspective regarding swine wastewater treatment (Review), Science of the Total Environment, 776, 145958.

II.2.1. Application of advanced oxidation processes for swine wastewater treatment

The exponential world population growth allied to the industrial and economic development of modern societies enhance meat demand worldwide (FAO, 2019). The climatic changes problematic also raises questions related with meat production impact (Nordgren, 2012). According to Nordgren (2012) the greenhouse gases (GHG) emission for cow beef production is about 12.14 kgCO_2eq./kg while for pork it reaches 4.45 kgCO_2eq./kg. Although pork meat production has a lower carbon footprint, its impact may not be neglected. Moreover, pork and poultry meat consumption is increasing worldwide. As an example, related to 2019, about 109 and 128 million tons were consumed (OECD, 2020). The highest worldwide pork production is in China, about 38.8 %, followed by the European Union with 24.5 % (USDA, 2020). This intensive pork production and current requirements in the European Union related with animal welfare are responsible by a high amount of swine wastewater (Sáez et al., 2017). This wastewater is characterized by high organic matter and nutrients (mainly nitrogen and phosphorous) (Table II.2.1), as well as several toxic compounds such as heavy metals, antibiotics and hormones (Zhang et al., 2016). This wastewater results from faeces, urine, wash water and animal feed waste (Zhang et al., 2019a). The swine wastes can be used as fertilizer or even for irrigation in some developed countries (Huang et al., 2017). However, the main part of this effluent is applied as fertilizer for agriculture fields and, due to the transportation cost, is typically used by farmers near the pork production facility (Malomo et al., 2018). Meanwhile, this proximity promotes the overload of lands which may be problematic due to the high concentration of nutrients (Joshi and Wang, 2018). In fact, the macronutrients load in the swine wastewater is related with a small assimilation by pigs, being excreted. Therefore, the continuous discharge of this waste in soils results in the contamination of lands which after leaching will contribute for ground and surface water eutrophication (Huang et al., 2017).

Table II.2.1. Typical characterization of swine wastewater.

Parameter	Value	References
pH	6.77-8.90	Garcia et al., 2020; Liang et al., 2021; Huang et al., 2019; Wu et al., 1999; Huang et al., 2020; João et al., 2020; Han et al., 2021
COD (mg/L)	910-19380	
TN (mg/L)	264-1450	
TP (mg/L)	18.4-918	
Turbidity (NTU)	360-4350	

Nowadays, swine wastewater is treated by different ways according to the installation dimension, the proximity of farmlands, geographic area and even the local legislation. The most common technologies are solid-liquid separation, aerobic and anaerobic lagoons, composting and anaerobic digestion (Santonja et al., 2017). Also, the scientific community is studying the treatment and reuse of the biomass produced during the swine wastewater treatment as a circular economy approach (Cheng et al., 2020a,b).

This exponential swine demand is leading to pork massive production in small spaces, such as confined animal feeding operations (CAFOs) (Radon et al., 2007). However, to enhance the pork production in small structures an increase on antibiotic (and other pharmaceuticals) consumption is required to face against diseases (Sarmah et al., 2006; D. Cheng et al., 2020a). Tretracyclines and sulfonamides are the main pharmaceutical groups used in this activity (Cheng et al., 2020a,b). Antibiotics and hormones are difficult to be absorbed and a part is excreted, reaching the surface and ground water through the waste disposal. This can be dangerous for aquatic species and human health (Cheng et al., 2018). In fact, the presence of antibiotics in the environment promotes the appearance of antibiotic resistant bacteria and genes (Michael et al., 2013; Rizzo et al., 2013). The traditional wastewater treatment plants seem to be not efficient to remove such contaminants due to their refractory character (Fiorentino et al., 2019). This way, these compounds are reaching the water courses at dangerous concentrations. Therefore, swine wastewater should be treated before reaching municipal wastewater treatment plants or water courses. On the other hand, the conventional wastewater treatment plants should be upgraded to be able to treat such refractory compounds. These two rhetorical sentences are the basis of the challenges for water recovery from swine wastewater reclamation since pork production is highly water consuming: to produce 1 kg of pork meat about 4.8 m^3 of water is needed (Hoekstra and Chapagain, 2008).

Advanced oxidation processes could be a suitable solution to remove refractory compounds from swine wastewater since the hydroxyl radicals can promote mineralization (Oller et al., 2011; Gomes et al., 2017). Among others, ozonation, Fenton’s process, photocatalysis, electrochemical oxidation, electrochemical coagulation and UV/hydrogen peroxide can be considered. These processes, besides the hydroxyl radical production, can also use ozone and hydrogen peroxide as well as other reactive compounds that can be helpful on the refractory compound’s conversion (Oller et al., 2011; Gomes et al., 2017; Garcia et al., 2020).

Considering this and the water scarcity, the increase on swines production must be the stimulus to improve the swine wastewater treatment. This improvement will allow wastewater reclamation without prejudice for the agriculture fields, namely soils, the aquatic species and human health. The aim of present paper is to give an overview about the advanced oxidation processes (AOPs) applied on the swine wastewater treatment and comparison with conventional treatment in terms of organic matter removal. The biological treatment selected for comparison was anaerobic digestion since it is a treatment widely used in the problem of swine wastewater. Regarding the AOPs, Fenton’s process, photo-Fenton, ozone, electrochemical processes and photocatalysis were considered. The application of these methods was also analyzed while combined with other technologies to enhance the swine wastewater treatment. Pharmaceutical compounds (such as antibiotics) removal efficiency was also analyzed by different treatment methodologies since it is a crucial factor for water recovery. Moreover, water recovery strategies were also considered. Finally, it was proposed and explored future perspectives for the swine wastewater highlight the benefits of AOPs for swine wastewater treatment.

II.2.2. Swine wastewater treatment

As previously referred, the methodologies currently applied for swine wastewater treatment cannot treat completely this kind of effluents. Among solid-liquid separation, aerobic and anaerobic lagoons, the best available technology seems to be the anaerobic digestion. This approach seems to be a suitable solution since related to the high biodegradability is inherent the biogas production which means that energetic integration may be possible. Moreover, the solid fraction (digestate) provided from this process can be recovered for soils application in agriculture field.

This effluent is highly charged by solids due to the straw, hay and animal feed waste presence. Therefore solid-liquid separation technologies allow a great reduction in the solid content (González-Fernández et al., 2008). From this separation results a solid fraction that can be used to produce compost while the liquid fraction is usually applied on-farm as fertilizer (Santonja et al., 2017). However, this methodology is inefficient for nutrients and dissolved organic matter removal.

The aerobic digestion can remove the biodegradable organic matter but needs a high amount of space to threat this complex wastewater since high hydraulic retention times are required.

Anaerobic digestion seems to be the most advantageous solution since can promote the biodegradable organic matter removal. Moreover, can reduce the number enteric pathogens and the emission of GHG since the biogas produced may be applied for electricity or heat generation (Khalil et al., 2019; Pramanik et al., 2019). On the other hand, the coupling of anaerobic digestion with solid-liquid separation may be advantageous. This way, the digestate (solid fraction coming from anaerobic digestion) may be sent to composting while the liquid fraction can be used for the farmland irrigation (Santonja et al., 2017). However, refractory compounds such as antibiotics, chelators (source of heavy metals) and hormones may persist after these processes. Therefore, the application of advanced oxidation processes will be required to remove such biorefractory compounds. Due to the high efficiency of anaerobic digestion (although the drawbacks mentioned), this process was selected as comparison to AOPs. Thus, the following section is devoted to this technology.

II.2.2.1. Anaerobic digestion

Anaerobic digestion is one of the most applied technologies to threat the raw swine wastewater due to the binomial benefit treatment costs and energy recovery (Khalil et al., 2019; Pfluger et al., 2019). In fact, the swine farm can be a source of gases with high environmental impact, such as methane, ammonia and nitrous oxide (Ramírez-Islas et al., 2020) that must be controlled. Anaerobic digestion leads to a controlled production of biogas that can be used for energy production and heat recovery without a decontrolled release of dangerous gases (Pfluger et al., 2019).

In anaerobic digestion, swine wastewater goes through different stages to produce biogas through the microorganism’s action (Pramanik et al., 2019). The steps are: Hydrolysis, where the complex organic substances are converted in simple molecules; Acidogenesis, the substances provided from previous stage are transformed in volatile fatty acids (VFAs); Acetogenesis, which consists in the transformation of VFAs in acetate, carbon dioxide and hydrogen. The final stage is the methanogenesis where the acetate, CO_2 and H_2 are converted into biogas (Pramanik et al., 2019). Typically, the biogas produced is composed mainly by methane (50-70%) and carbon dioxide (30-50%), and other compounds in very low amount (Paritosh et al., 2018). The production of biogas can be affected by different parameters such as temperature, VFAs concentration, C/N ratio, pH and presence of inhibitory compounds (Chen and Hashimote, 1996; Hattori, 2008). Moreover, as previously referred, the anaerobic digestion also produces a digestate that can be used as an organic fertilizer for agriculture purpose typically after further stabilization through composting.

Different types of reactors (Figure II.1.1.) can be used in this process such as sequencing-batch reactor (SBR) (Yang et al., 2016), sequencing-batch biofilm reactor (SBBR) (Hai et al., 2015), self-agitated batch reactor (Jiang et al., 2019), upflow anaerobic sludge blanket (UASB) (Zhao et al., 2016) membrane bioreactor (MB) (Padmasiri et al., 2007) and sequencing-batch membrane bioreactor (SMBR) (Han et al., 2018; Xu et al., 2019).

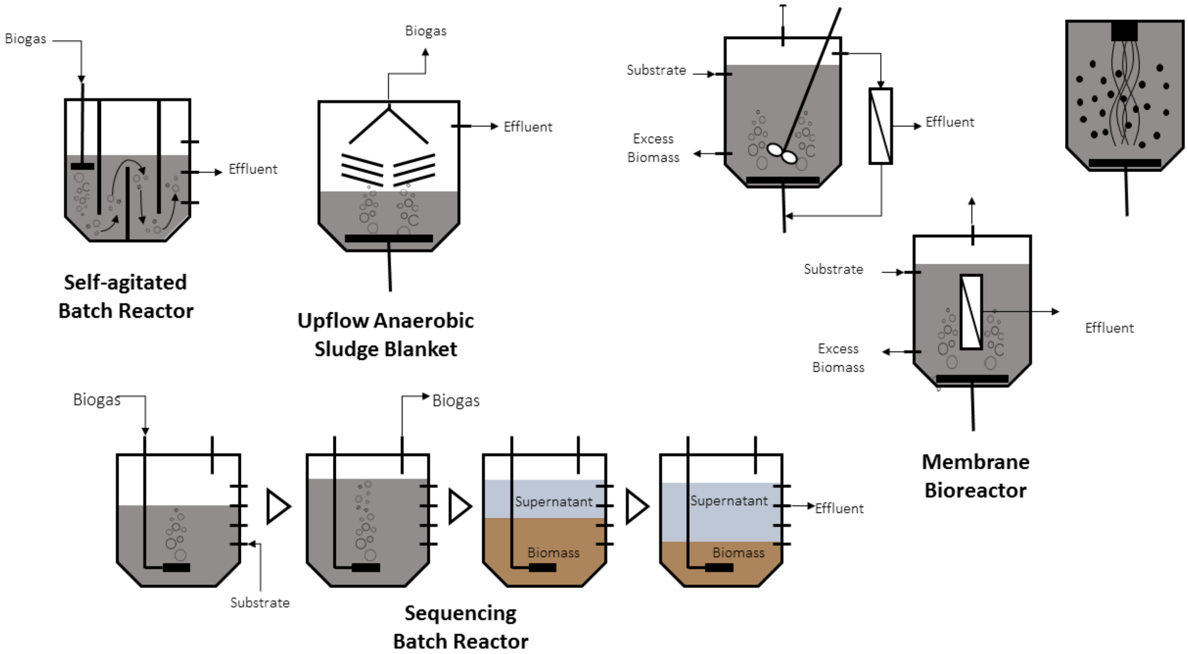


Figure II.2.1. Different types of reactors used in anaerobic digestion.

The efficiency of these processes is dependent upon composition of swine wastewater, since ammonia and VFAs concentration, the fraction of C/N, as well as the organic matter concentration can be different. The increase in the organic load rate (OLR) in a SBR can promote a decrease in the COD removal efficiency (Yang et al., 2016). Yang et al. (2016) using a SBR with hydraulic retention time (HRT) of 10 days for a OLR of 4.5 kg VS/m^3.d achieved a COD removal efficiency of about 80% at 20 ºC. On the other hand, Schievano et al. (2016) using also a SBR for swine wastewater treatment for an OLR of 7.8 kg COD/m^3.d and 41 days of HRT just removed 49% of COD. In fact, the higher OLR can represent a significant reduction on the COD removal efficiency.

Yang et al. (2019) used a self-agitated anaerobic batch reactor to treat swine wastewater and for 10 days of HRT achieved a total COD removal of 66%. Zhao et al. (2016) using a UASB treatment for a HRT of 2 days and OLR of 0.83 kg COD/m^3.d achieved 54.8% of removal. Moreover, the combination of UASB and upflow anaerobic sludge bed-filter (UBF) allows improving the efficiency obtained for OLR 2.63 kg COD/m^3.d leading to about 83.6% of COD removal (Zhao et al., 2016). Moreover, Yang et al. (2019) made the comparison between three different reactors for anaerobic treatment of swine wastewater, an anaerobic sequencing batch reactor (ASBR), an upflow anaerobic sludge bed-filter (UABF) and an upflow solid reactor (USR). For example, USR presented the worst methane yield production performance (Yang et al., 2019). Regarding to COD removal, the ASBR and UABF achieved about 90 % for OLR 2 kg TS/m^3.d while for USR the efficiency decreased to 85 % at the same conditions (Yang et al., 2019). According to these results the impact of anaerobic reactor type in the COD removal is not so significant compared to the OLR since the increase to 10 kg TS/m^3.d promoted the decrease in the COD removal efficiency, from 90% to 73% (Yang et al., 2019).

Besides the widely application of anaerobic digestion for swine wastewater treatment the removal efficiency of organic matter is low since the organic loading rates must be small so that the efficiency is high (Sakar et al., 2009). Thus, to maximize the anaerobic digestion efficiency, biocatalytic activity can be improved by employing granular sludge provided from other wastewater treatment industries (Wang et al., 2018; Lu et al., 2019; Zeng et al., 2019). Zeng et al. (2019) studied the effect of exogeneous granular sludge (EGS) from pulping wastewater treatment to enhance anaerobic digestion of swine wastewater. The EGS system promoted in 10 days an increase on COD removal efficiency from 37 to 85 % comparing to the indigenous anaerobic sludge (IAS) system (Zeng et al., 2019). Moreover, to achieve the same COD removal (85%) the IAS system takes about 20 days more (Zeng et al., 2019). This difference is related with the different composition of microbial community, since the EGS systems can have more syntrophic bacteria and methanogens (Zeng et al., 2019). In fact, De Vrieze et al. (2015) verified that, besides the high VFA and ammonia concentration, the Methanobacteriales can have significant impact on the biogas production yield. Moreover, typically such processes can only remove less than 90 % COD and have difficulties to remove the nitrogen and phosphorous (Abdel-Raouf et al., 2012; Cheng et al., 2020a,b). In fact, COD removal is not completely achieved or at least until legal levels for the effluent discharge in water courses. On the other hand, for these processes it can be also evaluated the performance regarding to methane yield as function of COD amount (Heidrich et al., 2011). However, in this review article this parameter will not be evaluated since the advanced oxidations processes cannot produce methane from organic matter degradation. Table II.2.2. summarizes the studies referred to in this section.

Table II.2.2. A brief summary of research studies in which anerobic digestion process was used for treating livestock and swine wastewater

Effluent	Reactor	Optimal conditions	Optimal COD Removal	Reference
Swine wastewater	SBR	HRT 10 days; OLR 4.5 kg VS/m^3.d; 20 ºC	80 %	Yang et al. 2016
Swine wastewater	SBR	OLR 7.8 kg COD/m^3.d; HRT 41 days	49 %	Schievano et al. 2016
Swine wastewater	Self-agitated anaerobic batch reactor	HRT 10 days	66 %	Yang et al. 2019
Swine wastewater	UASB	HRT 2 days; OLR 0.83 kg COD/m^3.d	54.8 %	Zhao et al. 2016
Swine wastewater	EGS system	HRT 10 days;	85 %	Zeng et al. 2019
Swine wastewater	IAS	HRT 30 days	85 %	Zeng et al. 2019

Besides this, it is important to consider for these technologies the pharmaceutical compounds removal capacity due to their problematic for human health due to (for example) the antibiotic-resistant bacteria and genes (Ben et al., 2009; Pan et al., 2011). This will be further discussed in the following sections where advanced oxidation processes are considered.

II.2.2.2. Fenton´s process

Fenton’s oxidation is a commonly used advanced oxidation process mostly applied for the removal of organic compounds from liquid effluents (Pera-Titus et al., 2004; Domingues et al., 2018). This is a cost-effective method, easy to apply and effective for improving the biodegradability and reducing the toxicity of bio-refractory effluents, such as the agro-industrial wastewaters (Martins et al., 2010a).

The oxidation mechanism in the Fenton’s process consists on the formation of hydroxyl radicals in an acid medium from the decomposition of hydrogen peroxide by the action of an iron-rich catalyst. This catalyst can be homogeneous or heterogeneous depending on its state in the reactional medium (Domingues et al., 2018; Jain et al., 2018). This can represent a significant impact on the yield of Fenton’s process over to the organic matter degradation in the real wastewaters.

The reactive hydroxyl radical unselectively reacts with organic substances, which are based on the carbon chains or rings and contain hydrogen, oxygen, nitrogen, or other elements.

The reaction mechanism is as follows (Barb et al., 1951; Kang et al., 2000; Xu et al., 2004) (Eq. II.6-9):

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {\cdot}OH$ II.6

$RH + {\cdot}OH \rightarrow R^{\cdot} + H_2O$ II.7

$R^{\cdot} + Fe^{3+} \rightarrow \text{product} + Fe^{2+}$ II.8

$Fe^{2+} + {\cdot}OH \rightarrow Fe^{3+} + OH^{-}$ II.9

Fenton's process is well-described in the literature, but most of the papers reported the use of synthetic wastewater. Nevertheless, the industrial effluents are constituted by complex matrices, which may contribute to a decrease in process efficiency (Wang et al., 2016). According, to previous studies with real effluents the homogeneous Fenton's process seems better than the heterogeneous process (Martins and Quinta-Ferreira, 2011b). On the other hand, Martins and Quinta-Ferreira (2011a) concluded for a synthetic olive mill wastewater that the Fenton´s process through the heterogeneous process presents similar results to the homogeneous system regarding COD removal. This may indicate that the limiting step is the chemical reaction instead diffusional mass transference into catalyst active sites. However, the presence of inhibitory species may be controlled in synthetic effluents, while some radical scavenging moieties are surely present in real wastewater. Martins and Quinta-Ferreira, (2011b) verified an efficiency decrease comparing homogeneous and heterogeneous Fenton's process for the treatment of real olive mill wastewaters. In fact, COD removal decreases from to 70% to 20%, respectively. This efficiency reduction can be related to the adsorption of inhibitory agents onto the catalyst surface, such as organic matter, heavy metals, that will block the active sites.

For the treatment of wastewaters derived from livestock farms, including cattle, swine and poultry farms, the authors Park et al. (2006) resorted to Fenton and Photo-Fenton processes. They studied COD, color, and fecal coliform removal efficiencies. These authors verified that under the optimal conditions for Fenton and photo-Fenton processes (pH of 4 and 5, an Fe^{2+} dose of 0.066 M and 0.01 M, a concentration of hydrogen peroxide of 0.2 M and 0.1 M, a molar ratio (Fe^{2+}/H_2O_2) of 0.33 and 0.1 and the reaction time of 60 and 80 min, respectively) were approximately 70–79%, 70–85% and 96.0–99.4%, respectively. Photo-Fenton process was associated to lower iron sludge production compared to conventional Fenton process. Moreover, it shows a lower color removal efficiency, but it has a higher COD and fecal coliform removal.

A high-strength livestock wastewater (with an initial CODcr of 5000–5700 mg/L, total solids (TS) 5126–5900 mg/L and color 2.1 AU (measured at 287 nm)) was treated by Fenton´s process (Lee and Shoda, 2008). Under optimal conditions (H_2O_2 dose 1.05 of the initial CODcr concentration, Fe^{2+} dose of ca. 4700 mg/L, initial pH 3.5–4, 30 min of reaction time and the H_2O_2/Fe^{2+} molar ratio of 2) the authors achieved about 80 and 95% of CODcr and color removal, respectively. They also proved that a single addition of Fenton's reagents is as efficient as adding it in aliquots.

Riaño et al. (2014) evaluated the Fenton’s process applied to a biologically pretreated swine manure in terms of color and organic matter removal. An initial effluent with a 0.8 AU (measured at 475 nm) of color and 769 mg/L of tCOD was subjected to Fenton’s process (with a dosage of 100 mg/L of Fe^{2+} and 800 mg/L of H_2O_2, an initial pH 3 during 30 min), resulted in about 78% tCOD and 96% color reductions. The iron source is iron sulphate which guarantee a homogeneous Fenton´s process. The authors compared the molecular weight distribution of the biologically pre-treated swine manure at pH 3 with the one after Fenton’s process for different hydrogen peroxide dosages. It was verified that the reduction of colorants increased when H_2O_2 dose raised from 200 to 800 mg/L. Fenton´s process simple operation and design was attested and, when compared to other AOPs, such as ozonation, also has a lower operational cost as a posttreatment method. Therefore, besides the COD removal efficiency one of the parameters to select one or other AOP process, can be the operational cost process.

A brief summary of the application of the Fenton process in the treatment of wastewater swine can be found in Table II.2.3.

Table II.2.3. A brief summary of research studies in which Fenton process was used for treating livestock and swine wastewater.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
Biologically pretreated swine manure (0.8 AU at 475 nm) of color and 769 mg/L of TCOD)	Fenton	$[Fe^{2+}]$ = 100 mg/L $[H_2O_2]$ = 800 mg/L pH=3 t = 30 min	78% tCOD and 96% color reductions	Riaño et al. 2014
Livestock wastewater (CODcr of 5000–5700 mg/L, TS 5126–5900 mg/L and color 2.1 AU (at 287 nm))	Fenton	H_2O_2 dose 1.05 of the initial COD_{cr} concentration Fe^{2+} dose of ca. 4700 mg/L pH = 3.5–4 t = 30 min H_2O_2/Fe^{2+} molar ratio of 2	80 of COD_{cr} and 95% of color removal	Lee and Shoda, 2008
Livestock farms, including cattle, swine and poultry farms	Fenton and Photo-Fenton	pH = 4 and 5 $[Fe^{2+}]$ = 0.066 and 0.01 M $[H_2O_2]$ = 0.2 M and 0.1 M Fe^{2+}/H_2O_2 = 0.33 and 0.1 t= 60 and 80 min,	70–79, 70–85 and 96.0–99.4% of COD, color, and fecal coliform removal, respectively	Park et al. 2006

Fenton process performed successfully in removing color and organic matter from real swine wastewater. However, other parameters must be considered to evaluate the possibility of this treated wastewater to be used for irrigation of agriculture soils in a water recovery approach. In fact, the use of toxicity indicators as the level of ecotoxicity over the vegetables and aquatic species can be beneficial for irrigation potential evaluation. Moreover, one of the drawbacks of the Fenton’s process was not addressed in these works, the iron sludge production (Domingues et al., 2019). Therefore, one alternative to mitigate this iron sludge formation is the use of heterogeneous Fenton’s process (Martins and Quinta-Ferreira, 2011b). Despite the possibility of efficiency reduction this must be weighted according to the quality of treatment and adjacent costs. On this way, further research should be addressed to reduce the operational costs that allow presenting Fenton’s process as a cost-competitive technology. Alternatively, for this heterogeneous Fenton´s process the iron can be doped or supported into a semiconductor catalyst (such as titanium dioxide or zinc oxide) so that photo-Fenton´s process can be applied (Shen et al., 2008; Park et al., 2019). Hydroxyl radical’s production can also be enhanced in homogeneous process by using UV radiation (Park et al., 2006). Meanwhile, the color of real swine wastewater should be at least slightly reduced to allow the penetration of sunlight radiation, UV or visible radiation to activate the photocatalytic process. The use of light and/or heterogeneous catalysts may give an important push to overcome Fenton’s process drawback related to iron sludge production.

II.2.2.3. Ozonation process

The strong odor of livestock wastewater is one of the main problems involved in this kind of effluent, causing a great distress to the population of the surrounding areas and representing a human and environmental health hazard (Donham, 2010; Bildsoe et al., 2012). Different compounds can be found in the air emissions of swine wastewater and are responsible for these detrimental effects, such as phenols, indoles, methane (CH_4), ammonia (NH_3) and hydrogen sulfide (H_2S) (Donham, 2010). Ozone is a powerful oxidant capable to degrade refractory compounds and can act in direct pathway through molecular ozone or an indirect pathway due to the production of hydroxyl radicals through ozone decomposition (Kasprzyk-Hordern et al., 2003; Gunten 2003). pH can significantly affect the pathway action of ozone since at pH lower than 7 prevails the direct action and at pH higher than 7 the hydroxyl radical is the predominant species. On this way, it is important to consider the pH in the swine wastewater treatment, since this kind of effluents has the typical pH of 7 (Zhang et al., 2016; H.H. Cheng et al., 2020a). Moreover, ozone presents potential to treat the swine wastewater regarding to COD and color removal as well as gases emission reduction.

Bildsoe et al. (2012) investigated the use of low dose ozonation (< 200 mg O_3/L) to remove malodorous substances from pig slurry. An ozone dose of only 20 mg/L was able to reduce in 96% H_2S emission rate compared to the control (simple mixing). Although, the NH_3 emissions increased with an increasing ozone dose, mainly above 20 mg/L, which could be associated with an increase in the surface pH and a consequent change in the NH_3 mass transfer and dynamic equilibrium with the pH gradient. The volatile fat acids concentration was not affected, and ozone concentrations of 80 and 200 mg/L achieved up to 10% and 42% of p-cresol and indole reduction.

Wu et al. (1999, 2002) conducted a sequence of tests involving the application of ozonation to eliminate malodourous metabolites in swine manure. In a first study, in a pilot-scale ozonation system, 0.25-1.0 gO_3/L were applied to fresh and stored manure (1-3 weeks). The concentrations of phenol, p-cresol, p-ethylphenol and skatole were assessed and an odor panel was used to evaluate the odor intensity. The concentrations of ammonia and the evaluated metabolites, except for skatole, increased during storage as well as the determined bad odor. An ozone dose of 0.5 g/L was significantly effective in reducing the manure malodor, but a concentration of 1.0 gO_3/L was necessary to remove the most persistent metabolites. The addition of hydrogen peroxide was also investigated but did not provide further benefit. In the different ozone applications, the addition of hydrogen peroxide can enhance the wastewater treatment since it can produce more hydroxyl radical species (Kasprzyk-Hordern et al.,2003). However, the presence of high organic matter and inorganic species can inhibit the action of hydrogen peroxide (Zwiener and Frimmel, 2000).

In its following study, Wu et al. (2002) also assessed the oxidation kinetics of phenolic (phenol, p-cresol, p-ethylphenol) and indolic (indole and skatole) compounds during ozonation in both real and synthetic swine wastewater. An ozone dose of 0.5 g/L was enough to completely remove the compounds from the synthetic effluent, while, due to a higher COD and ozone scavengers, 1.5 g/L of ozone were necessary to achieve the same result in the real effluent. With an increasing pH, the reaction rates also increased, which can be associated to the competition kinetics with ozone as well as the compounds ionic state, for example, the phenolate ion reaction rate constant towards ozone is more than 106 times higher than phenol.

Consistent characteristics of swine and general livestock wastewaters are the relative high organic load and nutrients concentration, with ranges of chemical oxygen demands (COD) of 3-15 g/L, ammonia concentrations of 0.4-1.4 g/L and total phosphorous of 0.10-0.25 g/L (Cheng et al., 2020a). These facts could result in a high energy consumption in the treatment of these wastewaters by AOPs such as ozonation. Thus, commonly, these technologies are combined with other techniques, as pre- or post-treatment, enhancing the global efficiency of the process. Table II.2.4. summarizes the overview on scientific works dealing with ozonation process for treating the swine wastewater.

Table II.2.4. A brief summary of research studies in which Ozonation process was used for treating livestock and swine wastewater.

Effluent	**Process**	**Optimal conditions**	**Results**	**Reference**
Pig slurry	Ozonation	20 mgO_3/L	Reduce in 96% the H_2S emission rate	Bildsoe et al. 2012
Synthetic swine wastewater	Ozonation	0.5 gO_3/L	Completely remove phenolic (phenol, p-cresol, p-ethylphenol) and indolic (indole and skatole)	Wu et al. 2002
Swine manure	Ozonation	1.5 gO_3/L	Completely remove phenolic (phenol, p-cresol, p-ethylphenol) and indolic (indole and skatole)	Wu et al. 2002

Ozone action seems to be a suitable for swine wastewater treatment specially regarding odor removal. Moreover, besides the conditions previous referred, the ozone action can be improved by the presence of UV radiation (Silva et al., 2019), sunlight radiation (Chávez et al., 2016), or even with catalysts, that can be heterogeneous and/or homogeneous (Kasprzyk-Hordern et al., 2003). On this way, the presence of this external approaches can also improve the decomposition of molecular ozone into hydroxyl radical or even other reactive oxidative species, such as ozonide and/or hydroperoxyl radical (Mehrjouei et al., 2015). The presence of these adjuvants with ozone can enhance the degradation of organic matter, but the real wastewaters can reduce significantly the capacity of ozonation due to the inorganic and organic species that can act as scavengers (Martins and Quinta-Ferreira, 2011b). Moreover, for the radiation coupling, the process can be improved by the first action of ozone alone to remove the color and then the radiation can be added to improve the COD removal of swine wastewater (Riaño et al., 2014). The technologies can be suitable applied if it is possible to take advantages of all parts involved in the integrated treatment process.

II.2.2.4. Photocatalysis

The use of photocatalytic systems for the treatment of a variety of contaminated air and water streams has been vastly and successfully explored (Kang et al., 2018; Basavarajappa et al., 2019; Chen et al., 2020; Fernandes et al., 2020; Zhao et al., 2020). Besides the common AOPs benefits, such as an elevated production of oxidative radicals the affinity with different pollutants allows it to achieve a high mineralization level. Different and low-cost materials can be applied, assisted with a radiation source, which can be natural or artificial, to activate the photocatalyst and promote the electronic excitation and consequent radicals formation. Moreover, heterogenous photocatalysis is one of the most explored routes, employing solid catalyst that can be easily removed post reaction and reutilized. The catalyst in these processes needs to be a semiconductor to allow the photogeneration of electron and holes to produce indirectly the hydroxyl radical and other reactive oxidative species (Pelaez et al., 2012).

A polymeric carbon nitride framework incorporated with copper was applied for the photocatalytic degradation under visible light of chlortetracycline hydrochloride (CTC-HCl), a very common antibiotic used in livestock production (Wang et al., 2020). The influence of the water matrix was studied, being prepared solutions of 20 mg/L CTC-HCl in deionized, river and tap water, and in a swine wastewater (SW). The degradation efficiency in SW was considerably lower than at the remaining matrices, 33% compared to 46%, 68% and 90% in tap, river and deionized water, respectively. The main factor pointed out as the cause for the lower removal was the presence of a higher concentration of NO_x-N and NH_3-N. These compounds present scavenging effect on hydroxyl radicals. The respective catalytic system was also able to remove 21% of the initial TOC present in the SW.

TiO_2 is the most used photocatalyst due to its lower cost, great chemical and physical stability and a high photoactivity (Salimi et al., 2017). Thus, a high number of photocatalytic studies focus on the use of different forms of TiO_2. Garcia et al. (2020) applied powdered Aeroxide® TiO_2 for the treatment of SW. Regarding COD removal three factors were optimized: catalyst dosage, wastewater concentration and irradiation time. The irradiation source used was a mercury lamp emitting in the UV and visible spectrum. The optimal conditions stipulated were a TiO_2 dose of 1.16 g/L, 1.68% of SW concentration, which had an initial COD of 13.11 g/L, and an irradiation time of 9.2 h, achieving 91.7% COD removal. The influence of the parameters over the photocatalytic COD removal efficiency were analyzed by fitting a second-order polynomial model, being most influential the SW concentration and the quadratic effect of SW concentration and irradiation time. The obtained removal was indeed very high, but it is important to evidence the high dilution of the initial effluent and irradiation time, which are factors that crucially influence the process overall cost and thus the further application of these configuration at larger scale.

Another method used in the photocatalytic treatment of swine effluents is the appliance of TiO_2-based paints and coatings for the degradation of pollutants present in the gas streams. As livestock effluents are associated with a high production of volatile organic compounds (VOCs), greenhouse gases (i.e. CH_4, N_2O, CO_2), H_2S and NH_3, which pose a strong odor nuisance and a risk to environmental and human health, the treatment of its gaseous emission are crucial.

Using a flow-through reactor with a TiO_2-based coating (~10.8 mL/m^2) and equipped with black UV lights, Maurer et al. (2019) studied the treatment at pilot-scale of the exhaust air stream of a swine barn. With a residence time of 47.2 s, the treatment resulted mainly in the degradation of 22% of p-cresol, 8% of N_2O and a total reduction of the odor of 16%. In their previous study (Zhu et al., 2017), the treatment of a synthetic effluent containing 6 different VOCs (p-cresol, Guaiacol, Butyric acid, DMTS, DEDS, DMDS), achieved similar reductions of p-cresol, but regarding the other contaminants no significant removals were found in the pilot-scale study. The lower treatment time reduces the process cost and increases its feasibility, but the influence of multiple factors over the treatment efficiency with the increasing of its applicated scale needs to be further analyzed.

Another advantage of the photocatalytic paints for air streams treatment is that they can be applied over the already existing systems or facilities, not needing necessarily many additional equipment. Costa et al., (2012) applied a TiO_2-based paint over the inside walls of a swine weaning unit, at an amount of 70 g/m^2, equipped also with sunlight simulating lamps. The respective unit was compared with an equivalent facility, with identical ventilation systems, being recorded the variations of temperature and humidity, ventilation rate, key compounds concentration and the animal's productivity performance. Over 48 h, no significant differences were found for the environmental and ventilation conditions between both units, but the one containing the photocatalytic paint presented 27% and 16% lower emission of, respectively, CH_4 and PM_{10} (particulate matter with diameter lower than 10 µm). Moreover, possibly due to the better air quality, in the treated unit, the piglets feed conversion ratio, which is the ratio between food consumed and weight gain, was 12% higher. Thus, the treatment of gaseous emissions resulting from livestock farms not only reduces the production of GHGs and other contaminants but can also improves its productivity. Table II.2.5. summarizes the main photocatalysis studies for the treatment of swine wastewater found in literature.

Table II.2.5. A brief summary of research studies in which photocatalysis process was used for treating livestock and swine wastewater.

Effluent	Process	Optimal conditions	Results	Reference
20 mg/L CTC-HCl in deionized, river, tap water, and in a swine wastewater	Photocatalysis: polymeric carbon nitride framework incorporated with copper	Visible light	Degradation of 33%, 46%, 68% and 90% in SW, tap, river and deionized water, respectively; 21% of the initial TOC in the SW	Wang et al., 2020
Swine wastewater	TiO_2 dose of 1.16 g/L 1.68 % of SW concentration which had an initial COD of 13.11 g/L Irradiation time of 9.2 h	Mercury lamp: UV and visible spectrum	91.7% COD removal	Garcia et al., 2020
Exhaust air stream of a swine barn	Flow-through reactor with a TiO2-based coating (~10.8 mL/m^2) and equipped with black UV lights	Residence time of 47.2 s	Degradation of 22% of p-cresol, 8 % of N_2O and a total reduction of the odor of 16%	Maurer et al., 2019
Swine unit air	TiO_2-based paint over the inside walls of a swine weaning unit	70 g/m^2 with sunlight simulating lamps	27% and 16% lower emission of, respectively, CH_4 and PM_{10}; the piglets feed conversion ratio was 12% higher	Costa et al., 2012

Considering the results, it is possible to antecipate the potential of this technology for the swine wastewater treatment. On the other hand, this treatment can be enhanced if a pre-treatment was used for the color removal allowing a more efficient light penetration to activate the photocatalyst. Besides, photocatalysis can be incorporated at the pig farms in order to improve the air quality which revealed to be important for piglet’s growth.

II.2.2.5. Electrochemical oxidation

Electrochemical advanced oxidation processes (EAOPs) can be considered a relevant treatment for the removal of organic and nitrogen-containing compounds in swine wastewater. Most of the literature refers electrochemical oxidation in the swine wastewater treatment with two purposes: ammonium oxidation by active chlorine species, and organic oxidation via electrogenerated or active chlorine species (Garcia et al., 2020). Chloramines are emerging as alternative to chlorine as disinfection agents, since chloramines reduce significantly the formation of organochlorinated by-products. Inorganic chloramines result from the reaction of active chlorine species with ammonia, which may give rise to monochloramines, dichloramines and trichloramines (Crittenden et al., 2012). Garcia-Seguro et al. (2009) studied different sources to generate chloramines, such as ammonium chloride, urea and synthetic urine matrix, under different conditions ammonia to chloride ratio and pH. On the other hand, electrochemical processes show efficiency in removing nitrates, which are present in swine wastewater. The main disadvantage is that the platinoid materials (PGEs), although they are excellent electrocatalysts for nitrate reduction, are expensive and endangered elements due to their high cost and limited availability as resources in our planet. Recent studies have been conducted with the aim of overcoming these difficulties and have shown that Earth abundant elements, such as carbon and tin, could be a low-cost and sustainable bet for wastewater disposal (Fajardo et al., 2021).

The pollutants can be degraded by both direct and mediated electrochemical oxidation onto the anode surface or in a bulk solution, in association with the electrochemical generation of highly reactive hydroxyl radical $^{\cdot}$OH or other oxidants depending on the electrolytes added in the treatment (Sirés et al. 2014; Moreira et al. 2017).

The type of electrode material is an essential parameter in the efficiency of electrochemical oxidation. Bejan et al. (2005) demonstrated that electrolytic oxidation can ameliorate the odor of the swine wastewater. They compared the performance of various types of anodes in terms of odor and TOC removal. The best results were obtained with an anode composed of tin dioxide coated on a base of titanium and boron-doped diamond (BDD), which has exceptional stability to oxidize and reduce electrolytic conditions. Later in another study, Bejan et al. (2008) found that hydroxyl radical forming anodes (BDD and Ebonex® (titanium oxide ceramic electrodes)) were the most effective, but these are new materials and are still unavailable on the market for industrial application. Evaluating the results of the number of total and anaerobic bacteria after 2 h with 200 mA treatment, the disinfection performance in terms of anode material confirms the oxidative superiority of BDD compared to Ebonex$^{®}$, graphite and RuO_2, respectively (Bejan et al., 2008).

Huang et al. (2019) analyzed the effect of various operating parameters on the electrochemical treatment of swine wastewater, namely anode material, cathode distance, cathode area, and wastewater volume. The performance in terms of COD removal of BDD-I, BDD-II, graphite/PbO_2, Ti/PbO_2, and DSA$^{®}$ was in the following order: BDD-I ≈ BDD-II > graphite/PbO_2 ≈ Ti/PbO_2 > DSA® (100%, 100%, 97%, 97%, and 90% at 150, 180, 240, 240, and 240 min, respectively). DSA® anodes incorporate in their structure nanostructured metal oxide coatings that allow enabling electrochemical generation of chlorine. BDD anode demonstrated similar performance as a commercial anode for the electrochemical COD and NH_3-N removal COD from swine wastewater. Other anode materials were tested, IrO_2/Ta_2O_5 and PbO_2 exhibited the lowest performance in terms of COD and NH_3-N removal, except PbO_2 for NH_3-N removal. NH_3-N removal increased with the increasing distance between electrodes and the increased cathode area. In terms of energy required, the lowest specific energy consumption (32 kWh/kgCOD) was obtained by increasing the wastewater volume and lowering the current density.

In terms of current densities, the results presented above are corroborated in the work of Cho et al. (2010) and Bejan et al. (2005). Both found that the increase in current density favors the removal of NH_3-N and COD in the first case study and the removal of TOC in the second work.

Huang et al. (2018) studied the effects of chloride addition, electrolyte (NaCl vs. Na_2SO_4), anode material (boron-doped diamond (BDD) vs. PbO_2), current density (0.10–0.50 A/cm^2), and anode area (2–6 cm^2) on the electrochemical abatements of organic pollutants (in terms of TOC or COD) and ammonia nitrogen in swine wastewater. The results showed that TOC degradation was higher in the absence of chloride. However, higher NH_3-N electrochemical abatement was observed in the presence of chloride. Using Na_2SO_4 also resulted in better TOC degradation along with worse NH_3-N removal. NH_3-N removal efficiencies were similar for BDD and PbO_2 anodes although the former exhibited better TOC degradation than the latter. In the presence of chloride, it was not possible to detect nitrite while in the presence of Na_2SO_4, or in the presence of chloride on PbO_2 at 0.25 A/cm^2 and on BDD at 0.50 A/cm^2, small amounts of nitrite were detected. The COD and NH_3-N removal pseudo-first-order rate constants ranged from 4.57×10^{-4} – 1.35×10^{-3} and 1.91×10^{-4} – 1.37×10^{-3} s^{-1}, respectively; the general current efficiency (GCE) and the specific energy consumption (ESP) were 9% – 32% and 4 – 11 kWh/kgCOD, respectively, on BDD at 25 ^oC and 0.10 – 0.50 A/cm^2.

The effect of NaCl addition was also studied by Cho et al. (2010) and Lei and Maekawa (2007) and they proved that the addition of NaCl enhances the removal of pollutants in the swine wastewater. Cho et al (2010) reported that under 0.05% (8.56 mM) NaCl, the optimal concentration, the average removal efficiencies of NH_4-N, soluble nitrogen, PO_4-P, sTOC, and color were 99%, 94%, 59%, 64%, and 93%, respectively. However, in the case of PO_4-P removal, the proportionality is not verified until the referred optimum concentration. Lei and Maekawa (2007) verified that ammonia could be completely removed in about 5 h with the addition of 1% NaCl dosage. However, there was no decrease in TOC which indicates that mineralization is not achieved by electrogenerated hypochlorous acid.

Regarding pH, Wang et al. (2019) used plant ash to adjust the pH in the method of corrosion magnesium metal and verified that increasing pH can effectively remove the phosphate from the swine wastewater and recovery it by struvite precipitation. Diaz and Botte (2012) reported that with alkaline pH the ammonia conversion was more efficient. pH strongly influences the efficiency of the electrochemical processes since it rules the active chlorine speciation (Garcia-Segura et al., 2019). In Table II.2.6. some studies of electrochemical oxidation are presented for the treatment of the swine wastewater.

Table II.2.6. A brief summary of research studies in which electrochemical oxidation process was used for treating livestock and swine wastewater.

Effluent	Process	Optimal conditions	Results	Reference
SW	Electrochemical oxidation	BDD anode, IrO_2/Ta_2O_5 and PbO_2	BDD-I ≈ BDD-II > graphite/PbO_2 ≈ Ti/PbO_2 > DSA® (100%, 100%, 97%, 97%, and 90% at 150, 180, 240, 240, and 240 min, respectively for COD removal; NH_3-N removal increased, increasing distance between electrodes and the increased cathode area	Huang et al. 2019
SW	Electrochemical oxidation	NaCl: under 0.05% (8.56 mM)	Removal of NH_4-N, soluble nitrogen, PO_4-P, sTOC, and color were 99%, 94%, 59%, 64%, and 93%, respectively	Cho et al. 2010
SW	Electrochemical oxidation	5 h with 1% NaCl	Ammonia is completely removed; there was no decrease in TOC	Lei and Maekawa 2007
SW	Electrochemical oxidation	Plant ash to adjust the pH	Increasing pH can effectively remove the phosphate and recover the phosphate in the form of struvite precipitation	Wang et al. 2019
SW	Electrochemical oxidation	Alkaline pH	Ammonia conversion was more efficient	Diaz and Botte 2012

The electrochemical oxidation can be a suitable solution for the nitrogen removal while for the remaining organic matter seems not so good alternative. Moreover, the materials (anode and cathode), used for these technologies can be a source of high economic investment due to the costs of acquisition. On the other hand, the usage of NaCl as electrolyte in real swine wastewater can be a source of organochloride compounds due to the presence of residual chloride.

II.2.2.6. Electrocoagulation oxidation

Typically, swine manure (feaces and urine) as excreted has a total of 10% solids. However, there are other types of water consumption in animal housing cleaning and operation, as well as manure decomposition. At the end the solid content decreases to a value between 1 and 5% (Ndegwa et al., 2001). Usually, swine wastewater is stored more than a half year in the barn before land application (Zhan et al., 2001). During the storage most of the large particles precipitate but an high number of fine particles, or colloids, remain in the liquid swine manure, 70–80% of the solids in raw pig slurry are smaller than 50 μm, while 50% of the total particles was associated to particles between 0.45 and 10 μm (Masse et al., 2005). This type of particles, due to their electrostatic force, repel each other, that is, not allowing them to stick together, thus making their separation difficult (Zhang and Lorimor, 2000). The mechanisms of chemical coagulation is based on the addition of chemicals to coagulate or flocculate particles, namely iron chloride, aluminum sulfate and aluminum chloride.. The hydroxylation compounds of iron or aluminum ions are very removal efficient, about 98%, but the dose of iron and aluminum ions also adds large amount of cations, which leads to the increase of sludge produced and causes more problems on sludge handling (Ebeling et al., 2003; Fernandes et al, 2012). Yielding results similar to chemical coagulation, electrocoagulation solves the problem using a direct current source between electrodes to promote the removal of pollutants via coagulation. In this case, coagulant is generated in situ and a lower amount of chemicals are required. During electrocoagulation can occur the formation of heavy or lighter particles. In the case of heavy particles, they will sediment, while in the case of light particles they will float, thus occurring electroflotation aided by the bubble gases formed in the process.

The electrocoagulation process essentially consists of three steps: (a) electrochemical reactions at the electrode surface and formation of coagulating species (electrochemistry); (b) destabilization of pollutants (e.g. colloids, emulsions, suspensions), aggregation of destabilized phases and flocculation (coagulation); and (c) removal of flocs by flotation and sedimentation (flotation) (Thirugnanasambandham, et al., 2015; Moussa et al, 2017). This process also has disadvantages such as the high operation cost due to electrical energy consumption and electrode replacement; a minimum conductivity of the wastewater is required; and wastewater pretreatment steps (pH adjustment, equalization, etc.) may it also be needed (Mollah et al., 2004, Kabdaşlı, et al., 2012).

Mores et al. (2016a) evaluated the effects of Al and Fe electrodes as anode and cathode for electrocoagulation. The particles removal efficiency was 92.9% and 96.3% for aluminum and iron electrode, respectively when treating swine manure digestate in a continuous system. Both electrodes proven to be very efficient in removing particles, but in this case the initial concentration of particles in the effluent studied was around 70 mg/L, which is lower than the general concentration in liquid swine manure (478–1756 mg/L) (Hernandez and Schmitt, 2012). In other study, Mores et al. (2016b) evaluated the performance of EC in a batch system in the treatment of swine wastewater digestate in terms of electrode distance (ED) and voltage applied (V). For the best operational condition, 2 cm with 5 V after 30 min, the removal efficiencies were 97%, 98%, 77% and 10% for color, turbidity, TOC and total nitrogen (TN), respectively.

With an initial effluent with 35.3 mg/L of particles concentration, Rahman and Bohran (2014) tested the electrodes of Fe-Fe, Al-Al and Fe-Al and all of them could achieve 100% of particles removal. However, with Fe electrodes they achieved the highest removal efficiency (85%) for TOC after 20 min at 21 mA/cm^2. Hybrid electrodes resulted in better COD removal for similar operating conditions.

Laridi et al. (2005) studied the application of Al electrodes instead of mild steel electrodes and found that Al electrodes, at low current, are more efficient in COD removal, about the double.

However, when high current densities were used, no significant differences were observed in COD removal.

Zhang et al. (2018) evaluated low carbon steel-based electrocoagulation for phosphorous separation in swine manure from two different swine wastewater, both with particles concentration higher than 400 mg/L. The results show that electrocoagulation pretreatment followed by one-day natural precipitation removed 72.6–86.3% of phosphorus from liquid swine manure, depending on the effluent. Sedimentation was improved and 90% of particles was removed. It was also found that large particles were formed after electrocoagulation and the viscosity of liquid manure decreased from 1.99 g/ms to 1.64 g/ms. Table II.2.7 overviews studies involving electrocoagulation in the treatment of swine wastewater.

Table II.2.7. A brief summary of research studies in which electrocoagulation process was used for treating livestock and swine wastewater.

Effluent	**Optimal conditions**	**Results**	**Reference**
Swine manure digestate in a continuous system	Al and Fe electrodes	The particles removal efficiency was 92.9% and 96.3% for aluminum and iron electrode, respectively.	Mores et al. 2016a
Swine wastewater digestate	2 cm, 5 V after 30 min	97%, 98%, 77% and 10% for color, turbidity, TOC and TN removal, respectively	Mores et al. 2016b
Swine wastewater: 35.3 mg/L of particles concentration	Electrodes of Fe-Fe, Al-Al and Fe-Al. 20 min at 21 mA/cm2.	All electrodes could achieve 100 % of particles removal. Fe electrodes demonstrate highest removal efficiency (85%) for TOC. Hybrid electrodes resulted in better COD removal.	Rahman et al. 2014
Swine wastewater	Al electrodes instead of mild steel electrodes	Al, at low current, are more efficient in COD removal, when high current densities were used.	Laridi et al. 2005
Swine wastewater: particles concentration >400 mg/L	Low carbon steel-based	Viscosity of liquid manure decreased from 1.99 g/ms to 1.64 g/ms.	Zhang et al. 2018

Although electrocoagulation is a promising process for swine slaughterhouse wastewater treatment some aspects must be considered as the toxicity of the materials, the aluminum toxicity will affect the growth of crop as well as human being's health (Koshian et al., 2005). In the final of the treatment ions are precipitated and generally the remaining ions in solution are way below maximum concentration levels even for drinking water quality standards. However, the solid waste requires a posttreatment and entails management.

II.2.3. Sequential methodologies

The application of sequential technologies is based on the reduction of treatment costs as well as the improvement of their global effectiveness due to synergy. This way, current legislation limits may be accomplished. Moreover, the combined methodologies can comprise a first step for solid fraction removal enhancing the treatment of liquid fraction by advanced oxidation processes afterwards. Table II.2.8 shows an overview on works dealing with processes integration for swine wastewater treatment.

João et al. (2020) studied the use of the Fenton process combined with ultrasound for the treatment of swine slaughterhouse wastewater in order to face conventional processes drawbacks. These technologies although efficient, require a high treatment area and yield high production of biological sludge. As a source of iron in the Fenton process, the authors used nails from civil construction. With the best conditions (pH 3, $[H_2O_2]$ = 90 mg/L and a nail unit (2.7 g in 200 mL of effluent) color, turbidity, COD, and BOD_5 removal of 98, 98.2, 84.6, and 98%, respectively, were obtained. The removal of nutrients, oils and greases was above 70%. The nails after six cycles of use showed a catalytic activity above 90%, revealing to be an efficient source of iron for the Fenton process. Moreover, ultrasound-assisted Fenton process may be an interesting alternative to the biological processes commonly used in the treatment of these effluents.

Park et al. (2019) evaluated the applicability of photo-assisted Fenton method for the treatment of real animal wastewater. The animal wastewater was pretreated by coagulation with 3000 mg/L of $FeCl_3$ with the aim to remove suspended solid (SS) components because these can interfere with UV light transmission. After pretreated the characteristics of effluent were: COD 1450 mg/L, color 0.1853 abs and coliform 1.2×10^{10} number/100 mL. In the photo-assisted Fenton the optimal conditions for degradation of animal wastewater were pH 3.5, $[Fe^{2+}]$= 0.01 M, $[H_2O_2]$= 0.1 M, light intensity 3.524 mW/m^2. These conditions allowed to achieve efficiencies of 91% on COD removal, sludge production 2.5 mL from 100 mL of solution, 80% on color removal and coliform removal efficiency was 99.5%.

Riaño et al. (2014) investigated the use of ozonation for color and organic matter removal from a biologically pre-treated swine manure. Applying ozone flowrates from 0.7 to 4.3 g/h, 59% to 89% color removals were obtained in 30 min reactions. Ozonation for color removal purpose is often used in wastewater treatment because the color is normally caused by the presence of humic-type compounds, which are aromatic molecules that easily react with ozone, being their direct oxidation the main reaction pathway. Regarding organic matter removal, both TOC and COD were found to be independent from the ozone dose used, with different flowrates achieving around 10% and 30% removals, respectively. As the natural effluent pH is basic (8.1), the decomposition of ozone into hydroxyl radicals ($^{\cdot}OH$) is favored, which has a higher oxidation potential than ozone. The high alkalinity of the swine manure (3200 mg $CaCO_3$/L) acts as $^{\cdot}OH$ scavenger, inhibiting the indirect reactions between these radicals and organic matter, causing the direct ozone oxidation to be the predominant pathway and the relative low removals.

As ozonation can significantly improve some target parameters, such as color and non-biodegradable substances, it can be used as a pre- or intermediate treatment capable to enhance a further biological process. Using a biological pre-treated swine piggery effluent resulting from a pond and constructed wetland system, Wang et al. (2017) investigated the enhancement of Vallisneria natans biofiltration activity by ozonation treatment, regarding nutrients (NH_4^+, TN, TP and NO_3^-), color and organic matter removal. Ozonation using different ozone concentrations (10-50 mg/L) by itself did not greatly affected the nutrients concentration, with only a small increase in NO_3^- load as possibly a result of the conversion of organic nitrogen species into inorganic forms. In the first 7 days of *Vallisneria natans* cultivation, NH_4^+, TN and TP removals were considerably improved after ozonation, with the effluent treated with 50 mgO_3/L achieving 85%, 49% and 93% removals, respectively, while the non-ozone treated effluent removed 67%, 35% and 81%. The higher NH_4^+ and TP removals can be associated with the acceleration of denitrification-nitrification process due to higher dissolved oxygen concentrations and a higher adsorption capacity by *V. natans* in ozonated waters. The NO_3^- concentrations presented a great increase in the first 7 days in all effluents, because of the nitrification process by the aquatic specie, but as cultivation time increased, as the other nutrients, the concentrations decreased, being always lower than the non-ozonated solution. The UV_{254} and UV_{436}, which determine, respectively, the presence of some organic components (e.g. lignin, tannin humic-type compounds) and color, presented a decrease with the increasing concentration of ozone in the effluent pre-treatment, presenting a similar evolution during the cultivation phase. Despite the higher UV_{254} removals, dissolved organic carbon concentration suffered no alteration, reaffirming the expected inability of ozonation to achieve total mineralization. As different reactive oxygen species (ROS) and by-products are formed during ozonation, its effects over the *V. natans* activity also had to be assessed. A higher production of O_2^- was found, mostly using a higher ozone dose (50 mg/L), and as this radical may be less stable, it is converted by dismutation into H_2O_2, having a possible toxic effect, as while 10 and 30 mgO_3/L treatments had a 50% and 32% increase in the specie biomass, the use of 50 mgO_3/L resulted in a decrease of 32%. The antioxidant activity of the *V. natans* was also affected by ozonation, as its protection mechanisms despite being active, could not prevent damages when subjected to solutions treated with a higher ozone concentration.

Kim et al. (2014) also studied the use of ozone to enhance the performance of *Scenedesmus quadricauda* microalgae in the treatment of a pre-filtered swine wastewater previously treated by anaerobic digestion. To study the ozone dose influence, up to 83 mgO_3/L was used in a 20 min treatment. With an increasing ozone dose, pH decreased from 8.7 to 7.9, possibly as a result of $^{\cdot}OH$ decomposition of ozone and $O_2^{\bullet-}$ formation. UV_{254} and color, presented 68% and 94% reductions, respectively. Specially in the first 10 min (~42 mgO_3/L), the effluent had a significant COD reduction from 3.1 g/L to 1.9 g/L (39%), reaching 1.6 g/L at the maximum used ozone dose, most likely as a result of the oxidation of inorganic compounds, such as H_2S and NO_2^-, which can be accounted in COD measurements. After 10 min treatment, the microalgae growth was significantly improved. This can be associated with a combination of the higher light transmittance due to color removal, which improved photoactivity, and the increase in the bio-convertibility of inorganic nutrients. The *S. quadricauda* dissolved organic carbon (DOC) uptake also increased for pre-ozonated effluent, indicating that ozonation was able to convert highly condensed species into more easily assimilative fractions. Membrane filtration systems also are indicated as promising livestock wastewater treatment techniques, principally in color removal, but are subjected to fouling and clogging problems and, except for reverse osmosis (RO), typically do not achieve complete color removal (Yoon et al., 2014). Additionally, even with RO being able to greatly treat color-rich effluents, it is a high-cost technology, and in the case of high-strength effluents such as swine manure, the disposal of by-product concentrate is also a disadvantage (Yoon et al., 2004).

To suppress these issues, Yoon et al. (2014) applied ozonation and peroxone (O_3+H_2O_2) as a post-treatment of previously biologically treated ultra-filtered (UFW) and nano-filtered (NFW) swine wastewater. The initial membrane process resulted in an effluent with < 600 mgO_2/L of COD and < 600 Pt-Co. To achieve 90% of color removal, UFW demanded an ozone dose of 240 mg/L while NFW used only 105 mg/L. The higher ozone usage of UFW can be assimilated with its radical scavenging due to the higher COD and, most importantly, alkalinity of 600 mg O_2/L and 3100 mg $CaCO_3/L$, respectively, compared to NFW, 450 mgO_2/L and 850 mg $CaCO_3/L$. The use of low H_2O_2/O_3 ratios had no effect over color removal, but while in NFW higher ratios decreased the process efficiency as H_2O_2 in excess can act as hydroxyl radical scavenger, in the UFW the ozone consumption decreased in 25 % for the same color removal. Comparing the capital and operating costs of all the process evaluated and reverse osmosis, ozonation applied in the NFW represented a 60% and 30% decrease, respectively, and peroxone applied to UFW had a 55% and 25% decrease compared to RO.

Hong et al. (2005) evaluated the performance of physicochemical processes for biologically pre-treated livestock wastewater. In the first phase, the biodegradable organic matter is removed in the biological process. Later, to cope with the non-biodegradable matter, different processes were combined: chemical coagulation, activated carbon adsorption, Fenton oxidation and ozonation. Based on the results, the authors found that ozone is the effective technology for color removal. A single process, whether biological or physicochemical, is not the definitive treatment solution for livestock wastewater. However, the combination of Fenton oxidation and ozonation would be an efficient alternative as a post-treatment as chemical coagulation followed by ozonation or Fenton oxidation process. In Figure II.2.2 and Table II.2.8 different possibilities of process integration are presented to treat the swine wastewater.

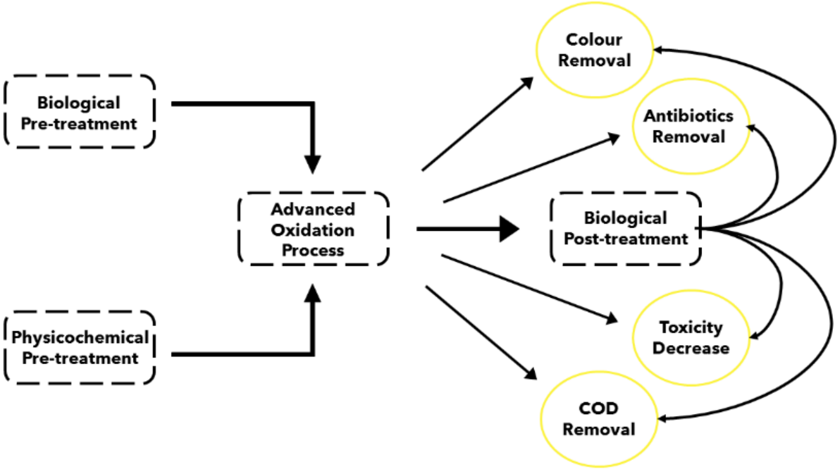


Figure II.2.2. Different integrated methodologies for swine wastewater treatment.

Table II.2.8. A brief summary of research studies for integrated methodologies in livestock and swine wastewater.

Effluent	Process	Optimal conditions	Results	Ref.
Swine slaughterhouse wastewater	Fenton process with ultrasound	pH 3; [H_2O_2] = 90 mg/L and a nail unit (2.7 g)	Color, turbidity, COD, and BOD_5 removal of 98, 98, 85, and 98%, respectively; Removal of nutrients, oils and greases was >70%; The nails after six cycles showed a catalytic activity above 90%.	João et al., 2020
Real wastewater pretreated by coagulation with 3000 mg/L $FeCl_3$: COD 1450 mg/L, color 0.1853 abs and coliform 1.2×10^{10} number/100mL.	Photo-assisted Fenton	pH 3.5; [Fe(II)] = 0.01 M; [H_2O_2] = 0.1 M Light intensity: 3.524 mW/m^2.	91% on COD removal; Sludge production 2.5 mL from 100 mL of solution; 80% on color removal and coliform removal efficiency was 99.5%.	Park et al. 2019
Biologically pre-treated swine manure	Ozone	Flowrates from 0.7 to 4.3 g/h; 30 min reactions.	59% to 89% color removals were obtained; 10% and 30% of TOC and COD removals.	Riaño et al. 2014
Biological pre-treated swine piggery effluent	Ozone	50 mg O_3/L	85, 49 and 93% NH_4^+, TN and TP removals after 7 days of *V. natans* cultivation	Wang et al. 2017

Pre-filtered swine wastewater	Ozone	up to 83 mgO_3/L; t = 20 min	With an increasing ozone dose, pH decreased from 8.7 to 7.9, as well as UV254 and color, which presented, respectively, 68% and 94% reductions.	Kim et al. 2014
Biologically treated ultra-filtered (UFW) and nano-filtered (NFW) swine wastewater: <600 mg O_2/L of COD and <600 Pt-Co	Ozonation and peroxone ($O_3+H_2O_2$)	240 mgO_3/L for UFW; 105 mgO_3/L for NFW	90% of color removal	Yoon et al. 2014

II.2.4. Pharmaceuticals removal

The pharmaceutical compounds and particularly antibiotics are a group of contaminants of serious concern in swine wastewater. These contaminants can be problematic for human health when reaching the agriculture soils or water sources due to the formation of antibiotic resistant bacteria and genes. On this way, the swine wastewater treatment needs to be improved to guarantee the complete removal of such contaminants. This is crucial in a water recovery strategy since these compounds are dangerous if reaching ecosystems. Thus, to enable wastewater reclamation for irrigation (for example) it must be ensured their efficient depletion.

Biological treatment methods, such as anaerobic digestion (AD), sequencing batch reactors (SBR) and constructed wetlands, are often applied in these types of effluents for the reduction of macropollutants due to its relative low-cost and maintenance needed (Han et al., 2020).

Han et al. (2020) reported the use of anaerobic and aerobic biodegradation to veterinary antibiotics removal. They found that concentrations between 99.2 and 339.3 μg/L of antibiotics are present in the swine wastewater. Laboratory tests showed that anaerobic digestion is essentially efficient in the removal of COD (95%) while aerobic biodegradation acts essentially in the removal of antibiotics (92% after a hydraulic residence time of 3.3 days). The authors also verified that the typical swine wastewater treatment (AD followed by the storage tank) even under long hydraulic residence time (2-3 months) is not totally effective in antibiotics removal. The sequencing batch reactor (SBR) is very efficient in organic matter removal (> 95%), (Kim et al., 2004; Li et al. 2008). Regarding antibiotics, Collado et al. (2013) reported that SBR is ineffective in its removal, they only managed to remove < 50% of sulfamethoxazole using this technology.

Xu et al. (2019) also studied the antibiotics removal by sequencing-batch membrane reactor (SMBR) for swine wastewater treatment. The author reported that SMBR is efficient in sulfonamides and tetracyclines removal (> 90%), while for fluoroquinolones the removal is less than 70%. The main mechanism for the total removal of antibiotics by SMBR is biodegradation

/ biotransformation although there is also a small contribution of sludge adsorption and membrane retention. SMBR still can remove > 60% of organic matter and nutrients.

Considering this, the advanced oxidation processes seem to be a suitable alternative for the biological treatments regarding to antibiotic removal. The efficiency of Fenton's process in the removal of existent antibiotics in swine wastewater has been previously verified. Ben et al. (2009) tested the potential of the Fenton process in removing sulfathiazole, sulfamethoxazole, sulfamethizole, sulfadimethoxine, sulfamethazine and tiamulin fumarate spiked in a sequencing batch reactor pretreated swine effluent. Under optimal conditions (1.5:1 molar ratio of $[H_2O_2]/[Fe^{2+}]$, initial pH 5, initial concentration of antibiotics 1 mg/L) the treatment effectively removed the studied antibiotics (> 90%). Besides this, the process was able to remove 40% of total organic carbon (TOC), toxic heavy metals (78% As, 36% Cu and 18% Pb) and 89% of total phosphorus (TP), which finally decreased in 20% the immobilization of Daphnia magna.

Different effluent´s parameters also have a significant influence on Fenton's process efficiency due to the interference in the radical's formation and activity, such as the organic matter content, solids characteristics, different ions and elements. Ben et al. (2009) also verified that an increasing concentration of COD and SS have a detrimental effect over the degradation of the studied antibiotics, reaching a removal reduction of up to 20%.

The combination of biodegradation and advanced oxidation processes can also enhance the treatment of veterinary antibiotics in swine wastewater. Qian et al. (2020) concluded that the use of citric acid in Fenton´s reaction promotes the formation of metal complex increasing the solubility of Fe^{2+}/Fe^{3+}, under nearly neutral conditions, and favoring the $^{\cdot}OH$ formation. In this study, the authors showed that Fenton-like is more efficient (about ~65%) in the antibiotics removal (sulfadiazine, sulfathiazole, sulfamerazine, trimethoprim, sulfamethazine, sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfamonomethoxine and sulfamethoazole-D4) than the conventional Fenton reaction at pH 6. Using optimal conditions ($[H_2O_2]$ = 2.9 mM, $[Fe^{2+}]$:[CA]:$[H_2O_2]$ = 1:1:3, pH = 6, reaction time of 120 min) Fenton-like reaction removed up to 74% of antibiotics.

The degradation of estrogens and antibiotics from livestock manure using Fenton oxidation technique was analyzed by Wang et al. (2019). Once again Fenton´s process proved to be an efficient methodology for removing these compounds that are harmful to human health and the environment. Considering optimal conditions ($[H_2O_2]$ =10.5 mmol/g slurry, an Fe^{2+}/H_2O_2 molar ratio of 0.067 mol/mol, a stirring rate of 100 rpm, the feeding of an identical amount of H_2O_2

in two steps (at 0 and 15 min), a manure/reactor ratio of 1:25, and a reaction time of 100 min) in swine manure the removal of estrogens (estriol (E3), Busphenol A (BPA), estradiol (17-E2), ethinyl estradiol (EE2)), and antibiotics (sulfadimethoxine (SDM)) is about 70% except for E3 which is lower.

Ben et al. (2012) studied the use of ozone as a post-treatment of swine wastewater after SBR spiked with a mixture of commonly used veterinary antibiotics (sulfathiazole, sulfamethoxazole, sulfamethizole, sulfadimethoxine, tetracycline hydrochloride, oxytetracycline hydrochloride, sulfamethazine, chlortetracycline hydrochloride and tiamulin fumarate) at a concentration of 200 µg/L each. In a first synthetic effluent test, an ozone dose of 1.38 mg/L achieved more than 98% of antibiotics removal. As expected, in the SBR effluent, the ozone consumption was much higher, with a dose of 37.3 mg/L achieving 85-100% removals, due to the higher matrix complexity. The lower efficiency in the SBR effluent is greatly related to the higher COD, as tests determined that a solution with a COD of 175 mg/L required the double amount of ozone to achieve total removal compared to other with 103 mg/L of COD. Different concentrations of suspend solids had no significant effect on the reaction and the addition of hydrogen peroxide reduced the process efficiency, indicating that the antibiotic degradation is mainly due to direct ozone oxidation. Table II.2.9 shows a brief overview on literature reports regarding pharmaceuticals removal from livestock and swine wastewater.

Table II.2.9. Brief summary of research studies for removing antibiotics in livestock and swine wastewater.

Effluent	**Process**	**Optimal conditions**	**Results**	**Ref.**
Sulfathiazole, sulfamethoxazole, sulfamethizole, sulfadimethoxine, sulfamethazine; tiamulin fumarate	Fenton	$[H_2O_2]/[Fe^{2+}]$= 1.5:1 molar ratio; pH= 5; initial antibiotics concentration 1 mg/L	Removal: >90% of antibiotics; 40% of TOC toxic heavy metals (78% As, 36% Cu and 18% Pb) and 89% of TP; decrease in 20% the immobilization of *D. magna*.	Ben et al. 2009
Sulfadiazine, sulfathiazole, sulfamerazine, trimethoprim, sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfamonomethoxine and sulfamethoazole-D4	Fenton-like	$[H_2O_2]$= 2.9 mM; $[Fe^{2+}]:[CA]:[H_2O_2]$ = 1:1:3; pH = 6; t = 120 min	~65% in the antibiotic's removal than the conventional Fenton; removed up to 74% of antibiotics	Qian et al. 2020
Livestock manure: estrogens (estriol (E3), Busphenol A (BPA), estradiol (17-E2), ethinyl estradiol (EE2)), and antibiotics (sulfadimethoxine (SDM)	Fenton	$[H_2O_2]$=10.5 mmol/g; Fe^{2+}/H_2O_2 molar ratio of 0.067; stirring of 100 rpm; feeding of an identical amount of H_2O_2 in two steps (at 0 and 15 min); a manure/reactor ratio of 1:25; t= 100 min	the removal of estrogens and antibiotics is about 70% except for E3 which is lower	Wang et al. 2019

Swine wastewater after SBR spiked with mixture of veterinary antibiotics (sulfathiazole, sulfamethoxazole, sulfamethizole, sulfadimethoxine, tetracycline hydrochloride, oxytetracycline hydrochloride, sulfamethazine, chlortetracycline hydrochloride and tiamulin fumarate) at 200 μg/L each	Ozone	37.3 mgO_3/L	85-100% antibiotic removal	Ben et al. 2012
Swine wastewater with 99.2 and 339.3 μg/L of antibiotics	Anaerobic digestion	---	95% COD removal; AD followed by the storage tank even under long hydraulic residence time (2-3 months) is not effective in the antibiotic removal.	Han et al. 2020
Swine wastewater with 99.2 and 339.3 μg/L of antibiotics	Aerobic degradation	3.3 days	92% of antibiotics removal	Han et al. 2020
Swine wastewater with 99.2 and 339.3 μg/L of antibiotics	Sequencing -batch membrane reactor	---	Sulfonamides and tetracyclines removal (>90%); fluoriquinolones removal < 70%; >60% of organic matter and nutrients removal	Xu et al. 2019

II.2.5. Advanced oxidation processes limitations

Although the several advantages of the advanced oxidation processes when compared to biological technologies, such as anaerobic digestion, for swine wastewater treatment, some limitations and/or disadvantages may be considered. In this section some of these limitations are discussed.

Fenton's process is a promising choice to reduce toxicity while converting toxic and biorecalcitrant contaminants into biodegradable by-products. Moreover, this technology enables color removal and promotes mineralization of the organic pollutants (Domingues et al., 2018). Although generally it performance is positive, depending on the catalyst used, some limitations may be encountered. In the case of homogeneous Fenton´s process the main drawback is the need for removing the dissolved iron from the treated effluent. At the end of the treatment, the effluent is usually alkalinized, which leads to the precipitation of iron $Fe(OH)_3$ and some coagulated organic compounds, leading to the formation of the so-called iron sludge. This iron-sludge may have a negative environmental impact and may constitute a second source of pollution, as its management usually consists in drying and landfilling it. Thus, reuse of the catalyst is not possible (Cao et al., 2009). Two approaches have been studied to minimize the production of sludge as a by-product of the Fenton process. Those include heterogeneous catalysts (Domingues et al., 2019) and the reuse of the iron-containing sludge (Bolobajev et al., 2014; Domingues et al., 2020a,c). However, the catalytic activity of heterogeneous materials is usually weakened after repetitive use due to iron leaching or the decay of active catalytic sites (Bolobajev et al., 2014). Narrow optimal pH range, high H_2O_2 consumption are also disadvantages of Fenton´s process. In neutral pH conditions a low efficiency of such systems can be observed. This low efficiency is mainly due to the presence of insoluble forms of Fe(III) under neutral pH conditions which produce very low H_2O_2 decomposition yield (Pignatello et al., 2007). The use of light in the so-called photo-Fenton may enhance hydroxyl radical's production while decreasing the catalyst dosage required, which will effectively reduce the formation of iron sludge (Giri et al., 2014). The utilization of solar or UV light for photo-Fenton can increase the utilization of H_2O_2 and enhanced the degradation of organic molecules. However, photo-Fenton still has some disadvantages, such as the request for UV radiation which may increase the energy costs demanded. Although, the use of sunlight radiation may reduce the energy costs, it has the disadvantage associated to building a specific reactor capable to take advantage from sunlight. Besides, strategies must be drawn whenever the solar radiation is not enough to promote a suitable treatment.

Ozone can readily react with electron-rich molecules, but in complex water matrices, the presence of many different species may reduce its efficiency. Thus, it can lead to incomplete oxidation of refractory compounds and even producing by-products that can be more toxic than the initial contaminants (Gomes et al., 2019; Rekhate and Srivastava, 2020). Regarding the economic aspects of the process, the main drawback is the energy consumption involved in the production of the necessary ozone quantity for the treatment. Thus, specific studies need to be conducted to determine the overall cost in each treatment, as several parameters influence the ozone dosage required. Taking the conditions stablished by Wu et al., (2002) and as the power consumption of ozone generator is typically around 16 kWh/kgO_3, the swine wastewater treatment to complete removal of phenolic and indolic pollutants would entail an energy consumption of 24 kWh/m^3. Moreover, considering in Portugal the electricity cost of 0.14 €/kWh (Henriques et al., 2020) can be estimated the price for swine wastewater treatment with ozone of about 3.36 €/m^3 (Table II.2.10). This value is much higher than the one required by Fenton's process (Domingues et al., 2021a) using the conditions established by Riaño et al. (2014) ($[Fe^{2+}]$ = 100 mg/L and $[H_2O_2]$ = 800 mg/L).

Still in what concerns ozonation, when dealing with a gas/liquid system one must bear in mind the mass transfer limitations which entails the need of implementing suitable gas/liquid contactors. This implies capital and maintenance costs. The dose of ozone required must be carefully selected so that its waste is minimized. In fact, since ozone is a dangerous gas at the stratosphere, a gas control device must also be considered to destroy remaining ozone before releasing the stream to atmosphere.

Table II.2.10. Estimated cost to treat 1 m^3 of swine wastewater by Homogeneous Fenton´s process and Ozonation.

Process	**Reagents**	**Price**	**€/m^3 of treated effluent**
Homogenous Fenton	H_2O_2	0.60 €/kg	0.288
	$FeSO_4$	0.25 €/kg	0.068
Ozonation	Ozone	0.14 €/kWh	3.360

Photocatalysis is another promising advanced oxidation process. This is especially true if sunlight radiation can be applied. However, since light must reach the catalysts, one of the limitations of this process on the treatment of real swine wastewater is the high turbidity, particles density and dark color of the effluent. Thus, an initial filtration or equivalent step or even the dilution or mixing with other effluents are often an option, which indeed increases the global treatment process costs.

Electrochemical systems have several advantages such as operation at ambient temperature and pressure as well as robust performance and capability to adjust to variations in the influent composition and flow rate. Usually, it is not necessary the use of chemicals and no waste is produced. Electrochemical processes can be adapted to various applications and can be easily combined with other technologies (Garcia-Segura et al., 2018). However, electrochemical treatment has relatively high costs related with electrodes and energy consumption. Moreover, there are some concerns about the presence of toxic byproducts in the treated water. Chlorine and bromine species formed at the anode can produce toxic organic chlorine and bromine-containing transformation products. Besides the presence of chloride in wastewater may yield toxic chlorate and perchlorate compounds (Bergmann at al., 2014; Palo et al., 2014).

The crucial points of electrochemical treatment for environmental applications is the need to reduce energy consumption and electrodes cost. These can be achieved by improving long-term stability and electrocatalytic performance and reducing the cost of electrode materials. These are the aspects where developments in materials science and nanotechnology may be most important (Martinez-Huitle and Panizza, 2018).

Electrocoagulation is a technology where simple equipment is required, which is easy to operate and automate. It involves short hydraulic time, high sedimentation velocity and a reduced amount of sludge produced (Fajardo et al., 2017). However, Electrocoagulation also presents some disadvantages like the sacrificial anodes need to be replaced when exhausted, the oxide film can passivate the electrodes and the aqueous media needs to be conductive (Babu et al., 2019).

Conventional anaerobic digester, for swine wastewater treatment is usually conducted in anaerobic ponds to ensure enough removal of organic materials and pathogens. The biggest disadvantage of this process, considering the growth of this type of effluent load, is the long retention time and large treatment area required for an effective depuration. This leads to increasing investment and operating costs (Van et al., 2020). Moreover, not all the swineries have the required area for that.

II.2.6. Applications at pilot and full scale

The growing studies of the application and optimization of AOPs to livestock wastewater shows their great advantages as a wide range and efficient treatments (Cheng et al., 2020a). With the positive lab-scale results of Ozone and Fenton treatments, the scale-up is the next step to fully establish these technologies as efficient wastewater treatments. The main drawbacks to their full-scale application are the high production cost of ozone and the large sludge formation and pH changes regarding Fenton's reaction (Trovó et al., 2013; Malik et al., 2020;). Different approaches have been pursued to optimize and understand key aspects to achieve a broader application of these technologies.

Some characteristics that have major influence on the scaling-up phase is the presence and formation of ions and radicals. In advanced oxidation processes, different reactions occur leading to the formation of many species but more importantly $^{\cdot}OH$, and the ratios and concentrations of the reactants are key aspects, principally because of the scavenging effect, that may occur due to species both from the water matrix but also formed during reactions. In the case of the Fenton process, as hydroxyl radical's production is principally due to H_2O_2 decomposition, which is manly activated by the iron source, the degradation efficiency is highly dependent on these reactants ratio. Although efficiency increases with the ratio, this occurs until a certain point. As a high iron load promotes a self-scavenging of $^{\cdot}OH$, H_2O_2 may also self-decompose and hydroxyl radicals consuming side reactions increase without the actual degradation of target substances (Trovó et al., 2013). Thus, a precise optimization of this ratio is fundamental to maintain the process efficiency as it changes during the scaling-up due to the increase of different interferences, such as the temperature fluctuation that affect peroxide decomposition.

Ozonation, as a more devised technology, is already implemented in some municipal wastewater treatment plants. For its use in livestock wastewaters, the interaction between ozonation active species and typical substances and characteristics of the water matrix is crucial (Kharel et al., 2020; Zimmermann et al., 2011). Many studies already highlighted the influence of different species over ozonation, such as chloride and sulfate ions, bicarbonate and others, that can alter the reactions kinetics and interact with ozone, increasing its consumption and consequently the cost of the treatment (Zimmermann et al., 2011; Cheng et al., 2020a; Fernandes et al., 2020). Both Yoon et al. (2014) and Riaño et al. (2014) indicated that a high concentration of bicarbonate (> 3000 mg$CaCO_3$/L) in swine manure reduces the ozonation efficiency and induces the need of a higher ozone concentration, as it acts as a strong inhibitor of reactions between formed radicals and organic matter.

The combination with other techniques enhances both the efficiency of the AOPs as well as its economic aspects. The most used solution is the combination with biological process, as an initial biological treatment may reduce the concentrations of more readily degradable contaminants, which then allows a more efficient degradation of the remaining substances by the AOPs, as their competition towards the active radical species is reduced (Ben et al., 2012; Cheng et al., 2020a; Qian et al., 2020). By applying ozone and peroxone as a color removal post-treatment after filtration processes, Yoon et al. (2014) compared the capital and operating costs involved in these process to the reverse osmosis (RO) technology currently used in the selected pig farm. Comparing to RO, ozonation applied in the nano-filtered wastewater represented a 60% and 30% decrease in, respectively, operating costs and capital requirements, while the best conditions for peroxone were a 55% and 25% decrease when applied to ultra-filtered wastewater. As comparison, Riaño et al. (2014) analyzed the operating costs of both Fenton and Ozonation for organic matter and color removal of a biologically pre-treated swine manure. In their study, the Fenton treatment had 58% lower operating costs than ozonation, as it also achieved a higher COD removal. In general, Fenton process presents a simpler operation and design, with higher costs associated with the sludge treatment or disposal and acid consumption, representing, respectively, 38% and 46% of the calculated total operating cost.

The incorporation of an irradiation source onto the process is also an interesting combination to enhance ozonation and Fenton's reaction, as, in the presence of both artificial and solar light, the production of oxidative radicals increases. Solar photo-Fenton and photolytic ozonation are then an option to reduce the overall treatments costs, as different studies at pilot and further scale already demonstrate the improvement of the degradation of several contaminants and organic matter, reducing the reactants amounts needed and using a natural and cheaper irradiation source (Michael et al., 2012; Roccamante et al., 2019; Solís et al., 2019).

II.2.7. Conclusions

Swine production effluent management is a growing problem with high environmental impacts. The commonly used processes for its treatment require space and time. The anaerobic digestion for 80% of COD removal needs about 3 to 10 days of hydraulic retention times. Besides, these traditional techniques are not efficient regarding persistent compounds removal such as antibiotics. Literature reveals that AOPs have proven efficiency on the degradation of a wide variety of pollutants in general and antibiotics in particular. However, these studies have been carried out essentially on a laboratory scale. Thus, it is crucial to show their performance at pilot scale in order to infer about their stability along a long-term use.

Industrially, these processes are considered expensive when compared with current depuration technologies. In this sense, future research involves trying to minimize the costs of these processes in order to become industrially more attractive. The integration of processes, the reduction of energy costs by developing catalysts activated by sunlight (visible light) and the recovery of the sludge resulting from the processes, namely Fenton, may be the key to the greater use of AOPs.

This overview shows the potential of such technologies on the depuration of swine effluents shading light on the future pathway so that their wider industrial application may be boost.

II.3. Sulfate radical based advanced oxidation processes for agro-industrial effluents treatment: A comparative review with Fenton's peroxidation

The Sulfate radical based advanced oxidation processes for agro-industrial wastewater treatment, compared to Fenton´s process, is now overviewed. This section is based in the publication: Domingues, E., Silva, M.J., Vaz, T., Gomes, J., Martins, R.C. (2022) Sulfate radical based advanced oxidation processes for agro-industrial effluents treatment: a comparative review with Fenton's peroxidation (Review), Science of the Total Environment, 832, 155029.

II.3.1. Sulfate radical based advanced oxidation and Fenton processes for agro-industrial effluents treatment

Water scarcity is an important issue that is aggravated through the increasingly prolonged droughts related to climate change (Amor et al., 2019). Thus, water protection is an emerging concern that should be tackled by science and industry and this path goes through suitable wastewater treatment and management technologies.

To face population growth, there is a strong intensification of industrial and agricultural activities to increase the supply of food. Agro-industries such as olive mill, wine, fruit processing, coffee, dairy, palm oil and pulp mill industries, are important agricultural activities in different countries and are the biggest water consumers among the industrial sector which is also reflected in a significant environmental problem related to wastewater that is generated along the different production steps (Martins et al., 2014). Effluents from many agro-food industries are a hazard to the environment and require appropriate and a comprehensive management approach (Rajogopal et al., 2013). Consequently, the treatment of agro-industrial wastewaters must be an important focus since the discharge of untreated wastewater into the environment will cause serious harm to humans and the environment (Martins et al., 2014; Mo et al., 2018).

The agro-industries wastewater treatment processes can be based on conventional technologies (physical, biological and chemical methods) or advanced technologies (e.g. membrane processes and advanced oxidation technologies) (Oller et al., 2011). The selection of a treatment process depends on the characteristics of the effluent like self-purification capacity of streams, permissible levels of pollutants in water bodies and the economic interests of industries (Rahim et al., 2015).

As for physical processes, these only promote the pollutants phase transfer, that is, they can remove the organic matter from the liquid phase. However, they are not able to degrade it. Regarding biological processes, although most of the organic content may be biodegradable, the biorecalcitrant character or the toxic contribution of some compounds, as well as an inadequate proportion of C:N:P, make it difficult to achieve an acceptable removal efficiency by just applying biological treatments (Santos et al., 2014; Solís et al., 2018). Besides, even though in the first months after grape harvest, the wastewaters may be treated by actived sludge or anaerobic treatment, due to the rich composition in biodegradable compounds, afterwards the WW become richer in alcohols and phenols, which reduce their biodegradability (Rodríguez–Chueca et al., 2017b). Therefore, the high variability in flow and composition of WW, during processing time, are a challenge for the wastewater treatment (Souza et al., 2013; Rodríguez–Chueca et al., 2017b).

Considering the danger that these wastewaters present and the lack of efficiency that generally the conventional approaches based on biological oxidation show, the investigation of suitable treatment methods becomes imperative. Advanced oxidation processes, in particular Fenton process, appear as interesting alternatives. However, to overcome some of these technologies drawbacks, S-AOPs have been the object of study of recent investigations.

Bearing in mind the emergency of developing suitable technologies to remove the contaminant load of agro-industrial wastewater, and the high expectations shown in literature regarding S-AOPs for this aim, this work intends to perform a critical review on works dealing with these technologies for agro-industrial effluents depuration. In this context, the effect of operating conditions will be evaluated; the role of the activating strategy will be analysed; light will be shaded on how sulfate radicals react with organic matter and which are the characteristics of the treated wastewater. Besides, since S-AOP operates at similar conditions to Fenton’s process, these two technologies will be compared.

II.3.2. S-AOPs

S-AOPs can be applied to remove or degrade resistant pollutants, such as, antibiotic resistant microorganisms, drugs and non–biodegradable organic matter (Qiu et al., 2020). The sulfate radicals ($SO_4^{\bullet-}$) bind with the pollutants by removing hydrogen from the saturated carbon, by adding it in the double bonds or by electrons transfer, causing partial or total mineralization of the organic matter (Genç et al., 2020). When compared to Fenton’s process, the use of S-AOP has some advantages, such as:

– Sulfate radicals have a greater stability and thus a longer life span than the hydroxyl radical ($HO^{\bullet}$), which is the radical formed in the Fenton process;
– The oxidant agent necessary to generate $SO_4^{\bullet -}$ is solid at room temperature, which facilitates its transport and storage;
– The range of pH values of the S-AOP is wider than those used in the Fenton process (usually pH must be around 3);
– Sulfate radicals have a bigger solubility, in aqueous solution, than $^{\cdot}OH$;
– The hydroxyl radicals react through unselective multi–step pathways which limits the process efficiency (Brienza et al., 2017; Ioannidi et al., 2020; Gormez et al., 2020).
However, some authors reported that although sulfate radicals have a greater stability and have an oxidation potential like that of hydroxyl radicals, the reaction rate between $SO_4^{\bullet -}$ and organic matter is slower than the one observed between $^{\cdot}OH$ and organic compounds (Waclawek et al., 2017; Giannakis et al., 2021). Nevertheless, there is still no consensus in this matter as other authors, found out that the reaction between the organic matter and the sulfate radicals is faster than the one with hydroxyl radicals (Brienza et al., 2017).

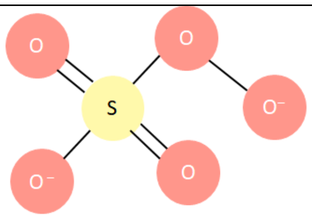
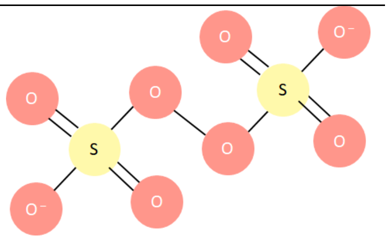
S-AOPs, like other AOPs, can produce toxic by-products, in some cases, the global toxicity of the treated effluent may be increased substantially, indicating that some by-products are more hazardous than the original matrices. A way to work around or minimize this problem is to combine with other treatment processes to reduce the impurities, like merging membrane technologies with S-AOPs to improve detoxification (Ganiyu et al., 2015), and as a post-treatment, to decrease the organic byproducts, adding activated carbon. Activated PS (peroxidisulfate) and PMS (peroxymonosulfate) were largely applied in the laboratory scale for disintegration of waste activated sludge (Liu et al., 2018) and anaerobically digested sludge (Wacławek et al., 2016), they are undesired products of the biological wastewater treatment. The sulfate radicals can react very fast with the sludge flocs as well as cell membranes. This leads to the improvement of dewatering ability and often improvement of other sludge properties. However, there is a lack of reports regarding the toxicity of such oxidized sludges. Considering the published studies, it is clear that there is a great interest in the combination of AOPs with conventional treatments, in particular biological ones, due to the economic benefits and due to the economic benefits and the effectiveness of inactivating the antibiotic-resistant bacterial load. The biological processes most studied to be integrated with AOPs, either as pre- or post-treatment, are membrane bioreactors (MBRs) and activated sludge systems (Dhangar et al., 2020; Rostam et al., 2020). The position that AOPs should occupy with regard to the biological treatment, as pre- or post-treatment, depends on the characteristics of the wastewater.

If the effluent to be treated has recalcitrant compounds in his composition or inhibitory compounds, an AOP as pre-treatments is usually needed in order to increase the biodegradability or to eliminate the toxic compounds that prevent the metabolism of microorganisms in the biological treatment (Oller et al., 2011; Giwa et al., 2020). For refractory organic pollutants in wastewater Yan et al. (2021), in another point of view, studied the coupling of membrane technology with persulfate/peroxide-based in situ chemical oxidation (ISCO). They verified real advantages of pollutant filtration and degradation. In terms of PS activation, Liu et al. (2022) made a revision on metal-free carbonaceous materials catalysts for green remediation. The authors showed that a proper heteroatom doping into metal-free carbonaceous materials is a real way to improve PS activation performance.

II.3.2.1. Oxidant Agents for S-AOPs

Sulfate radials are generated through the activation of an oxidant agent, like persulfate (PS – $S_2O_8^{-2}$ or peroxymonosulfate (PMS –HSO_5^-), whose properties are present in Table II.3.1.

Table II.3.1 Properties of persulfate and peroxymonosulfate (Manos et al., 2020).

Properties	PMS	PS
Chemical Structure		
Formula	$HSO_5^{\,-}$	$S_2O_8^{\,-2}$
Reactive Oxygen Species (ROS)	$\cdot OH/SO_4^{\bullet -}/SO_5^{\cdot -}$	$\cdot OH/SO_4^{\bullet -}/SO_5^{\cdot -}$
Molecular Weight (g/mol)	113	192
Solubility in Water at 20 °C (g/L)	> 250	730
Oxidation Potential (V)	1.8	2.01

The most common form of PMS is a triple potassium salt, $2KHSO_5.KHSO_4.K_2SO_4$, commonly called Oxone. It is easily dissolved in water, stable over a wide pH range and is nontoxic. However, two of the three sulfur salts are inactive and do not participate in the activation reaction. It should be noted that, during the PMS activation process, in addition to the sulphate radicals, hydroxyl radicals ($\cdot OH$) and sulfur pentoxide radicals ($SO_5^{\bullet -}$) can also be formed (Ghanbari et al., 2017; Manos et al., 2020), as can be seen ins equations II.10-12.

$$HSO_5^- + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{\bullet -} + OH^- \qquad \text{II.10}$$

$$HSO_5^- + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{2-} + \cdot OH \qquad \text{II.11}$$

$$HSO_5^- + M^{(n+1)+} \rightarrow SO_5^{\bullet -} + M^{n+} + H^+ \qquad \text{II.12}$$

The PS has a symmetrical structure, unlike the PMS, thus being more stable and requiring more energy for its activation (Xiao et al., 2020; Giannakis et al., 2021). The most common and stable form of PS is crystalline salts like sodium persulfate ($Na_2S_2O_8$) or potassium persulfate. For water decontamination, the most used salt is sodium persulfate, which is more soluble in water than PMS (Manos et al., 2020). It should be noted that, during the PS activation process, besides the formation of sulfate radicals ($SO_4^{\bullet-}$), hydroxyl radicals ($^{\cdot}OH$) can also be formed (Qui et al., 2020; Xiao et al., 2020).

In addition to the symmetry of the molecules, another difference between the PMS and the PS is the redox potential. As observed in Table II.3.1, PS presents a higher oxidation capacity than PMS. Even so, both agents have been studied because of their advantages, such as, high aqueous solubility, environmentally friendly nature and cost effectiveness relationship (Xiao et al., 2020). It should be noted that, to take advantage of the potential of these agents they must be activated to generate sulfate radicals.

II.3.3. Activation Techniques for S-AOPs

As mentioned before, persulfate and peroxymonosulfate are moderate oxidizing agents and thus must be activated to form sulfate radicals with higher redox potential. These agents can be activated by heat, ultrasound, microwave, photolysis and catalysis (Rodriguez et al., 2012; Ioannidi et al., 2020; Qui et al., 2020). The most usual activation modes will be discussed in the following sections.

II.3.3.1. Iron catalysis

Regarding the activation of PS and PMS through catalytic processes, the most common is the use of Fe (II) as homogeneous catalyst, as shown in Equations II.14 and II.15. It should be noted that according to Anipsitakis and Dionysiou (2004) silver is the best catalyst to activate PS and in the case of PMS, the most efficient catalyst is cobalt. However, given the toxicity associated with it usually iron is a prefereable catalyst (Brienza et al., 2017; Manos et al., 2020), the abundance of iron and the non–toxicity of this material at the concentrations usually applied in these processes, combined with the known efficacy of this compound in the activation of PS and PMS, have made this metal the target of studies in the generation of sulfate radicals (Xiao et al., 2020).

It is important to point that during the activation process, besides the formation of sulfate radicals, other radicals can be formed, as described in Equations II.15- 17 (Manos et al., 2020; Qui et al., 2020; Xiao et al., 2020).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \tag{II.13}$$

$$HSO_5^{-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + OH^{-} + Fe^{3+} \tag{II.14}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} + H^{+} \tag{II.15}$$

$$HSO_5^{-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + HO^{\bullet} \tag{II.16}$$

$$HSO_5^{-} + Fe^{3+} \rightarrow Fe^{2+} + SO_5^{\bullet-} + H^{+} \tag{II.17}$$

The activation of PS and PMS using iron can be carried out in homogeneous or heterogeneous systems. Homogeneous systems usually lead to faster reactions since mass transfer resistances are negligible. Nevertheless, some unwanted side reactions take place and ferrous sludge is formed at the end of the process since iron must be removed from the treated wastewater. Heterogeneous systems emerged with the aim of eliminating the disadvantages of homogeneous systems, namely the formation of iron sludge (Manos et al., 2020; Xiao et al., 2020). Still, the size of the particles, which are the source of iron, the deposition of molecules on their surface and the agglomeration of particles influences the speed of oxidant activation (Brienza et al., 2017; Xiao et al., 2020). Thus, currently, despite the disadvantages associated with homogeneous systems, they are more effective, compared to heterogeneous catalytic processes for PS and PMS activation (Giannakis et al., 2021).

In these processes, it is necessary to consider the effect that pH, the iron catalyst load, the persulfate / peroxymonosulfate concentration and the initial pollutant concentration have on their performances. Regarding pH, for homogeneous systems, the degradation process is favored in acidic environments. However, for pH values below 2.5, the formation of ferrous complexes is verified and for values above 3, the precipitation of Fe^{2+} occurs, according to Equation II.18 (Xu et al., 2010; Hoa et al., 2020; Xiao et al., 2020).

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet-} \quad \text{and} \quad Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \tag{II.18}$$

If the reaction occurs in heterogeneous systems, depending on the source of iron its precipitation is not a shortcoming. Even so, at acidic pH the process is favored, since for higher pH values a layer of complexes is formed on the catalyst surface, which reduces the rate of degradation (Xiao et al., 2020).

Besides this, at alkaline pH, the formation of radicals with a lower oxidative power is verified (Xu et al., 2010; Hoa et al., 2020; Xiao et al., 2020). It was also reported that at a pH value lower than 5, hydrogen ion scavenges sulfate and hydroxyl radicals, according to Equations II.19 and II.20 (Ghanbari et al., 2017).

$$HO^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \qquad \text{II.19}$$

$$SO_4^{\bullet -} + H^{+} + e^{-} \rightarrow HSO_4^{\bullet -} \qquad \text{II.20}$$

Besides, must be taken when using heterogeneous iron-based catalysts at acidic conditions since low pH favors metal leaching which will promote the catalyst deactivation.

Regarding the effect of the catalyst load, an increase in this parameter results in an increase of the process efficiency until a certain point. When there is excess of iron in the medium, Fe^{2+} will react with the sulfate radicals, according to Equation II.21. It should be noted that the rate of reaction of consumption of sulfate radicals, in comparison with the rate of formation, is five to eight times higher. This will result in a decrease of the organic matter removal efficiency.

$$Fe^{2+} + SO_4^{\bullet -} \rightarrow SO_4^{2-} + Fe^{3+} \qquad \text{II.21}$$

As for the contribution of the oxidant concentration, it has a similar effect since an increase in the oxidant concentration induces an increase in the efficiency, until there is an excess of oxidant in the solution. The excess of persulfate and peroxymonosulfate will react with the sulfate radicals, according to the Equation II.22 and II.23. It is important to note that the scavenger effect due to PS or PMS excess is less noticeable than the scavenger effect due to iron excess (Ghanbari et al., 2017; Hoa et al., 2020; Xiao et al., 2020).

$$S_2O_8^{2-} + SO_4^{\bullet -} \rightarrow S_2O_8^{\bullet -} + SO_4^{2-} \qquad \text{II.22}$$

$$HSO_5^{-} + SO_4^{\bullet -} \rightarrow SO_4^{2-} + SO_5^{\bullet -} + H^{+} \qquad \text{II.23}$$

In homogeneous systems, to avoid the scavenger effect, an appropriate molar ratio between the oxidant agent and the catalyst should be adopted. The molar ratio 1:1 is recommended, considering that this is the stoichiometry of the reactions of interest (Equation II.14 and II.15). Other strategies to be adopted are the sequential addition of Fe^{2+}, instead of adding the total amount at the beginning of the process, and the introduction of chelating agents and/or reducing agents, which promote the conversion of Fe^{3+} to Fe^{2+} (Rodriguez et al., 2012; Xiao et al., 2020).

In heterogeneous systems, when using zero valence iron, it acts as a source of iron with controlled and slow release and, therefore, minimizing the scavenger effect (Waclawek et al., 2017; Xiao et al., 2020). Some investigators propose that high-valent iron-oxo species of $\equiv$ Fe Ⅳ$=$ O could be also formed in iron-based Fe(Ⅱ)/PDS and Fe(Ⅱ)/PMS activation processes. Wang et al. (2018) validate that, at acidic conditions and even at circumneutral pH, Fe(IV) rather than $SO_4^{\bullet -}$ is the main reactive intermediate in the Fe(II)/PS process. In this study it has been revealed that Fe(IV) can react with organic compounds (aromatic substrates and aliphatic alcohols) via electron or atom transfer (hydride, hydrogen, or oxygen) and inorganic ions (NO_2^-,Cl^-,Mn^{2+}, and HSO_3^-) . However, the reaction rate of substrates is lower than those with $SO_4^{\bullet -}$ and $HO^{\cdot}$ (Mártire et al., 2022). Lai et al. (2020) carried out a study using iron-based mineral, natural titanomagnetite, as catalyst to activate peroxydisulfate (PDS) for the removal of atrazine (ATZ) in water. The authors with quenching experiments, EPR tests and UPLC/ESI–MS/MS analysis showed that free radicals ($SO_4^{\cdot -}$ and $^{\cdot}OH$) and high-valent iron-oxo species were the main reactive oxygen species (ROS). The high-valent iron-oxo species, $\equiv$ FeIV$=$O and $\equiv$ Fe V $=$ O, could be produced from the $\equiv$ Fe(II) and $\equiv$ Fe(III) present on titanomagnetite through a nonradical way. The mechanism of $SO_4^{\cdot -}$ and $^{\cdot}OH$ generation followed a single electron transfer process, while the formation of $\equiv$ FeIV$=$O and $\equiv$Fe V $=$ O followed two-electron transfer reactions. A study conducted by Li et al. (2018) proposed a PMS activation with Fe(III) doped g-C_3N_4 (CNF) as catalyst. This combination was able of selectively degrading phenolic compounds in a large pH range (3−9) via nonradical way. The study demonstrates that singlet oxygen ($^1O_2$) in the PMS/CNF_3 (3.46 wt % Fe) system has an irrelevant role in 4-CP degradation, and high-valent iron oxo species fixated in the nitrogen pots of g-C_3N_4 ($\equiv$FeV$=$O) was the dominant reactive species. The mechanism was assumed that $\equiv$FeV$=$O was generated by activation of PMS by binding to Fe(III)-N, which efficiently reacted with 4-CP via electron transfer. These studies are relevant in the development of new heterogeneous complex iron catalysts for PS/PMS activation to degrade organic contaminants through a nonradical pathway.

Finally, regarding the amount of pollutant introduced, a larger amount of organic matter can induce a decrease in the performance of the process, if the number of radicals generated is insufficient (Gormez et al., 2020; Hoa et al., 2020).

Besides the effect of the variables described above, it is also necessary to consider the effect of the anions present in the waters, since they will react with the radicals and affect the effectiveness of the activation. Among them, it is worth highlighting the influence of chlorides, bicarbonates, carbonates and phosphates. Chlorides (Cl^-), as shown in Figure II.3.1a, reacts with the sulfate radicals forming chlorine, whose radicals have a smaller redox potential and prefer to react with aromatic compounds. However, since the reaction between Cl^- and $SO_4^{\bullet -}$ is reversible, its negative influence is dependent on its concentration. Contrary to chloride, carbonates, bicarbonates and phosphates, as shown in Figure II.3.1b, have a negative effect on the performance of the process, regardless of their concentration, since they have a strong buffering capacity and are known scavengers of $SO_4^{\bullet -}$. In addition, when using solid catalysts, these anions can be adsorbed on the catalyst surface, by electrostatic forces, occupying the active centers for the generation of sulfate radicals (Manos et al., 2020; Xiao et al., 2020; Giannakis et al., 2021). It has been reported that the order of inhibitory effect of some anions is $S_2O_3^{-2} > HCO_3^{-} > CO_3^{-2} > Cl^{-} > H_2PO_4^{-} > SO_4^{-2}$ (Xu et al., 2010; Ghanbari et al., 2017).

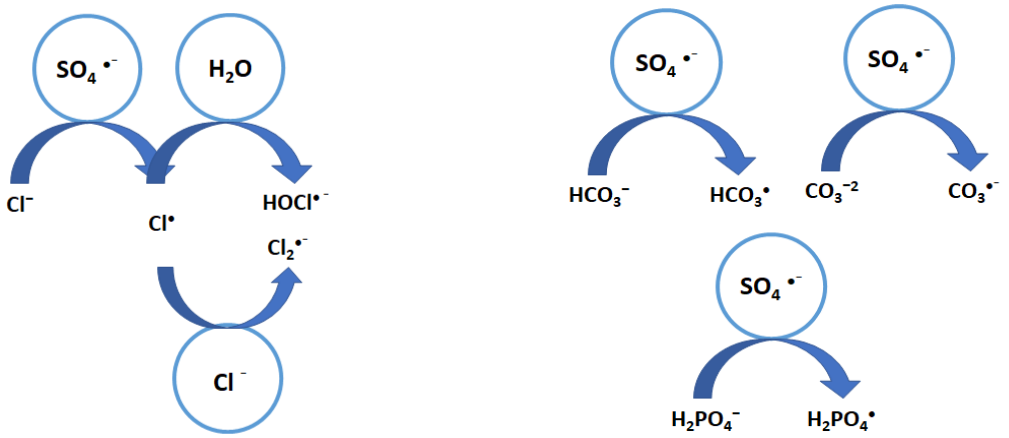


Figure II.3.1. Influence of a) chloride in the activation process b) carbonates, bicarbonates and phosphates in the activation process.

The concentration of dissolved oxygen in the waters is another parameter that must be considered. The oxygen acts as an electron acceptor and thus when reacting with the catalyst generates superoxide radicals. These can react with PS or PMS to generate $SO_4^{\bullet -}$, as illustrated in Figure II.3.2. So, the presence of oxygen can facilitate the decomposition of organic matter. However dissolved oxygen in excess acts as an electron inhibitor, making the activation process more difficult (Xiao et al., 2020).

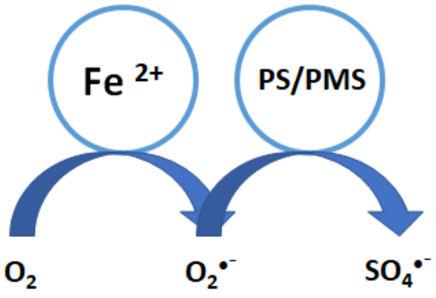


Figure II.3.2. The influence of oxygen in the activation process.

II.3.3.2. Carbon based catalysis

Although the catalytic activation technique with iron based on heterogeneous systems has some advantages over homogeneous systems, it still suffers from some drawbacks, such as, particle aggregation due to high surface energy and inherent magnetic forces, easy oxidation in air of the catalyst and the occurrence of leaching of iron ions. To overcome these disadvantages, the catalysts can be distributed on various supports (Brienza et al., 2017; Xiao et al., 2020).

One of the most applied types of support is based on carbon materials. These materials have emerged as a promising alternative to metal catalysts since they prevent secondary contamination of water by leaching of metals. In addition, carbon materials have other benefits, such as, large surface areas, good stability in both acidic and alkaline environments and structural stability at high temperatures (Waclawek et al., 2017; Vieira et al., 2020; Xiao et al., 2020).

Activation of PMS/PS through carbon-based materials can happen by different ways, regarding the reactive oxygen species (ROS): radical generation (Equations II.24 and II.25), the formation of charge transfer complex, generation of singlet oxygen ($^1O_2$), and/or direct catalysis by nonradical pathway or by combination of radical and non-radical pathways (Xiao et al., 2018, Pedrosa et al., 2019). In addition, these materials usually have a strong adsorption capacity, so they have the advantage to eliminate a fraction of the contaminants by itself (Duan et al., 2018).

$$S_2O_8^{-2} + e^- \rightarrow SO_4^{\bullet -} + SO_4^{-2} \qquad \text{II.24}$$

$$HSO_5^- + e^- \rightarrow SO_4^{\bullet -} + HO^- \qquad \text{II.25}$$

Pedrosa et al. (2019) verified that the catalytic mechanism, in metal-free catalytic membrane as activator of PS, is processed by both the radical and the non-radical pathways, but there is a greater contribution observed from the non-radical way ($^1O_2$).

Zhu et al. (2018) studied N-doped graphitic biochars (N-BCs) as low-cost catalysts for peroxydisulfate (PDS) activation and the degradation of diverse organic pollutants in water treatment (as well as Orange G, phenol, sulfamethoxazole, and bisphenol A) and they verified that singlet oxygen and nonradical pathways (surface-confined activated persulfate–carbon complexes) dominate the oxidation processes in N-BC derived at 900 °C. There are clearly advantages in the use of carbon-based materials for the activation of PMS and PS, but there is still some resistance to its large-scale implementation due to high price to synthesize the material and it is also necessary to better understand the activation mechanisms and study its performance in the presence of a mixture of pollutants, since most studies analyze its use for the degradation of a single contaminant. (Guerra Rodrúguez et al., 2018).

Among the carbon–based catalysts used in the activation of persulfate and peroxymonosulfate, those based on reduced graphene oxide and activated carbon are the ones that have been the target of most research (Waclawek et al., 2017; Vieira et al., 2020).

The application of these materials has been carried out in the form of powders and membranes. The membrane application is more advantageous, since it allows the process to be carried out continuously. However, this is a recent technology and is still under investigation. In addition, membranes also have the disadvantage of obstruction and disintegration due to use (Vieira et al., 2020).

II.3.3.3. Radiation activation

The radiation used to activate PS or PMS can be microwave, solar radiation and ultraviolet radiation (UV). The radiation, besides allowing the formation of radicals, contributes to the solubility increase of organic matter and to the increase in temperature, which allows the reaction rate increase and decrease the processing time (Qi et al., 2014).

In this technology, the effect of the pH value, the concentration of the oxidizing agent, the initial concentration of the pollutant, the temperature (or power), as well as the composition and chemical structure of the pollutant, must be considered.

The effect of pH is dependent on the characteristics of the target molecule, since several compounds have different structures depending on the pH of the mixture and the structure of the molecules influences their reactivity with the radical. In addition, as previously mentioned, the concentration and the species of radical formed are dependent on the pH (Qi et al., 2014; Persaheb et al., 2019).

Regarding temperature / power, an increase in this variable induces an increase in the reaction speed and, consequently, a decrease in the process time. It is important to note that at low temperatures (< 20 °C) the formation of radicals is small (Qi et al., 2014; Genç et al., 2020; Amor, et al., 2021).

Activation of persulfate and peroxymonosulfate with visible or near ultraviolet radiation is not as effective as activation by UV with a wavelength of 245 nm. Regarding the photolysis of peroxymonosulfate, it allows to obtain one mole of $SO_4^{\bullet-}$and one mole of ·OH, for each mole of oxidant, while persulfate photolysis allows to obtain two moles of $SO_4^{\bullet-}$for each mole of oxidant, as represented in Equations II.26 and II.27 (Chueca et al., 2017a; Amor et al., 2021).

$$HSO_5^- \xrightarrow{hv/\Delta} SO_4^{\bullet-} + HO\cdot \tag{II.26}$$

$$S_2O_8^{-2} \xrightarrow{hv/\Delta} 2SO_4^{\bullet-} \tag{II.27}$$

Ultraviolet radiation does not penetrate easily in water and is not easily transported in wastewaters, so the activation of persulfate and peroxymonosulfate by other types of radiation is also target of study (Qi et al., 2014). Microwave radiation (MW) is an economic technology for water treatment, soil remediation and sediment decontamination. MW are selective and provide rapid degradation processes. Unlike conventional heating, which is based on passive heat transfer to the depth of the material, microwaves convert energy into heat by irradiation and increase the reaction rate (Qi et al., 2014; Genç et al., 2020).

II.3.3.4. Combined activation techniques

Persulfate and peroxymonosulfate activation can be enhanced by combining different techniques. For example, in the specific case of iron catalysis activation, it can be favored by the application of external energy, such as ultrasound, electric fields, magnetic fields and ultraviolet radiation (Xiao et al., 2020).

Regarding the use of ultrasounds, when this method is applied to an aqueous solution, microbubbles can form, grow and collapse violently. Acoustic cavitation can result in sonoluminescence and hot spots, where extreme conditions of high temperature and pressure are generated. Some volatile organic compounds can be directly decomposed under ultrasonic irradiation. In addition, the radicals $SO_4^{\cdot-}$ and $\cdot OH$ can be produced, simultaneously, through the direct activation of persulfate or peroxymonosulfate, and $\cdot OH$ can also be formed through the decomposition of water. When applied in heterogeneous systems, this technique can also promote the dispersion of particles in the system, clean the oxidized surface and facilitate the contact between the catalysts and the oxidizer. It should be noted; however, that a too high of an input can lead to inhibition of the activation process, due to the formation of large bubbles that block the transmission (Xiao et al., 2020).

As for the application of electric fields, in this method, are formed electrons that can be used to reduce Fe^{3+} to Fe^{2+}, achieving high activation efficiencies. In addition, the introduction of an electric field makes it possible to overcome the pH dependence of the activation process, allowing its application at neutral pH (Xiao et al., 2020).

II.3.4. Fenton process

Fenton is considered an effective advanced treatment process for the removal of many organic pollutants in wastewater, surface water, and groundwater. These pollutants, such as volatile phenols, benzene, and benzene derivatives, are considered highly toxic and low biodegradable and result from contaminated soil, agricultural runoff, industrial wastewater, and hazardous compounds storage leakage (Babuponnusami et al., 2014).

The conventional Fenton technologies involves the following steps as illustrated in Figure II.3.3, including acid regulation, catalyst mixing, oxidation reaction, neutralization, and solid–liquid separation.

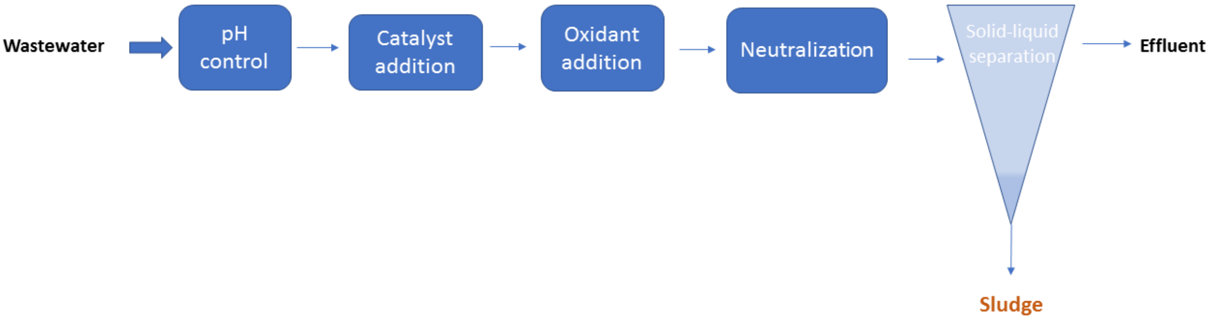


Figure II.3.3. Fenton process scheme.

In this process, the hydroxyl radical (·OH) is generated from the reaction between aqueous ferrous ions and hydrogen peroxide (H_2O_2), and it can destroy refractory and toxic organic pollutants in wastewater (Lucas et al, 2007). The hydroxyl radical (·OH) has a strong oxidation capacity (standard potential = 2.80 V versus standard hydrogen electrode) (Oturan and Aaron, 2014). Hydroxyl radicals can effectively oxidize refractory organic pollutants in wastewater and even completely mineralize them into CO_2, water, and inorganic salts (Gallard and De Laat, 2000). Meanwhile, the iron complex produced in the treatment of wastewater by Fenton will play the role of flocculant. The traditionally accepted Fenton mechanism is represented by Eqs. (II.28) – (II.34) (Neyens and Baeyens, 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad k=63.5\ M^{-1}\cdot s^{-1} \qquad \text{II.28}$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{2+} + OH^- \qquad k=3.2\times 10^{8}\ M^{-1}\cdot s^{-1} \qquad \text{II.29}$$

$$RH + \cdot OH \rightarrow H_2O + R \rightarrow \text{further oxidation} \qquad \text{II.30}$$

$$R\cdot + Fe^{3+} \rightarrow Fe^{2+} + R^+ \qquad \text{II.31}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot OOH + H^+ \qquad k=0.001\text{–}0.01\ M^{-1}\cdot s^{-1} \qquad \text{II.32}$$

$$\cdot OH + H_2O_2 \rightarrow \cdot OOH + H_2O \qquad k=3.3\times 10^{7}\ M^{-1}\cdot s^{-1} \qquad \text{II.33}$$

$$\cdot OH + \cdot OH \rightarrow \cdot OOH + OH^- \qquad k=6.0\times 10^{9}\ M^{-1}\cdot s^{-1} \qquad \text{II.34}$$

According to equation (II.28), ferrous iron (Fe^{2+}) is rapidly oxidized to ferric ions (Fe^{3+}), while Fe^{2+} is regenerated from the so-called Fenton-like reaction between Fe^{3+} and H_2O_2 at a very slow rate. Equation II.28 is usually considered as the core of the Fenton reaction.

Fenton's main oxidant (hydroxyl radicals) may be scavenged by an excess of iron (equation II.32) or hydrogen peroxide (equation II.33), which may reduce the process efficiency. This means that the ratio between H_2O_2/Fe^{2+} must be carefully selected in order to avoid the scavenging effect (Domingues et al., 2018).

Fenton process presents many advantages for organics oxidation (Bigda, 1995) (such as its high performance and simple operation. Moreover, it occurs at room temperature and atmospheric pressure besides the non-toxicity of the reactants applied (Duarte et al., 2011). However, Fenton also has some inherent disadvantages, which limit its wider application at full-scale. For example, strict pH range (acidic pH), high H_2O_2 consumption, and the accumulation of ferric sludge that affect the oxidation efficiency (Wang et al., 2016; Domingues et al., 2018). To overcome these disadvantages, the enhancement of the Fenton process has attracted much attention from researchers. Some heterogeneous catalysts were used to replace homogeneous Fe^{2+}, including ferric oxide (Matta et al., 2007), iron minerals (Shinya et al., 2007), and nano zero-valent iron (Martins et al., 2012). Also, Fenton’s process efficiency can be enhanced through the addition of some external energy leading to photo-Fenton/Fenton-like processes, electro-Fenton-like processes (Pouran et al., 2015; Domingues et al., 2019), sono-Fenton by Wang et al. (2015) and microwaves by Carta and Desogus (2013). This way, the amount of catalyst required will be reduced leading to lower loads of ferrous sludges.

II.3.5. Application of S-AOP and Fenton´s process for agro-industrial wastewater treatment

In the following sections, the application of S-AOP and Fenton’s process for depuration of several agro-industrial wastewaters will be analyzed and compared in order to shade light about the most suitable approach for the full-scale treatment technology.

II.3.5.1. Wastewater from the winery industry

Wine industry is one of the largest agro-industries around the world, with a global production, in 2019, of 25.6 million m^3 of wine, which represents a decrease of 7.4% when compared to the 2015 production of 27.5 million m^3 (Solís et al., 2018; OIV, 2020). However, there is an annual increase in market value, although production remains fixed at the average value. For example, from 2017 to 2020, there was an increase in the market value of 38.4%, reaching, in 2020, a value of 417.85 billion $US (Zion Market Research, 2019; Grand View Research, 2021).

Wine is the product obtained from the total or partial alcoholic fermentation of fresh grapes, whether crushed or not, or of grape must. Producing wine requires the implementation of a biotechnological sequence involving several unit operations – grape reception, crushing, fermentation, conservation, stabilization and filtration (Brito et al., 2007; Lucas et al., 2010), as shown in Figure II.3.4. White wine is normally produced by the fermentation of a clarified must, which is obtained after grape stem removal, pressing of the resulted grape berries, and subsequent clarification. The production of red wines is usually conducted in non–clarified musts (Brito et al., 2007).

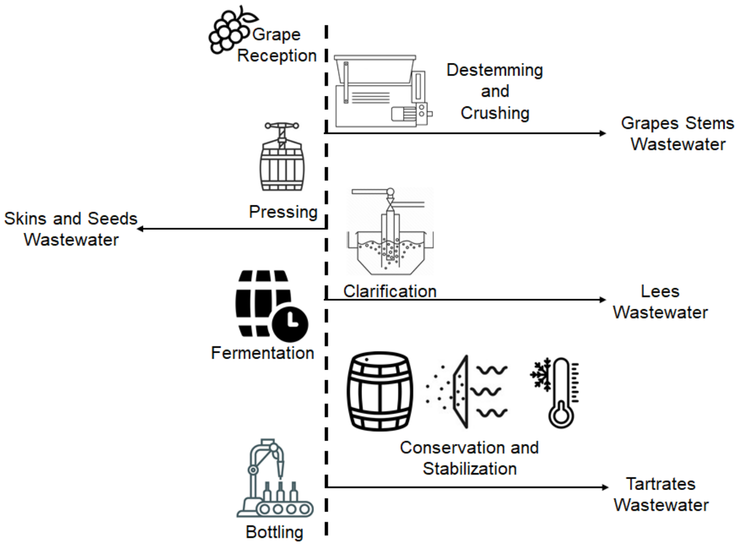


Figure II.3.4. Wine production scheme.

Wineries annually generate large volumes of wastewater, designated winery wastewaters (WW). These mainly originate from various washing operations, from the crushing and pressing of grapes to the stabilization of the product, as well as rinsing of fermentation tanks, barrels, and other equipment or surfaces (Brito et al., 2007; Strong and Burgess, 2008; Lucas et al., 2010). It is estimated that the winery industry generates 1.2–9.25 m^3 of wastewaters and 27.4 kg of residues per m^3 of wine produced. However, 43% of the residues are revalorized (Brito et al., 2007; Solís et al., 2018).

The WW are characterized by high organic load and an acidic pH, as shown in Table II. 3.2. Moreover, the examples shown in Table II.3.2 reveal that the organic load of WW is highly variable. The organic content of WW consists of highly soluble sugars, alcohols, acids and recalcitrant high molecular weight compounds, such as, polyphenols, tannins and lignins. The sugars make up a large portion of the chemical oxygen demand, whereas organic acids play a more prominent role in the acidity of the wastewaters (Strong and Burgess, 2008; Lucas et al., 2010: Santos et al., 2014). These wastewaters also vary in color from yellow to dark red, due to the phenolic compounds content (Strong and Burgess, 2008).

Table II.3.2. Winery wastewaters characterization.

Parameter	**Rodríguez–Chueca et al. 2017a**	**Lucas et al. 2010**	**Amor et al. 2019** [a]	**Santos et al. 2014**	**Heredia et al. 2005**
pH	4.3 ± 0.4	4.0	4.4 ± 0.2	4.9 ± 0.2	3.76
COD (mg/L)	5000 ± 1000	4650	600 ± 30	3820 ± 115	15750 ± 750
Phenols (mg/L)	51 ± 7	103	40 ± 2	–	550 ± 150
TSS (mg/L)	1030 ± 150	–	–	1215 ± 120	–
BOD_5 (mg/L)	–	–	145 ± 5	2110 ± 105	–

[a] after evaporation process, for 12 h at 80 ºC, to remove possible volatile organic compounds

Note that, WW production is seasonal, and a higher amount of wastewater is generated in the first 3–4 months, after grape harvesting. Furthermore, the spatiotemporal variations are very significant, in the composition and quality of WW formed, such as the conditions used during fermentation, such as, for example, the type of yeast and grape used (Souza et al., 2013; Rodríguez–Chueca et al., 2017b).

Some of the environmental impact associated with the WW discharge are the degradation of soil, reduction of soil alkalinity and manganese availability, water pollution, blocking the sunlight, damage to vegetation, seed germination inhibition and odors emissions. WW can also cause eutrophication of water resources, due to the high COD, nitrogen and phosphate content, and suffocation of aquatic and amphibious life. It is worth to mention that even though phenolic compounds are a relatively small portion of the organic load of winery effluents, they can cause significant environmental damage if released untreated in the environment since some of these compounds are toxic to human, animals and many microorganisms, even at relatively low concentrations, and they are also particularly resistant to degradation (Mohana et al., 2009; Ioannou et al., 2015).

The European Directive 91/271/EEC classifies these effluents as similar to urban wastewater. For this reason, some winery industries use wastewater treatments methods resembling those used in Municipal Wastewater Treatment Plants (MWTP) or mix their wastewater with the municipal wastewaters, before their discharge into MWTP (Rodríguez–Chueca et al., 2017a; Rodríguez–Chueca et al., 2017c). In contrast, the wastewaters from rural wineries are often irrigated onto fields, with very little treatment or none, resulting in deleterious side effects (Strong and Burgess, 2008).

Conventional wastewater treatments do not work satisfactorily, due to the seasonal variability and the high organic concentration of winery effluents, and suffer from serious drawbacks, such as, high cost and the formation of toxic by–products (Strong and Burgess, 2008; Rodríguez–Chueca et al., 2017b; Rodríguez–Chueca et al., 2017c).

For these reasons, Advanced Processes (S-AOPs and AOPs) are gaining importance in the treatment of these effluents, due to the capacity of generating free radicals, which can attack and degrade the complex molecules found in WW (Rodríguez–Chueca et al., 2017c).

Even though S-AOP was only recently considered for treatment of agro–industrial effluents, in the last 4 years some advances have been made. Amor et al. (2019) studied the performance of S-AOP in the treatment of a real winery wastewater, with an initial COD of, approximately 600 mg/L, after the removal of volatile compounds. For this purpose, the following parameters were analyzed: the pH value (3–11), the operating temperature (20–60 ºC), the persulfate load (5–25 mM), the activation technique, the metal used and the metal load (5–10) mM. It was concluded that, for the metal activated PS, the optimal operating conditions were a pH of 4.5, a PS load of 5 mM, an iron load of 5 mM and a temperature of 40 ºC. At these conditions 55% COD and 40% TOC removal were achieved. It was also found out that, the UV activated persulfate method was more efficient, achieving 96% and 71% of COD and TOC removal, when the PS load and the pH used were 25 mM and 7, respectively, during 260 min.

Rodríguez–Chueca et al.(2017a) studied the S-AOP performance in the treatment of a real winery wastewater, with an initial COD of 5 g/L. In this study, the pH was kept constant and equal to 5 and the following parameters were analyzed: metal used, metal (0.1–5 mM) and peroxymonosulfate (PMS) load (0.1–10 mM). From this investigation, it was concluded that a PMS load of 10 mM and a cobalt load of 10 mM allow to achieve the maximum COD removal of 23%. It was also concluded that the sulfate radical has disinfection capacity since a PMS and an iron load higher than 0.5 mM allow to remove almost 100% of *Bacillus mycoide*s, *Staphylococcus aureus* and *Escherichia coli*. Cobalt catalyst is shown to have a greater efficiency in COD removal, but iron achieves better results in terms of disinfection.

The performance of the S-AOP for the treatment of a synthetic winery wastewater, with an initial COD of 513 mg/L, was studied by Rodríguez–Chueca et al.(2017b). In this investigation, the following aspects were analyzed: the oxidant agent used (PMS; $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$; KPS; $K_2S_2O_8$; PS; $Na_2S_2O_8$), the metal used (iron or cobalt), the oxidant load (1–50 mM), the metal load (1–50 mM) and the pH value (4.5, 7). It was concluded that a 10 mM load of sodium peroxymonosulfate, an iron load of 10 mM and a pH value of 4.5 allow to achieve a 50% TOC and an 87% COD removal.

Rodríguez–Chueca et al.(2017c) studied the S-AOP for the treatment of a real WW, with an initial COD of 5 g/L. For this study, the following parameters were evaluated: peroxymonosulfate load (1–20 mM), iron load (0.1–8 mM), pH value (2–8) and the operating temperature (20–50 ºC). With this investigation, it was concluded that a PMS load of 2.5 mM, an iron load of 1mM, a pH value of 6.5 and a temperature of 50 ºC allow to achieve 51% COD removal. The enhancement of the S-AOP with an UV radiation was also analyzed, and it was concluded that a UV–LED 70W/m^2 lamp can remove up to 80% COD, 63% TOC and 23% phenolic compounds. The studies mentioned above are summarized in Table II.3.3, which lists the process applied, the conditions tested, the optimum conditions and the results obtained for each investigation.

Table II.3.3. Application of Sulfate Radical based Advanced Oxidation Process to treat winery.

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Metal-Heat or UV activated PS	COD_0=600 ± 300 mg/L^b Co^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} [PS]=[5, 25] mM [Metal]=[5, 10] mM t={90, 240} min pH={3, 4.5, 7, 11} T=[20, 60] ºC	For metal activated PS: [PS]=5 mM $[Fe^{2+}]$=5 mM pH=4.5 t=90 min T=40 ºC For UV activated PS: [PS]=25 mM pH=7 t=240 min	For metal activated PS: 55% COD removal 40% TOC removal For UV activated PS: 96% COD removal 71% TOC removal	Amor et al. 2019
Metal and UV activated PMS	COD_0= 5 ± 1 g/L Fe^{2+}, Co^{2+} PMS=[0.1, 10] mM [metal]=[0.1, 5] mM t=120 min pH=5 T=22 ºC UV-A LED 23 W/m^2	For organic better degradation: [PMS]=10 mM $[Co^{2+}]$=5 mM For disinfection: [PMS]≥0.5 mM $[Fe^{2+}]$≥0.5 mM	23% COD removal 99.97% *B. mycoides* and *S. aureus* removal 99.99% *E. coli removal*	Rodríguez–Chueca et al. 2017a
Metal and Solar activated oxidant agents	COD_0=513 mg/L^a PMS, KPS, PS Fe^{2+}, Co^{2+} [oxidant]=[1, 50] mM [metal]=[1, 50] mM t=180 min pH=4.5, 7	PS and Fe^{2+} [oxidant]=10 mM [metal]= 10 mM pH=4.5	50% TOC removal 87% COD removal	Rodríguez–Chueca et al. 2017b
Iron or Iron/UV activated PMS	COD_0=5 g/L $[HSO_5^-]$=[1, 20] mM $[Fe^{2+}]$=[0.1, 8] mM t=90 min pH=[2, 8] T={20, 60} ºC UV-A LED 70W/m^2, UV-A LED 23W/m^2, UV mercury lamp	$[HSO_5^-]$=2.5 mM $[Fe^{2+}]$=1 mM pH=6.5 T=50 ºC UV-A LED 70W/m^2	80% COD removal 63% TOC removal 23% phenolic compound removal The use of 20 mM PMS and 8 mM of iron allow to achieve a higher phenolic compound removal (56%)	Rodríguez–Chueca et al. 2017c

[a] Simulated wastewater 10 times less concentrated that a real wastewater

[b] Real wastewater after volatile removal

When using iron-heat activated PS, a load of 1.6 gPS/gCOD allows to achieve 60% of COD removal. The application of higher PS-loads in the heat-activated experiments lead to better performances. However, the effect of PS concentration was not evaluated in the metal-heat activated PS process. It was also possible to find out that the UV activated PS consumes a higher amount of oxidant agent – 3.2 gPS/gCOD – than the metal-heat activated PS (1.6 gPS/gCOD), to achieve the same removal efficiency – 60%.

The source of UV radiation and the temperature of the solution play an important role on the PMS load required. From the results comparation of Rodríguez–Chueca et al. (2017a) and Rodríguez–Chueca et al. (2017c), it is verified that, a higher intensity and a higher operating temperature led to a higher removal and a lower consumption of PMS per gram of initial COD. When using a UV-A LED 23 W/m^2 lamp and an operating temperature of 20 ºC, Rodríguez–Chueca et al. (2017a) reported a PMS load of 0.23 gPMS/gCOD, while Rodríguez–Chueca et al. (2017c) used 0.06 gPMS/gCOD, when applying a UV-A LED lamp (70 W/m^2) and 50 ºC as the operating temperature value. It should be considered the global economics of the process since, even though a lower PMS load is required in the latter approach, in this case higher energy consumption will be required for operating the UV lamp and to warm up the reactor.

Comparing the results from Rodríguez–Chueca et al. (2017b) and Amor et al. (2019), it is verified that the iron activated PS achieves a similar COD removal to the iron activated PMS, 50% and 55%, respectively. However, the PMS system requires a lower oxidant agent consumption with UVA-LED.

From the studies that evaluated the efficiency of different metals to activated S-AOP, it was concluded that both iron and cobalt show similar removals, with the use of cobalt achieving slightly higher removals. However, Co is less abundant and more expensive than iron, and this should be considered while deciding which the is best catalyst.

Several studies have been carried out with the aim of evaluating the effectiveness of the Fenton process to treat WW, such as Ormad et al. (2006) and Lucas et al.(2009a).

The effectiveness of the Photo–Fenton–like process for the treatment of synthetic effluent was analyzed by Ormad et al. (2006). The synthetic WW was created from the dilution of red wine and grape juice, to obtain a synthetic wastewater with characteristics like real ones. In this study, the pH value of the solution (3.5), the operating temperature (35 °C) and the light intensity (500 W/m^2) were kept constant, and the effects of the following parameters were analyzed: H_2O_2 concentration (0.02–0.5 M), iron concentration (5–500 mg/L), initial organic load (5–10 g/L) and operating time (5–30 min). With this study, it was concluded that the use of 5 mg/L of Fe^{3+} and 0.5 M of H_2O_2 allows achieving a removal of 99% of TOC, after 5 min. With this study, it was also concluded that the effect of the concentration of reagents is more significant than that of the other variables analyzed.

Lucas et al. (2009a) evaluated the performance of the Solar Fenton process in the treatment of synthetic WW, with an initial COD of 4.45 g/L. Synthetic effluent was created by diluting red wine and grape juice. In these tests, the concentration of H_2O_2 (12 mM) and pH (3) were kept constant, and the concentration of iron (55, 110 mg/L) was varied. In addition, the influence of the concentration of ethanol present in the wastewater was also analyzed. It is concluded that, the use of 55 mg/L allows to achieve a TOC removal of 46% for effluents rich in ethanol and a TOC removal of 93% for effluents rich in sugars and poor in ethanol. Given the discrepancy in the efficiency of the treatment process, depending on the composition of the effluent, the removal of ethanol by air stripping and heating the solution was tested. With this system, there was a 70% reduction in TOC and a 96% of TOC, an 82% COD and a 92% of phenolic compounds removal efficiency, with the Solar–Fenton process, in the ethanol free effluent.

The application of integrated systems involving the Fenton process, as a pos–treatment, was studied by Yang et al.(2008), Lucas et al.(2009b), Ioannou et al.(2013) and Ioannou et al.(2014), and, as a pre–treatment, was studied by Heredia et al.(2005) Santos et al.(2014), Amaral–Silva et al.(2016) and Ferreira et al.(2017). The systems used are represented in Figure II.3.5.

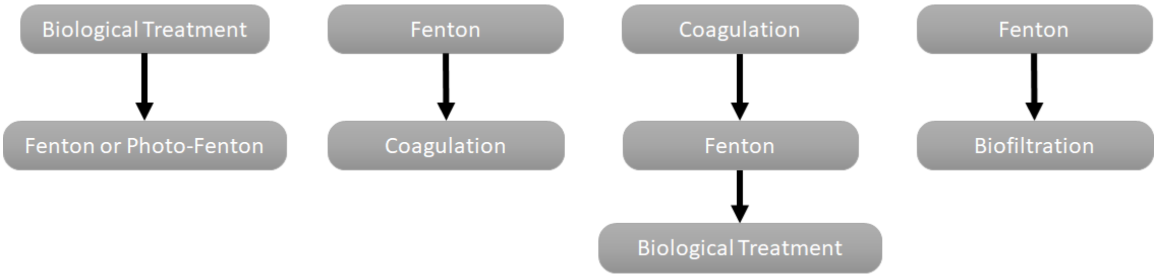


Figure II.3.5. Integrated treatment systems involving Fenton process.

Yang et al. (2008) investigated the use of the Fenton process in the treatment of a real WW, previously remedied by biological action, with an initial COD equal to 636 mg/L. In this study, the effect of iron loading (250–600 mg/L) and H_2O_2 (50–600 mg/L) introduced into the system were analyzed and it was concluded that, after 30 min, 75% of COD removal is achieved when using a concentration of iron and hydrogen peroxide equal to 450 and 500 mg/L, respectively.

Ioannou et al. (2013) analyzed the applicability of the Fenton process, after a biological treatment, for the removal of organic matter present in a real effluent from the wine industry, with an initial COD of 264 mg/L. In this study, the effect of the concentration of iron (5–20 mg/L) and hydrogen peroxide (50–1000 mg/L), temperature (15–40 ºC), and the use of radiation with different intensities (150–1000 W) were analyzed. It was concluded that the use of 5 mg/L of iron, 500 mg/L of H_2O_2, an operating temperature of 25 ºC and an irradiation power of 1000 W allowed to achieve, after 2 h, 71%, 71% and 50% of COD, phenolic compounds and color removal.

Lucas et al. (2009b) studied the performance of the Fenton process in the treatment of a real WW, with an initial COD of 1.56 g/L, after biological treatment. In this study, the influence of the concentration of iron (26–260 mg/L) and hydrogen peroxide (0.39–3.9 g/L) were analyzed, but the ratio between these compounds was kept constant and equal to 15. It was concluded that a 93.2% COD removal was achieved, when 260 mg/L of iron and 3.6 g/L of hydrogen peroxide were used.

Ioannou et al. (2014) analyzed the performance of the solar Fenton process for the treatment of a real WW, with a COD_0 of 180 mg/L, previously remedied by biological treatment. For this purpose, the effect of the iron concentration (1–5 mg/L) and the hydrogen peroxide concentration (250–750 mg/L) were analyzed and the pH value was kept constant (3). It was concluded that the optimal operating conditions are the use of 3 mg/L of iron and 350 mg/L of H_2O_2. Under these conditions, the process proved to be effective on a pilot scale and on an industrial scale, allowing to remove 85% COD, 65% DOC and 80% color, in 180 min.

Santos et al. (2014) evaluated the applicability of the integrated system *Cryptococcus laurentii*/Fenton for the treatment of a real WW with an initial COD of 3.82 g/L. In this study the biological treatment method system was used first because the wastewater showed 55% of biodegradability. After the biological process, the WW has a COD of 385 mg/L, which is equivalent to say that the biological process has an efficiency of 90%. During the Fenton tests, the influence of the hydrogen peroxide concentration (0.98–39.2 mM) was analyzed and the molar ratio H_2O_2/Fe^{2+} and the pH value were kept constant and equal to 15 and 3.5, respectively. With 39.2 mM of H_2O_2, after 30 min, an 80% COD and 90% phenolic compounds removal were achieved.

Heredia et al. (2005) studied the effectiveness of the Fenton process followed by a coagulation process in the treatment of a real WW, with a COD_0 of 16 g/L. In this study, the operating time (3 h) and the operating temperature (30 ºC) were kept constant and the effect of the concentration of hydrogen peroxide, (0.33–1.65 M), iron (5–100 mM) and the dilution factor (1.14–5.33) was analyzed. It was concluded that an iron concentration of 33 mM and a H_2O_2 loading of 0.5 M allow achieving a COD removal of 74% and a TOC removal of 60%, if the initial effluent is diluted with a dilution factor of 1.45. Under these conditions, the biodegradability of the effluent is increased to 40%.

Amaral–Silva et al. (2016) evaluated the effectiveness of the coagulation/Fenton process in treating a real WW, with an initial COD of 5.18 g/L. In this study, different coagulants were tested, and it was found that the use of 1500 ppm of iron sulphate and a pH of 3 allowed to remove 29.2% of the COD. As for the tests with the Fenton process, the hydrogen peroxide concentration (0.012–0.119 mol/L) and the operating time (0.5–12 h) were varied, and the pH value (2.4–3.2) and the iron concentration (920 mg/L) were kept constant at the inherent value at the end of the coagulation process. It was concluded that, the use of 0.024 mol/L of H_2O_2 allowed to remove 42% of the COD, after 8 h, and to increase the biodegradability of the effluent to 40%.

Ferreira et al. (2017) studied the performance of the Fenton/biofiltration (using the invasive clam *Corbicula fluminea*) system in the treatment of a real WW, with an initial COD of 1.99 ± 0.29 g/L. In this study, the effect of hydrogen peroxide (0.029–0.206 M) and iron (0.030–0.291 M) concentration was analyzed. It was concluded that, after 60 minutes, the use of 0.206 M of H_2O_2 and 0.030 M of Fe^{2+} allow to achieve the highest COD removal of 52%. As for the biofiltration tests, these were run for 10 days and the effect of the wastewater dilution factor was investigated. It was concluded that, after 2 days, the biofiltration process reached a maximum of COD removal (~100%), with and without prior dilution of the effluent. The biofiltration set was also important for the removal of dissolved iron and it was able to reduce its concentration from 1.50 mg/L to 0.02 mg/L. In the Table II.3.4 the referred studies were summarized.

Table II.3.4. Application of the Fenton Process to treat winery wastewaters.

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Photo–Fenton–like	COD_0=[5, 10] g/L^a / $[H_2O_2]$=[0.02, 0.5] M $[Fe^{3+}]$=[5, 500] mg/L / t=[5, 30] min pH=3,5 / T=35ºC I=500W/m^2	COD_0=10 g/L / $[H_2O_2]$=0.5 M $[Fe^{3+}]$=5 mg/L t=5 min	99% TOC removal	Ormad et al. 2006
Solar Fenton	COD_0=4.45 g/L^a / $[H_2O_2]$=12 mM $[Fe^{2+}]$={55, 110} mg/L / t=500 min pH=3	$[Fe^{2+}]$=55 mg/L	54% TOC removal	Lucas et al.2009a
Solar Fenton after biological treatment	COD_0=[150, 210] mg/L / $[H_2O_2]$=[0.25, 0.75] g/L $[Fe^{2+}]$=[1, 5] mg/L / t=180 min	$[H_2O_2]$=0.35 g/L $[Fe^{2+}]$=3 mg/L	Removal: 85% COD 68% DOC	Ioannou et al. 2014
Solar Fenton after biological treatment	COD_0=270 mg/L / $[H_2O_2]$=[0.05, 1] g/L $[Fe^{2+}]$=[5, 20] mg/L / pH=2.9 t=120 min / T=[15, 40] ºC P={150, 1000} W	$[H_2O_2]$=0.5 g/L $[Fe^{2+}]$=5 mg/L T=25 ºC P=1000 W	Removal: 71% COD 71% phenolic compounds 50% color	Ioannou et al. 2013
Fenton after biological treatment	COD_0=636 mg/L / $[H_2O_2]$=[50, 600] mg/L $[Fe^{2+}]$=[50, 120] mg/L / pH=3 t=30 min	$[H_2O_2]$=500 mg/L $[Fe^{2+}]$=90 mg/L	75% COD removal	Yang et al. 2008
Fenton after biological treatment	COD_0=1.56 g/L / $[H_2O_2]$=[0.39, 3.9] g/L $[Fe^{2+}]$=[42.8, 428] mg/L / H_2O_2/Fe^{2+}=15 pH=3.5 /T=30 ºC	$[H_2O_2]$=3.9 g/L $[Fe^{2+}]$=428 mg/L	93.2% COD removal	Lucas et al.2009b

Table II.3.4. Application of the Fenton Process to treat winery wastewaters (cont.)

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Fenton after biological treatment	COD_0=3.82 g/L / Cod $_{\text{after biological process}}$=385 mg/L $[H_2O_2]$=[0.98, 39.2] mM / H_2O_2/Fe^{2+}=15 pH=3.5 /t=30 min	$[H_2O_2]$=39.2 mM	Removal: 80% COD 90% phenolic compounds	Santos et al. 2014
Fenton prior to biological treatment and after coagulation	COD_0=5.18 g/L / COD $_{\text{after coagulation}}$=3.67 g/L $[H_2O_2]$=[0.012, 0.119] mol/L $[[Fe^{2+}]$= 920 mg/L; pH~3 t=[0.5, 12] h	$[H_2O_2]$=0.095 M t=8 h	Removal: 42% COD BOD_5/COD=0.4 74% COD after biological treatment	Amaral–Silva et al. 2016b
Fenton followed by coagulation	COD_0=16 g/L $[H_2O_2]$=[0.33, 1.65] M $[Fe^{2+}]$=[5, 100] mM Dilution factor=[1.14, 5.33] t=3 h T=30 ºC	$[H_2O_2]$=0.5 M $[Fe^{2+}]$=33 mM Dilution factor=1.45	Removal: 62% COD and 39% TOC after the Fenton process 74% COD and 60% TOC after coagulation BOD_5/COD=0.4	Heredia et al. 2005
Fenton followed by biofiltration	COD_0=1.99 ± 0.29 g/L $[H_2O_2]$=[0.029, 0.206] M $[Fe^{2+}]$=[0.030, 0.291] M t=1 h	$[H_2O_2]$=0.206 M $[Fe^{2+}]$=0.030 M	52% COD removal after the Fenton process 100% COD removal after biofiltration	Ferreira et al. 2017

[a] Synthetic wastewater prepared from the dilution of red wine and grape juice

Fenton process was applied as a pos–treatment after biological remediation and achieves high levels of organic matter removal, between 71% and 93% COD removal, which allows the disposal of the treated wastewater according with the Portuguese Decreto-lei nº236/98. From the results of these studies, it seems that, to achieve a high degree of degradation, with the Solar-Fenton process (Ioannou et al., 2014), a ratio of 1.9 g/g between the hydrogen peroxide and the initial COD load should be applied. As for the Fenton process, a ratio of 2.50 and 3.50 g/g between the hydrogen peroxide and the initial COD load should be used, when using a molar ratio H_2O_2/Fe^{2+} of 15, while, when considering a H_2O_2/Fe^{2+} molar ratio of 9, a ratio of 0.8 g/g between the hydrogen peroxide load and the initial COD load seems to be more appropriate. It can also be concluded that, when the Solar–Fenton process is applied, a smaller amount of iron is necessary to form hydroxyl radicals.

Fenton process was applied as a pre–treatment before a biological remediation. In two of the works, Fenton process did not achieve high levels of organic matter removal but lead to high levels of biodegradability which allowed an efficient biological post-treatment leading to a final effluent able to be discharged in the natural water courses (Amaral-Silva et al. 2016b; Ferreira et al. 2017).

From the results of these studies, it seems that, with the Fenton process, a ratio of 0.88–3.5 g/g between the hydrogen peroxide and the initial COD load should be applied. It is important to refer that, the process with the longest operating time requires a smaller ratio, while the fastest process requires a higher ratio.

In this section a comparison will be made between the two processes to try to define the most efficient one in terms of COD and TOC removal when applied for WW treatment.

In most cases, S-AOP, based either on PS or PMS, show a lower need for oxidant agent, than the similar Fenton process. As for the use of catalyst, it is not possible to make a comparison between the two processes, as the S-AOP uses both a smaller amount and a higher or similar amount. For example, when comparing the work done by Rodríguez-Chueca et al. (2017c) and the work by Ferreira et al. (2017), it seems that the S-AOP uses a smaller amount of iron, but, when evaluating the study by Rodríguez-Chueca et al. (2017c) and the study of Ioannou et al. (2014), both processes use the same amount of catalyst. And, by comparing the work of Amor et al. (2021) and Ioannou et al. (2013), it is verified that the S-AOP consumes a higher amount of iron than the Fenton.

By comparing the two processes, it was possible to conclude that, while Fenton's process prefers acidic media (pH=3), S-AOP prefers a pH media close to neutrality (pH = [5, 7]). Thus, in S-AOP, the pH change step, to start the treatment process, can be eliminated, since the initial effluent has generally a pH of, approximately, 5.

Although it is promising, the application of S-AOP for the treatment of WW is still scarce in the literature so that a throughout comparison with Fenton’s process is not possible. Special care must be taken regarding the final effluent characteristics. On one hand if the oxidation process is aimed to be applied as a pre-treatment for a further biological oxidation, it should be evaluated if an increase in biodegradability is achieved. On the other hand, if the goal is to discharge the effluent after the oxidation process, care must be taken on the potential toxic impact coming from the by-products resulting from the partial oxidation of the parent compounds.

II.3.5.2. Wastewaters from palm oil mills

The palm oil industry is one of the largest agro-industries around the world. Malaysia is the biggest producer and holds 50% of the world production (Ming and Chandramohan, 2002). The global production of palm oil, in 2020/2021, was 72.27 million tons of palm oil, which represents an increase of ~10% when compared to the 2016/2017 production of 65.17 million tons (Shahbandeh, 2021).

The production of palm oil is composed by several steps, as illustrated in Figure II.3.6, such as, the fruit reception, sterilization and striping, the digestion of the loose fruitlets, followed by the pressing of the oil-bearing cells of the mesocarp and lastly the palm oil clarification. From the pressing phase two currents are generated, the crude oil and the press cake. The press cake is sent to a depericarping unit to remove the nuts and then the residual fibers are transported to the nut cracking machine or plant. The nuts are then sent to a hydrocyclone to separate the shells and kernel. The kernel is stored for later oil extraction and the shells are sent, along with the fibers, to a boiler for power generation (Sani et al., 2020; Utama et al., 2020; Mohammad et al., 2021).

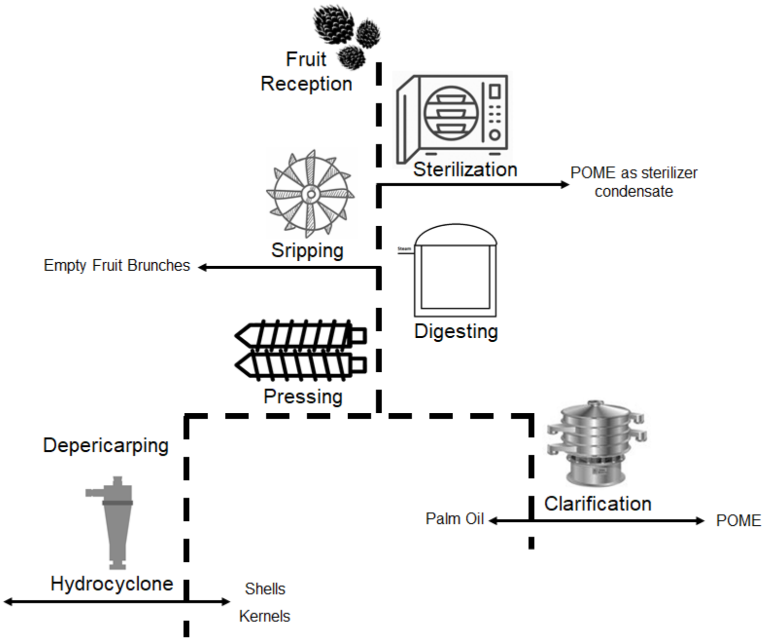


Figure II.3.6. Palm oil production scheme.

Most of the palm oil mills use the addition of water during oil extraction process, as a result, a considerable amount of wastewater is generated. It is estimated that 5–7.5 tons of water are required to produce 1 ton of palm oil, with more than 50% of the water ending up as palm oil mill effluent (POME) (Aris et al., 2008; Sani et al., 2020; Mohammad et al., 2021). For example, in major oil palm-producing nations such as Indonesia and Malaysia, the production of palm oil results in an annual production of up to 3 billion pounds of POME (Mohammad et al., 2021).

The sterilization process acts as one of the main contributors to the POME accumulation, in the form of sterilizer condensate. However, other processes such as, the oil clarification and the hydrocyclone also contribute to the POME generation. It is estimated that the sterilization process generates 36% of the POME, the oil clarification 60% and the hydrocyclone the remaining 4% (Sani et al., 2020; Mohammad et al., 2021).

It is important to keep in mind that POME represents most of the waste from the palm oil industry, about 60% of the total wastes. The remaining wastes being empty fruit brunches (23%), fibers (12%) and shells (5%) (Bashir et al., 2016; Sani et al., 2020).

POME main compound is water, which makes up for 94-96% of its composition, besides it is also constituted by oils (0.6-2%) and suspend solids (2-4%) (Utama et al., 2020; Mohammad et al., 2021).

Even though the composition of POME varies depending on the operating unit where it is produced, it is generally characterized by a high organic load and a low pH, as shown in Table II.3.5. The organic content of POME consists of lignin, hemicellulose, cellulose, carotene, pectin, tannin and phenolic (Bashir et al., 2016; Utama et al., 2020; Mohammad et al., 2021). POME is also hot, viscous and dark brown in color (Bashir et al., 2016; Mohammad et al., 2021).

Table II.3.5. POME characterization.

Parameter	**Mohammad et al. 2021**	**Sani et al. 2020**	**Aris et al. 2008**
pH	3.4 – 5.2	4 – 5	3.8 – 4.5
COD (g/L)	15 – 100	44.3 – 102.7	40 – 50
TSS (g/L)	5 – 54	18 – 46	–
BOD_5 (g/L)	10.25 – 43.75	25 – 65.71	20 – 30
Temperature (ºC)	80 – 90	80 – 90	80 – 90

The direct discharge of POME on the land results in clogging, water logging of the soil, and kills the vegetation on contact. Discharge of the effluent into waterway causes water depletion, resulting in aquatic pollution. In extreme cases, river water consequently turns brown with an unpleasant smell and viscous characteristic. Mortality of fish and other aquatic organism increases, and local people are deprived of the local water sources for domestic uses and fishing. Therefore, the effective techniques for POME treatment are of the uttermost significance (Mohammad et al., 2021).

Although POME is known as a non-toxic substance, due to its high organic load, it cannot be disposed of directly into the environment, without a proper treatment (Utama et al., 2020; Mohammad et al., 2021).

Since POME is biodegradable, biological treatment system is found to be the most suitable method (Aires et al., 2008). More than 85% of palm oil processing mills, in Malaysia and Indonesia, have adopted the ponding system to treat POME, and the result of wastewater treatment is own back to the plantation for fertilization (Sani et al., 2020; Utama et al., 2020; Mohammad et al., 2021).

The ponding system is relatively inexpensive and simple, although it requires a large area of land and long hydraulic retention time – 100 to 120 days (Utama et al., 2020; Mohammad et al., 2021). Besides this, the treated wastewater does not meet waste disposal standards (shown in Table II.3.6) and the ponding system is responsible for methane gas emissions, that result in the ozone layer depletion and insidiously fortify the impact of global warming (Aris et al., 2008; Bashir et al., 2016; Mohammad et al., 2021). Even though the implementation of CH_4 capturing systems provides various advantages such as reducing the greenhouse gaseous emission, generating renewable energy, and improving soil quality, the system is too costly (Mohammad et al., 2021).

Table II.3.6. Discharge limits by Malaysian government (Sani et al., 2020).

Parameters	**POME discharge limits**	
	Department of Environment [a]	**Environmental Quality Act [b]**
BOD_3 (mg/L)	50	100
COD (mg/L)	1000	1000
Total Suspended Solids (mg(L)	400	400
Oil and grease	50	50
pH	5	5 – 9
Temperature (ºC)	45	45

[a] Discharge limits set by the Malaysian Department of Environment in form 1986 onwards.

[b] Quality Environmental Act nº127 from 1974 in force by the Malaysian government.

The pale-yellow color of POME that remains even after the conventional ponding system reveals the presence of recalcitrant pollutants (Sani et al., 2020). A tertiary treatment is therefore needed to remove the color, ensure more effective degradation and mineralization, and further enhance the quality of the biologically treated POME (Aires et al., 2008; Sani et al., 2020). Advanced oxidation processes (AOP) can diminish the pollutants in the wastewater, as compared to other techniques which merely transfer them from one phase to another and are also seen as an economic method (Aires et al., 2008; Sani et al., 2020). Typically, the oxidation process has been exploited as a part of an integrating system with other wastewater treatment methods primarily to synergistically enhance the treatment efficiencies when dealing with wastewaters loaded with refractory organics (Bashir et al., 2016).

Hua et al. (2019) studied the activation of persulfate by heat, pH and transition metals to treat biologically treated POME, with a COD of 509 mg/L (Table II.3.7). To evaluate the effect of PS oxidation, the operational pH (3–12), the contact time (10–60 min), the temperature (40–60 ºC), the metal oxidation state and the metal dosage were investigated. For the pH activated PS, the best result – 30% COD removal – was obtained with a value of 12, after 20 min, while using

256 mg PS/200 mL of sample POME and 30 ºC as the operating temperature. For the iron (II)–heat PS activated system, the best result –70% COD removal – was obtained using a pH value of 9, a PS load of 1.28 g/L, an iron (II) load of 2.03 g/L mg and a temperature of 60 ºC, after 20 min. Lastly, for the iron (III)–heat PS activated system, the best result – 58% COD removal – was obtained using a pH value of 11, a PS load of 256 mg/L, a iron (III) load of 299 mg and a temperature of 50 ºC, after 20 min.

Lin et al. (2016) evaluated the efficiency of the alkaline activated PS as a post-treatment of biologically treated POME, with a COD of 3.29 g/L. For this study, the operational conditions of pH (3–12), contact time (5–240 min) and PS dosage (1.65–19.74 g/L) were investigated. It was concluded that a pH of 11 and a PS load of 6.58 g allowed to achieve a 37% COD removal, after 20 min.

Bashir et al. (2017) analyzed the electro persulfate oxidation to eliminate the remaining non-biodegradable compounds left in the biologically treated POME, with a COD of 2.42 g/L. For this study, the operational conditions of pH (3–5), contact time (10–60 min), PS dosage (0.5–4 g/L) and the current density (20–50 mA/cm^2) were investigated. It was concluded that a pH of 4, a PS load of 0.89 g and a current density of 45 mA/cm2 allowed to achieve a 77.7% COD removal, after 45 min, while using aluminum electrodes. In Table II.3.7 the main results regarding the application of S-AOP for palm oil mills wastewater treatment are presented.

Table II.3.7. Application of Sulfate Radical based Advanced Oxidation Process to treat POME.

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Iron II–Heat or Iron III–Heat	COD_0=509 mg/L [Iron II]=[37.33, 224] mg [Iron III]=[74.66, 448] mg pH=[3, 12] t=[10, 60] min T=[30, 60] ºC	For Iron II – Heat activated PS: PS=256 mg / [Iron II]=187 mg pH=5 / t=20 min T=60 ºC For Iron III – Heat activated PS: PS=256 mg / [Iron III]=299 mg pH=11 /t=20 min T=50 ºC	For Iron II – Heat activated PS: 70% COD removal 90% color removal For Iron III – Heat activated PS: 58% COD removal 90% color removal	Hua et al. 2019
Alkaline activated PS	COD_0=3.29 g//L PS/COD_0=[0.5, 6] g/g pH=[3, 12] t=[5, 60] min	PS/COD_0=2 g/g pH=11 t=20 min	37% COD removal	Lin et al. 2016
Electro – S-AOP	COD_0=2.42 g/L PS=[0.5, 4] g pH=[3,5] J=[20, 50] mA/cm^2 t=[10, 60] min	PS=0.89 g pH=4 J=45 mA/cm^2 t=45 min	77.7% COD removal 98% color removal 99.7% SS removal	Bashir et al. 2017

From the analysis of Table II.3.7, it seems that the iron (II) activated PS and the Electro-S-AOP are more efficient than alkaline activated PS. It is also noticed that, to achieve a 70-80% COD removal, with iron (II) activated PS and Electro-S-AOP, a 2.51 gPS/gCOD_0 and a 0.74 gPS/gCOD_0 mass ratio between PS added and the initial COD is needed.

As POME is considered a biodegradable effluent, most studies about the applicability of Fenton focus on its use as a post biological remediation treatment. However, some articles, concerning the individual use of Fenton and its use as a pre-treatment, are found in literature.

As shown in Table II.3.8, Gamaralalage et al. (2019) found out that, while using a mass ratio of 4 between H_2O_2 added and the wastewater initial COD, to treat a 100-fold diluted POME with an initial COD of 50 g/L, a 90% TOC removal is achieved, after 105 min. Meanwhile, Rajesh et al. (2015) achieved a 64% COD removal, after 30 min, while using a mass ratio of 12 between H_2O_2 added and the wastewater COD.

Regarding the use of Fenton as a pre-treatment, literature data is resumed in Table II.3.8. Babu et al. (2010) discovered that Electro Fenton can improve the biodegradability of the wastewater up to 80% and remove 46% of COD, while using a mass ratio of 0.25 between H_2O_2 added and the wastewater COD and while using Ti/RuO_2 as the anode and stainless steel as the cathode. Lim et al. (2017) also studied the use of Electro Fenton to treat a 100-fold diluted POME. In this study, it was concluded that a 94% COD removal is achieved, when using a mass ratio of 9.9 between H_2O_2 added and the wastewater COD and stainless steel as the anode and graphite as the cathode.

By comparing the two studies, to achieve a higher COD removal, smaller mass ratios between H_2O_2 and iron (II) should be used as well as a higher ratio between H_2O_2 added and the initial COD of the wastewater.

As previously mentioned, most works focus on the application of Fenton after the biological treatment, because POME is considered a biodegradable wastewater. Table III.3.8, shows the main results regarding such approach.

Aris et al. (2008) and Kanakaraju et al. (2017) concluded that Solar Fenton can reach COD removals higher than 80%. In the former work, this was achieved by using a mass ratio between H_2O_2 added and the wastewater COD of 0.93.

Komgnoo et al. (2012) used the Fenton process to treat POME and were able to achieve an 80% COD removal, after 5 min, while using a 0.61 mass ratio between H_2O_2 added and the wastewater COD and a 3.3 mass ratio between iron added and the H_2O_2 added. Aris et al. (2008) also evaluated the Fenton performance to treat POME with an initial COD of 1.5 g/L. While using a 0.77 mass ratio between H_2O_2 added and the wastewater COD and a 0.35 mass ratio between iron added and the H_2O_2 added, a 75% COD removal was achieved, after 1 h. Saeed et al. (2015) concluded that 85% of COD removal can be achieved after 90 min, when a 0.24

mass ratio between added H_2O_2 and the wastewater COD and a 4.1 mass ratio mass ratio between added iron and the added H_2O_2 were used.

Chairunnisak et al. (2017) evaluated the performance of Electro Fenton to treat a biologically treated POME with COD_0 of 9 ± 2 g/L. In this study a COD removal of 99.6% was achieved, after 36 min, while using iron electrodes and a mass ratio of 0.42 between H_2O_2 added and the wastewater COD.

Table II.3.8. Application of the Fenton Process to treat POME.

Process	Tested Conditions	Optimal Conditions	Results	Reference
Fenton	COD_0=50 g/L $[H_2O_2]$=[0.5, 3] g/L $[Fe^{2+}]$=0.5 g/L pH=[2, 5] t=[15, 180] min	$[H_2O_2]$=2 g/L pH=3 t=105 min	90% TOC removal	Gamaralalage et al. 2019
Fenton	COD_0=1408 mg/L $[H_2O_2]$=[0.1, 0.5] M Fe^{2+}/H_2O_2=0.5 g/g pH=3 t=30 min	$[H_2O_2]$=0.5 M	64% COD removal	Rajesh et al. 2015
Electro Fenton prior to biological treatment	COD_0=6.71 g/L $[H_2O_2]$=0.05 M $[Fe^{2+}]$=0.6 mM pH=5 t=2h J=0.05 A/cm^2	–	Electro Fenton: 46% COD removal BOD_5/COD=0.8 Biological treatment: 83% COD removal	Babu et al. 2010
Electro Fenton prior to biological treatment	COD_0=17.14 g/L $[Fe^{2+}]$=[0.01, 0.3] M $[H_2O_2]$=[0.05-0.2] M pH=3 t=[1, 6] h V=[1.5, 7.5] V	$[Fe^{2+}]$=0.01 M $[H_2O_2]$=0.05 M t=3 h V= 1.5 V	94% COD removal In the same optimal conditions, a 48% COD removal is achieved with Fenton	Lim et al. 2017
Fenton and Solar Fenton after biological treatment	COD_0=1.5 g/L $[Fe^{2+}]$=[50, 400] mg/L $[H_2O_2]$=[800, 1500] mg/L pH=3 t=1 h	Fenton: $[Fe^{2+}]$=400 mg/L $[H_2O_2]$=1.15 g/L Solar Fenton: $[Fe^{2+}]$=349 mg/L $[H_2O_2]$=1.40 g/L	Fenton: 75% COD removal 82.5% color removal Solar Fenton: 82.4% COD removal 92.1% color removal	Aris et al. 2008
Solar Fenton after biological treatment	COD_0=73.15 ± 0.12 g/L Fe^{2+}/H_2O_2=[1:10, 1:40] g/g pH=3 t=3 h	Fe^{2+}/H_2O_2=1:30	89% COD removal	Kanakaraju et al. 2017
Fenton after lagoon age	COD_0=[120, 638] mg/L $[Fe^{2+}]$=[0.2, 10] mM $[H_2O_2]$=[10, 150] mM pH=[3, 8.5] t=5 min	$[Fe^{2+}]$=1 mM $[H_2O_2]$=50 mM pH=3	80% COD removal 60% color removal	Kongnoo et al. 2012
Fenton	COD_0=2.8 g/L $[Fe^{2+}]$=[0.02, 0.08] M $[H_2O_2]$=[0.01, 0.05] M pH=[2, 5] t=[30, 150] min	$[Fe^{2+}]$=0.05 M $[H_2O_2]$=0.02 M pH=3.5 t=90 min	85% COD removal 90% color removal	Saeed et al. 2015
Electro Fenton after biological treatment	COD_0=[7, 11] g/L $[H_2O_2]$= [1.28, 3.84] g/L pH=2 t=[15, 45] min V=[10, 20] V [NaCl]=[0, 1] M Iron electrodes	$[H_2O_2]$=3.84 g/L t=36 min V=16 V [NaCl]=0.06 M	99.6% COD removal	Chairunnisak et al. (2017)

Gathering up all these results, it is possible to conclude that the Fenton process needs a mass ratio of ~0.25 between the H_2O_2 added and the initial COD of the wastewater, to achieve, after 60-90 min, a COD reduction of ~80%. To achieve the same efficiency, but with a faster process it is necessary to use of a higher ratio – 4.48 g H_2O_2/g COD_0. The solar Fenton uses 0.93 g H_2O_2/g COD_0, to achieve a removal of 82% within 1h, therefore consumes more H_2O_2 than the Fenton process. As for the Electro-Fenton, it can remove almost 100% of the COD, within 36 min, while using a ratio of 0.43 g H_2O_2/g COD_0. Therefore, with a slightly higher ratio than the one use in the Fenton process, the Electro-Fenton can achieve a higher efficiency in less time.

Comparing the two processes to treat POME, one can verify that S-AOP achieves similar COD removals when compared to the Fenton, after the same reaction time, but using a smaller mass ratio between oxidant added and the wastewater initial COD. As for the Electro-S-AOP and the Electro-Fenton, it is not possible to accurately perform a comparison, because some of the operation conditions are not the same, namely the operation time and the current density or voltage use. These parameters are crucial in what regards the process operating costs.

Throughout the work, it was also found that, while the Fenton process requires a pH adjustment step of the effluent to be treated, the S-AOP operates between a pH of 4 and 5, which encompasses the pH of the untreated wastewater and a pH correction step can be dismissed.

II.3.5.3. Olive mill: Industry andt its wastewaters

The olive oil industry is one of the largest industries worldwide and it is constantly growing. In 2018, the world production of olive oil reached 3.4 million tons, corresponding to an increase of 9.7% compared to the 2011 production of 3.1 million tons (Paraskeva et al., 2006; Espadas–Aldana et al., 2019). It should be noted that, 97% of this production came from the Mediterranean region. Consequently, this region is responsible for a large production of liquid and solid wastes, about 40 to 200 L of wastewaters per ton of olive oil and 400 to 800 kg of residues per ton of processed olive (Paraskeva et al., 2006; Giannis et al., 2007; Medouni–Haroune et al., 2018; Gormez et al., 2020).

The olive oil can be extracted by a discontinuous or a continuous process. The discontinuous process is also known as the traditional pressing process and the continuous process can be divided in two different technologies depending on the separation method used – two and three phase centrifugation process, as shown in Figure II.3.7 (Medouni–Haroune et al., 2018; Pantziaros et al., 2021).

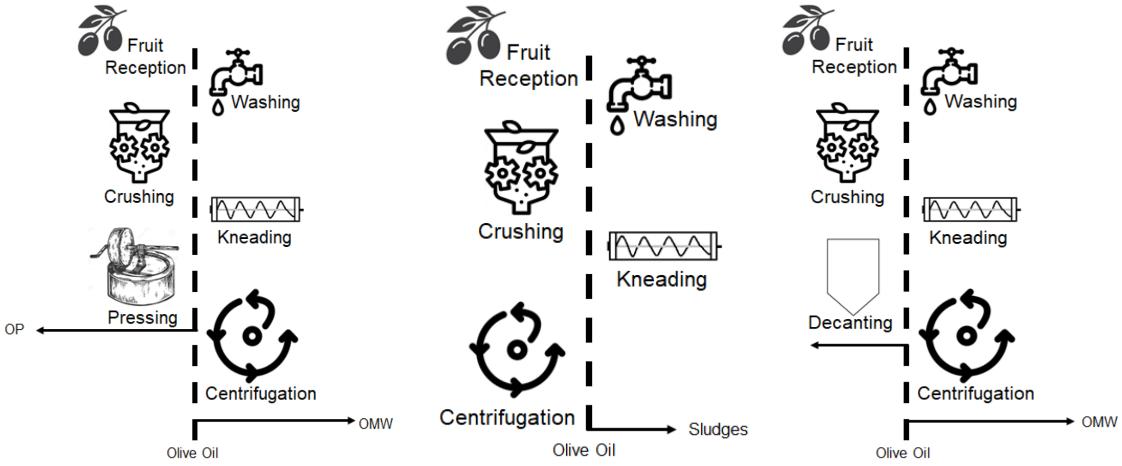


Figure II.3.7. Scheme of continuous olive oil production process.

In Table II.3.9, a comparison between the three different extractions systems is made based on the water consumption, olive oil production and generation of residues and wastewaters.

Table II.3.9. Comparison between the three different extractions systems for olive oil (Azbar et al., 2004; Medouni–Haroune et al., 2018).

Process	**Water consumption (m^3/ton olive)**	**OP production (kg/ton olive)**	**OMW generation (m^3/ton olive)**	**Olive oil production (kg/ton olive)**
Traditional	0.1 – 0.12	~400 (35% humidity)	0.4 – 0.7	200
Two-phase	0.1 – 0.12	~800 (60% humidity)	0.2	220
Three-phase	0.7 – 1.42	~500 (50% humidity)	1 – 1.6	210

The wastewaters, also known as OMW, are characterized by their rich composition in organic matter, as shown in Table II.3.10, and by their seasonality (Paraskeva et al., 2006; Giannis et al., 2007; Gormez et al., 2020).

Table II.3.10 OMW characterization.

Parameter	**Gormez et al. 2020**	**Paraskeva et al. 2006**	**Giannis et al. 2007**
pH	4.5 – 5.8	–	4 – 6
COD (g/L)	30 – 318	45 – 170	40 – 220
TOC (g/L)	–	–	25 – 45
BOD_5 (g/L)	–	35 – 110	35 – 110
Lignins and tannins (g/L)	–	52 – 180	–
Phenolic compounds (g/L)	1 – 10	0.5 – 24	0.5 – 24
TSS (g/L)	24 – 120	1 – 9	–

The solid residues, also known as olive pomace (OP), are characterized by their lignocellulosic matrix (cellulose, hemicellulose and lignin) composed with phenolic compounds, uronic acids, and oily residues, as shown in Table II.3.11 (Medouni– Haroune et al., 2018).

Table II.3.11. OP characteristics.

Parameter	Albuquerque et al. 2004	Leite et al. 2016	Innangi et al. 2017	Medouni-Haroune et al. 2018
Residual oil	–	3.5 %	–	4.5 – 9 %
Moisture	55.6 – 74.5 %	73.5 %	44.1%	25 %
Cellulose	140.2 – 249 g/kg$_{\text{dry weigh}}$	12.5 %	–	14 – 26 %
Hemicellulose	273 – 415-8 g/kg$_{\text{dry weight}}$	22.3 %	–	10 %
Lignin	323 – 556.5 g/kg$_{\text{dry weight}}$	43.2 %	–	27 %
Phenolic Compounds	6.2 – 23.9 g/kg$_{\text{dry weight}}$	8.4 g/kg$_{\text{dry weight}}$	4.5 g/kg$_{\text{dry weight}}$	0.3 – 5 %
pH	4.86 – 6.45	–	6.6	–

The characteristics of OMW and OP vary depending on the climate condition, types of olive trees, olive oil manufacturing process and the fertilizers and pesticides used (Albuquerque et al., 2004; Paraskeva et al., 2006). Although the composition of the OMW varies, it is characterized by having a high organic load (phenols, lipids, organic acids), a high chemical oxygen demand, a high suspended solids content, a low pH, an unpleasant odor and a dark color, due to the high lignins and tannins composition (Paraskeva et al., 2006; Gormez et al., 2020). OP composition is also highly dependent on several factors, but it is generally characterized by having a high organic load, a high content of phenolic compounds and a low pH (Albuquerque et al., 2004; Leite et al., 2016; Medouni–Haroune et al., 2018).

The OMW and the OP are considered a regional environmental problem due to their environmental impacts such as, blocking the passage of the sunlight by forming a colored layer on the surface of natural water, preventing oxygen transfer between the water and the atmosphere by forming an oil layer, changes in soil quality, emission of unpleasant odors and their toxic impact on aquatic life (Justino et al., 2012; Gormez et al., 2020; Duman et al., 2020; Genç et al., 2020).

The management of olive pomace is based on its valorization as a by–product of interest. Thus, it can be used as a fertilizer, a source of organic compounds for the pharmaceutical, food and cosmetic industries, a bioadsorber of heavy metals for water treatment, among others (Medouni–Haroune et al., 2018; Pantziaros et al., 2021). However, OP is usually sent to the extraction industry, to recover the residual oil in its composition (Medina et al., 2018; Domingues et al., 2021a).

In the olive oil extraction industry, OP is discharged into a large open–air pound. After this drying process, OP is subjected to a chemical extraction with hexane to produce crude pomace oil (Medina et al., 2018; Domingues et al., 2021a). During this process a new wastewater is produced, called the olive oil extraction industry wastewater (OOEIW), whose composition is shown in Table II.3.12 (Leite et al., 2016; Domingues et al., 2021a; Pantziaros et al., 2021).

Table II.3.12 OOEIW characteristics.

Parameter	**Domingues et al. (2021a)**
COD (g/L)	50.4 g/L
BOD_5(g/L)	8 g/L
Phenolic compounds (g/L)	4.3 g/L
TSS (g/L)	0.6 g/L
pH	4.6

Thus, the problem of the semisolid waste management is shifted from handling the liquids within the premises of olive mill to the treatment of semisolid waste in huge pomace oil companies. In addition, the OP management problem is not being fully resolved, as the most usual solution is responsible for the production of new wastewaters that need an effective treatment (Albuquerque et al., 2004; Pantziaros et al., 2021). Several methods have been applied for OMW treatment, such as physical, biological, thermal and physical–chemical. However, due to the high phenolic compounds content, the applicability of these techniques is limited (Kilic et al., 2019; Gormez et al., 2020). The molecules that make out the organic load, mainly phenolic compounds, are resistant to biodegradation and, in addition, these compounds can be polymerized into molecules of higher molecular weight, further hampering the degradation process (Gormez et al., 2020). Besides this, these technologies have a high cost and a low efficiency (Kilic et al., 2019; Gormez et al., 2020).

Although prohibited in some European countries, such as Spain, Portugal and Italy, the most common practice for OMW treatment consists of its disposal in lagoons, in which the OMW natural evaporation process takes places. The resulting sludge is then used as a fertilizer. Even though plants can benefit from the application of these fertilizer, seed germination can be inhibited, and plant growth can be delayed, due to the sludge inherent toxicity (Paraskeva et al., 2006; Genç et al., 2020; Gormez et al., 2020). Besides these disadvantages, this method has other drawbacks such as sludge–disposal problems and a low efficiency, because, instead of promoting organic matter degradation, concentrates the effluent (Amaral–Silva et al., 2016). Regarding physical methods, to achieve satisfactory removal rates, it is necessary to use several technologies in series, since the single use is not able to reduce organic matter and toxicity to acceptable values (Paraskeva et al., 2006; Genç et al., 2020). Regarding biological processes, they present several advantages such as being the most suitable from an environmental point of view and the cheapest (Justino et al., 2012). However, due to the low pH and the high phenol load that inhibit microbial growth, these methods are not very effective, moreover are time consuming (Genç et al., 2020; Gormez et al., 2020). Among the physical–chemical methods, advanced oxidation technology has received a lot of attention in recent years, due to its effectiveness in the degradation of resistant pollutants and the possibility of its integration with conventional processes to further increase its efficiency (Amaral–Silva et al., 2016; Justino et al., 2012; Gormez et al., 2020).

As for the treatment of OOEIW, there is a lack of research and information. However, considering their characteristics, it is expected that conventional techniques for treating wastewaters are ineffective, as in the case of OMW treatment.

Gormez et al. (2020) studied the performance of electro-S-AOP in the treatment of an OMW with an initial value of chemical oxygen demand (COD) of 62.65 g/L. An ANOVA model was developed based on a series of experiments, in which the concentration of persulfate ($S_2O_8^{-2}$) varied between 44.87 mM and 301.1 mM, the concentration of iron (Fe^{2+}) from 3.18 mM to 36.82 mM and the applied current between 132 to 468 mA and maintained the pH fixed at 5. Based on the ANOVA model, it was concluded that the influence of the current can be neglected and that the optimum conditions of the process would be a concentration of persulfate between 200 and 250 mM and a concentration of iron between 20 and 25 mM. Thus, these two conditions were tested for 3, 5 and 6 h. The best result was obtained after 6 h when a concentration of persulfate of 250 mM and an iron concentration of 25 mM were used. This way it was possible to obtain a removal of 71.2% of COD and a removal of 88% of the phenolic compounds.

Genç et al. (2020) evaluated the performance of microwave activated PS to treated OWM with an initial COD of 72.4 g/L. The following conditions were analyzed: PS dosage (33-266 g/L), power (120-700 W), pH (2-12) and time (2-28 min). It was concluded a 63% COD removal is achieved while using 266 g/L of PS, 567 W and a pH of 2, after 24 min.

Domingues et al. (2021b) submitted a synthetic olive mill wastewater to homogeneous and heterogeneous S-AOPs using iron sulfate and solid catalysts (red mud and Fe-Ce-O) as the source of iron. The homogenous process at the best conditions (pH 5, 300 mg/L of iron and 600 mg/L of persulfate) achieved 39%, 63% and 37% COD, phenolic compounds and TOC removal, respectively. About heterogeneous S-AOPs process the best performance was achieved by Fe-Ce-O, with an optimal load of 1600 mg/L. At these conditions, 27%, 55% and 5% COD, phenolic compounds and TOC removal were obtained, respectively. Toxicity tests on *Aliivibrio fischeri* and *Lepidium sativum* showed no improvements in toxicity from the treated solutions when compared with the original one. In this study also the compounds effectiveness of S-AOP was evaluated, for a synthetic OMW (Trans-cinnamic acid, 3,4-Dihydroxybenzoic, 4-Hydroxybenzoic, 3,4,5-Trimethoxybenzoic, and 3,4-Dimethoxybenzoic) treatment. They verified that S-AOP can completely degrade the 3,4,5-trimethoxybenzoic compound and can reduce the trans-cinnamic compound by 50% but cannot degrade efficiently the remaining three compounds. Such behavior may be due to the higher selectivity of sulfate radicals towards certain organic compounds when compared to that of the hydroxyl radicals (Brienza and Katsoyiannos, 2017). The mentioned studies were summarized in Table II.3.13.

Table II.3.13. S-AOP to treat OMW.

Process	Conditions Tested	Optimal Conditions	Results	Reference
Electro/Fe (II)/persulfate oxidation	COD_0=62.65 g/L [PS]=[44.87, 301.1] mM [Fe^{2+}]=[3.18, 36.82] mM I=[132, 468] mA pH=5 t={3, 5, 6} h	[PS]=250 mM [Fe^{2+}]=25 mM t=6 h	71.2% COD removal 88% phenolic compounds removal	Gormez et al. 2020
Microwave activated PS	COD_0=72.4 ± 10 g/L [PS]=[33, 266] g/L P=[120, 700] W pH=[2, 12]; t=[2, 28] min	[PS]=266 g/L P=567 W pH=2 t=24 min	63.4% COD removal 56.9% TOC removal BOD_5/COD=0.26	Genç et al. 2020
S-AOP Homogeneous process (synthetic OMW)	COD_0= 800 ± 64 mg/L [PS]=[400, 800] mg/L [Fe^{2+}]=[100, 600] mg/L pH=[3, 11]; t=30 min	[PS]=600 mg/L [Fe^{2+}]=300 mg/L pH=5 t=30 min	39%, 63% and 37% of COD, TPh and TOC removal	Domingues et al. 2021b
S-AOP Heterogeneous process (synthetic OMW)	COD_0= 800 ± 64 mg/L [PS]=600 mg/L [cat]=[1000, 1900] mg/L pH=5; t=30 min	[PS]=600 mg/L [Fe-Ce-O]=1600 mg/L pH=5; t=30 min	27%, 55% and 5% COD, TPh and TOC removal	Domingues et al. 2021b

Mert et al. (2010) studied the effectiveness of the Fenton process in the treatment of OMW, with a COD_0 of 115 g/L. It was concluded that an 81% COD removal is achieved, when using 3.5 g/L of H_2O_2, 600 mg/L of iron(II) and a pH of 3.

Lucas et al. (2009) found that the Fenton process allows to obtain a 69.4% COD reduction of an OMW with an initial organic load of 2 g/L, after the effluent has been diluted 30 times. For this purpose, a H_2O_2/COD_0 mass ratio of 1.75, a H_2O_2/Fe^{2+} molar ratio of 15 and a pH of 3.5 were use.

Reis et al. (2018) evaluated the performance of the Fenton process in the treatment of an OMW, with an initial COD of 8.545 g/L. The following parameters were analyzed: H_2O_2 concentration (1822-9110 mg/L), iron concentration (50-500 mg/L), pH (1.5-3.5) and operating time (1-4 h). It was concluded that a COD removal of 76% was achieved while using 9110 mg/L of H_2O_2, 500 mg/L of iron and a pH of 3.5, after 4h. To reduce the consumption of iron and, consequently, the formation of sludge, a new study was carried out in which the effect of the iron load (10-90 mg/L) and the iron (II)/H_2O_2 mass ratio (0.002-0-008) were studied. In this study, a COD reduction of 81% was achieved, when 50 mg/L of iron and a Fe^{2+}/H_2O_2 mass ratio of 0.002 were used, after 1 h.

Rivas et al. (2001) also analyzed the efficiency of the Fenton process to treat an OMW with a COD_0 of 14.65 g/L. It was concluded that an 85% COD removal is achieved, after 8h, while operating under the following conditions: 1 M of H_2O_2, 0.01 M of Fe(II), a pH of 2.8 and 40 ºC.

Domingues et al. (2021a) proposed a treatment of a real effluent from an olive oil extraction industry (OOEIW), using the Fenton's process integrated with coagulation. The studied effluent has a dark color, with an organic load of about 50 g/L of COD and high toxicity, with 9% of biodegradability. With the best conditions for coagulation (double phased addition of a total of 40 mg/L of coagulant) integrated with Fenton reaction (4 g/L of hydrogen peroxide, 2 g/L of iron (II) at pH 3 with 60 min of reaction) was possible to achieve about 45% of COD removal. With these two treatments the biodegradability increases to a ratio higher than 40% making possible a further biological treatment. In Table II.3.14 the range of conditions tested and the best results to treat OMW by Fenton process are presented.

Table II.3.14. Fenton process to treat OMW.

Process	**Conditions Tested**	**Optimal Conditions**	**Results**	**Reference**
Fenton	COD_0=115 ± 11 g/L $[H_2O_2]$=[0.5, 4] mg/L $[Fe^{2+}]$=[100, 700] mg/L pH=[2,7]; T=25 ºC	$[H_2O_2]$=3.5 g/L $[Fe^{2+}]$=600 mg/L pH=3	81% COD removal 86% phenolic compounds removal	Mert et al. 2010
Fenton	COD_0=2 g/L[a] H_2O_2/COD=[0.35, 1.75] g/g H_2O_2/Fe^{2+}=[7.5, 30] mol/mol pH=[2,9]; t=[10, 60] min	H_2O_2/COD=1.75 H_2O_2/Fe^{2+}=15 pH=3.5 t=60 min	69.4% COD removal	Lucas et al. 2009
Fenton	COD_0=8545 ± 428 mg/L $[H_2O_2]$=[1822, 9110] mg/L $[Fe^{2+}]$=[50, 500] mg/L pH=[1.5, 3.5]; t=[1, 4] h	$[H_2O_2]$=9100 mg/L $[Fe^{2+}]$=500 mg/L pH=3.5;t=4 h	76% COD removal	Reis et al. 2018
	$[Fe^{2+}]$=[10, 90] mg/L Fe^{2+}/H_2O_2=[0.002, 0.008] g/g pH=3.5; t=1 h	$[Fe^{2+}]$=50 mg/L Fe^{2+}/H_2O_2=0.002	81% COD removal 97% phenolic compounds removal BOD_5/COD=0.5	
Fenton	COD_0=14.65 g/L $[H_2O_2]$=[0.2, 1] M $[Fe^{2+}]$=[0.01, 0.1] M pH=[2.8, 7] t=8 h; T= [20, 50] ºC	$[H_2O_2]$=1 M $[Fe^{2+}]$=0.01 M pH=2.8 T=40 ºC	85% COD removal	Rivas et al. 2001
Fenton	COD_0=42.5 g/L $[H_2O_2]$=[2-28] g/L $[Fe^{2+}]$=[0.1, 3] g/L pH=3; t= 1 h	$[H_2O_2]$=4 g/L $[Fe^{2+}]$=2 g/L pH=3 t=1 h	30% COD removal	Domingues et al. 2021a

[a] The OMW was previously diluted 30 times
[b] The OMW was previously diluted 10 times with urban wastewaters

It can be concluded that, generally, S-AOP achieves the same removal as Fenton process to treat OMW. Besides this process seems to require less oxidant and less catalyst to achieve similar COD removals when compared to Fenton's process after similar reaction time. It should be considered that S-AOP can operate at the inherent pH of the wastewater which is an important advantage since no pH correction step will be required.

II.3.5.4. Dairy: Industry and its wastewaters

Global milk production reached in 2020 of 906 million tonnes, which represents an increase of 7.5%, when compared to the 2018 production of 843 million tonnes (FAO, 2021a; FAO, 2021b). The dairy industry produces large volumes of wastewaters, designed dairy wastewaters (DWW). DWW englobes the processing wastewater – composed mainly by whey[1] –, cleaning wastewater and sanitary wastewaters (Slavov, 2017; Sinha et al., 2019). DWW are characterized by fluctuations in their quantity and composition, due to the variety of products produced and since every product needs a separated technological line (Tikariha et al., 2014; Slavov 2017). However, it has been estimated that the dairy industry produces 2.5 m^3 of wastewaters per m^3 of milk produced (Slavov, 2017; Sinha et al., 2019). But, according it Karadag et al. (2015) and Akansah et al. (2020), the dairy industry can generate up to 10 times more DWW than milk industry.

According to Table II.3.15, the DWW are characterized by a high COD and BOD, large variations in pH, an unpleasant odour, a withe-yellowish colour and an average temperature of 18-25 ºC (Slavov, 2017; Sinha et al., 2019). Besides sanitizers and detergents used for washing, the effluent from dairy industry contains plenty of milk constituents (such as casein) and inorganic salts. It also has dissolved sugars, fats, proteins and possibly residues of additives (Sinha et al., 2019).

Table II.3.15. Characteristics of dairy industry wastewater.

Waste Type	COD (g/L)	BOD (g/L)	pH	TS (g/L)	Reference
Dairy effluent	1.9 – 2.7	1.2 – 1.8	7.2 – 8.8	0.9 – 1.35	Sinha et al. 2019
	5	2.8	7.1	3.88	Banu et al. 2008
	5.6	4.48	5.87	6.12	Akansah et al. 2020
	1.5 – 3	0.35 – 0.6	5.5 – 7.5	–	Sarkar et al. 2008
Whey	71.5	20.0	4.1	56.8	Sinha et al. 2019
	60	40	4.46	59	Gannoun et al. 2008

The organic constituents present in the DWW putrefy fast, diminishing the level of dissolved oxygen in the receiving water bodies creating anaerobic conditions and intense odour. Also, the receiving water becomes a breeding place for mosquitoes and flies, which can cause threatening diseases. The casein precipitation from the DWW decomposes further into odorous black sludge. Additionally, DWW promote the growth of certain algae and bacteria which eventually utilize oxygen present in the water, consequently leading to the death of fish due to suffocation (Sinha et al., 2019). Primary treatment mainly consists of removing unwanted components, which could disturb the successful functioning of the treatment plants, and it is usually

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[1] Whey is produced mainly in cheese manufacturing and its main constitute is lactose

composed by mechanical, physicochemical and chemical treatment (Slavov, 2017; International Dairy Federation, 2019). Mechanical treatment removes suspended solids from wastewater. Conventional mechanical procedures reduce insufficiently the organic load because of the low settleable solid concentration in dairy wastewater. Physicochemical treatment destroys and reduces milk fat and protein colloids. Chemical treatment removes mostly colloids and soluble contaminants from milk processing effluents (Slavov, 2017; Sinha et al., 2019). Some of the treatments implemented on a DWW treatment plant are screening, equalization tank, FOG trap, pH correction, coagulation-flocculation (Slavov, 2017; International Dairy Federation, 2019).

Secondary treatments based on biological phenomena may include aerobic and anaerobic solutions and is responsible for the removal of small colloids and soluble compounds (Slavov, 2017; International Dairy Federation, 2019). Conventional aerobic activated sludge systems are not appropriate for DWW treatment. The high soluble COD values in wastewater promotes the vast filamentous growth, which obstructs proper treatment and plant management. The high COD levels create conditions for the preference of anaerobic digestion over aerobic processes, although anaerobic treatment rarely produces clear streams (Slavov, 2017).

Tertiary treatments are applied to remove a particular residual pollutant after biological step (Slavov, 2017). In the dairy sector, nitrification/denitrification and biological or chemical phosphorus removal are the tertiary treatments most frequently encountered. Some dairy uses constructed wetlands to polish the treatment of wastewater (International Dairy Federation, 2019). Wetland systems use natural processes that include self-supported microbial communities. The main drawbacks of their application include the need for a large surface area, the potential risks for surface and ground water pollution, the presence of dangerous volatile substances and the presence of insects (Slavov, 2017).

The dairy industry often encounters difficulties to follow the requirements imposed by the stringent rules for wastewater discharge. Thus, the search for a low-cost technique that is effective is increasing and may contribute to reduce the environmental impacts generated by the dairy industry (Penteado et al., 2015).

S-AOP has not much been applied for DWW treatment. To the best of our knowledge only two works were published in this issue (Table II.3.16).

Panahi et al. (2020) investigated the effect of the following parameters in the efficiency of the sono-activated PS process: pH (3-11), PS load (50-750 mg/L), contact time (10-90 min) and intensity of ultrasound waves – US – (35 - 130 kHz). The highest efficiency – 74.5% COD removal – was obtained at pH 3, persulfate concentration of 500 mg/L, US intensity of US 130 kHz and contact time of 60 min.

Pramanik et al. (2019) studied the performance of UV-activated PS to degrade organics from an anaerobically treated dairy wastewater, as a pre-treatment prior to forward osmosis. A range of PS doses was tested (1-10 mM) for dissolved organic carbon and the optimum dose was 5 mM. The UV lamp used emitted light at 245 nm with a UV energy of 83 W and an intensity of 1.04 W/cm^2.

Table II.3.16 Application of Sulfate Radical based Advanced Oxidation Process to treat dairy wastewaters.

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Sono-activated PS	COD_0=720 mg/L [PS]=[50, 750] mg/L pH=[3, 11] t=[10, 90] min US=[35, 130] kHz	[PS]=500 mg/L pH=3 t=60 min US=130 kHz	74.5% COD removal	Panahi et al. 2020
UV-activated PS	DOC_0=54.8 ± 3.2 mg/L^a [PS]=[1, 10] mM T=20 ºC t=30 min	[PS]=5 mM	30% DOC removal	Pramanik et al. 2019

The radical ·OH generated during the Fenton reaction are highly reactive, and thus can completely degrade organic compounds by hydrogen abstraction. However, for high pollutant loads, this process requires a high consumption of chemicals and causes the generation of high metal sludge (Santos et al., 2015; Salari et al., 2018), which is not economically advantageous. Moreover, the use of AOPs isolated such as Fenton or electrochemical oxidation does not provide satisfactory treatment effectiveness (Vahid and Khataee, 2013, Asaithambi et al., 2020).

Prazeres et al. (2013) studied Fenton-like process as a post-treatment of pretreated cheese whey wastewater by $FeCl_3$ coagulation-flocculation or after $Ca(OH)_2$ precipitation plus aerobic digestion (activated sludge) of cheese whey wastewater (CWW). Raw CWW was firstly pretreated by $FeCl_3$ addition (9 x 10^{-4} M) with no pH change. Once the solid (mainly $Fe(OH)_3$) was settled down, the supernatant was oxidized in the presence of pre-calculated amounts of hydrogen peroxide and ferric chloride. In the case, the effluent was pretreated by lime addition instead of $FeCl_3$. The supernatant was thereafter aerobically biodegraded and, finally, after solids separation, the effluent was again processed in the presence of the system H_2O_2/Fe(III). In the case of coagulation-flocculation by $FeCl_3$ Fenton-like oxidation can reduce the initial to 80% of the initial value. 20% of COD shows recalcitrance to chemical oxidation regardless of the operating conditions used. CWW pretreated by $Ca(OH)_2$ precipitation plus aerobic digestion, the final oxidation system is capable of almost removing the total COD content of the effluent, rendering a relatively clean wastewater suitable for other uses.

Fenton process was evaluated in the treatment of dairy wastewater by Özgüven and Bayram (2021) considering reaction time, pH, Fe^{2+} and H_2O_2 concentrations effects on chemical oxygen demand (COD) and total organic carbon (TOC) removal. The application of advanced oxidation treatment before biological treatment methods seems to be advantageous because these processes play a protective and burden-reducing role in biological treatment systems as they remove toxic or difficult to decompose substances from the environment. According to the results obtained by the authors, the optimum reaction time, pH, Fe^{2+} and H_2O_2 concentrations were found to be 60 min, pH 3, 1 g/L, 1.5 g/L, respectively, while the COD and TOC removal efficiencies were 87% and 75%.

Loures et al. (2013) evaluated the efficiency of Photo-Fenton and Fenton processes in reducing organic matter of dairy effluent. The authors verified that after photochemical treatment, DOC, COD and BOD_5 percentage reduction were 91, 91 and 74%, respectively in the optimal conditions (0.343 mol H_2O_2/L; 0.0215 mol Fe^{2+}/L during 60 min at pH 3). According to the results it can be concluded that this method has a significant potential of application for the treatment of dairy effluent.

Heidari et al. (2021) proposed to design and evaluate the efficiency of the combined electro-Fenton (EF) process as one of the stages in a batch reactor (SBR) - (EFSBR) - process for the treatment of dairy WW. A hydraulic retention time (HRT) of 10 h, sludge retention time (SRT) of 15 d, mixed liquor suspended solids (MLSS) concentration of 3500 mg/L, and sludge volume index (SVI) of 89 were found to be suitable for the treatment of DW in the EFSBR system. Under the optimum conditions of the EFSBR, the simultaneous COD, TN, and TP removal efficiencies were greater than 95%. Therefore, the EFSBR not only allows the reduction of the HRT, SRT, and reaction time (t_R), but also increases the treatment efficiency compared with the sole use of biological or EF treatment. In Table II.3.17 the tested conditions and the optimal results are sumarized.

Table II.3.17. Application of combined Fenton´s process to treat dairy wastewaters.

Process	**Tested Conditions**	**Optimal Conditions**	**Results**	**Reference**
Fenton-like (after coagulation-flocculation with $FeCl_3$)	COD_0= 5.0 g/L $[H_2O_2]$=[0.2-1.07] M $[Fe^{3+}]$=[0.01-0.075] M t=350 min; T=20 ºC	$[H_2O_2]$=1.13 M $[Fe^{3+}]$=1.07 M t=10 min T=20 ºC	~80% COD removal	Prazeres et al. 2013
Fenton-like (precipitation with $Ca(OH)_2$ + aerobic degradation)	COD_0= 2.5 g/L $[H_2O_2]$=[0.2-1.13] M $[Fe^{3+}]$=[0.01-0.075] M t=350 min; T=20 ºC	$[H_2O_2]$=1.13 M $[Fe^{3+}]$=0.050 M t=4 min T=20 ºC	~100% COD removal; ~100% H_2O_2 conversion in 5-6 min	Prazeres et al. 2013
Fenton	COD_0= 4.225 g/L $[H_2O_2]$=[0.5-4.3] g/L $[Fe^{2+}]$=[0.35-4.3] g/L pH=[2-7] t=[0-90] min; T=25 ºC	$[H_2O_2]$=1.5 g/L $[Fe^{2+}]$=1 g/L pH=3 t=60 min	87% of COD and 75% of TOC removal	Özgüven and Bayram 2021
Photo-Fenton/Fenton	COD_0= 9-10 g/L $[H_2O_2]$=[0.255-0.343] M $[Fe^{2+}]$=[0.01808-0.0215]M UV=[0-28] W pH=[3-5] t=120 min; T=[20-35] ºC	$[H_2O_2]$=0.343 M $[Fe^{2+}]$=0.0215 M UV=28 W pH=3 t=120 min T=35 ºC	91, 91 and 74 % of DOC, COD and BOD_5 removal, respectively	Loures et al. 2013
Electro Fenton	COD_0= 3.225 g/L $[H_2O_2]$=[0.2-1.4] mM Current density=[0.5-5] mA/cm^2 pH=[3-11]; t=[5-120] min	$[H_2O_2]$=1 mM Current density=2 mA/cm^2 t=45 min pH=7	TN and TP removal rates were 46% and 37%, respectively	Heidari et al. 2021

For the treatment of DW, the main conclusions to be drawn are that sono activated PS leads to COD removal percentages comparable to Fenton process. The studies presented show that effectively S-AOP is not yet, for dairy wastewater treatment, an alternative with the same effectiveness as Fenton. However, still few studies have been done for this wastewater treatment using S-AOP. Other forms of persulfate activation can be studied and optimized for the same wastewater. Moreover, in such biodegradable and high organic charge streams the chemical oxidation technologies should be envisaged as final treatments to refine the quality of a biological processed wastewater. This way the costs associated to effluents treatment can be minimized.

II.3.5.5. Elderberry: Industry and its wastewaters

It is imperative to treat the huge volumes of wastewater caused by massive industrial production 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 with these technologies are normally a limiting factor for any company.

The elderberries are very interesting from a food point of view because they present a high content in anthocyanin and flavonoids, exhibiting a strong antioxidant potential, as well as anticarcinogenic, antibacterial and antiviral properties, they also are a source of natural food colorants (Cernusca et al., 2012; Szalóki-Dorkó et al., 2014). Elderberry is characterized for its high commercial value as a profitable product for pharmaceutical, medicine and biotechnology sectors (Stănciuc et al., 2018). The berries are essentially consumed as concentrates, food dyes, juices and occasionally are consumed in fresh (Fazio et al., 2013; Silva et al., 2017). The fruit has dark purple colour due to its high content in polyphenols and its growth is seasonal, ripening at the end of summer (Veberic et al., 2009; Sidor et al., 2015; Stănciuc et al., 2018).

Elderberry industry generates large amounts of solid wastes (25–40% of solid residues from total berry weight) and liquid effluent (Brønnum-Hansen et al., 1985). During the industrial process, the elderberry is washed after taking out the branches and stems. The effluent resulting from washing process has in its composition some recalcitrant compounds such as cyanogenic glycosides (namely sambunigrin and prunasin) and m-hydroxysubstituted glycosides (like zeirin and holocalin), which hydrolyse generating cyanide that is toxic and life-threatening, causing nausea, throw up and diarrhoea (Sidor and Gramza-Michałowska, 2015; Młynarczyk et al., 2018). Due to its characteristics, the presence of biorecalcitrant compounds, elderberry wastewater is classified as a complex agro-industrial wastewater characterized by a strong colour (Martins et al., 2012; Amaral-Silva et al., 2016c).

Advanced oxidation processes (AOPs), such as Fenton, photo-Fenton processes and persulfate, are options to remove toxicity and/or enhance the biodegradability of industrial wastewaters into less harmful substances leading to the mineralization in salts, water, and carbon dioxide (Krzemińska et al., 2015, Domingues et al., 2021b). However, few studies were reported regarding elderberry wastewater. The wastewater was characterized by a dark-brown color, high amount of suspended solids (inducing turbidity, a moderate COD value, low total phenol content (TPh) content and low biodegradability as presented in Table II.3.18.

Table II.3.18. Elderberry wastewater characterization.

Parameter	**Amor et al. 2021**	**Ferreira et al. 2020**	**Amaral-Silva et al. 2016c**
pH	5.03 ± 0.05	7-8	6.7
Turbidity (NTU)	2.86 ± 0.07	0.7-1.2	
Redox Potencial (mV)	87.1 ± 0.5		
Conductivity (µS/m)	85.2 ± 0.5	150000-180000	
TPh (mg gallic acid/L)	92.8 ± 1.		29.1
DOC (mg C/L)	457 ± 20	160-210	
TOC (mg C/L)	459 ± 2		
Inorganic Carbon (mg C/L)	1.95 ± 0.30		
COD (mg O_2/L)	1320 ± 45	550-580	680
BDO$_5$ (mg O_2/L)	397 ± 23		33
BDO$_5$/COD	0.30 ± 0.02	No	0.05
TSS (mg/L)	37 ± 2.0		370
Absorbance at 254 nm (diluted 1:10)	0.256 ± 0.004		
TDS (mg/L)			1160

As mentioned before, there are not many studies regarding the treatment of elderberry wastewater. However, Amaral-Silva et al. (2016c) studied the Fenton´s process to depuration of elderberry juice wastewater. The aim of the work was to attain a stream legally able to be discharged into the natural hydrological resources considering the operational costs of the process. The study confirms the effectiveness of Fenton's process as a method for elderberry juice production wastewater treatment reaching 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 operational conditions that allowed to obtain these results were pH= 3, $[H_2O_2]:[Fe^{2+}] = 5$, 20 mM Fe^{2+} and a retention time of 4 h leading to an effluent within the legal limits to discharge into hydric resources.

In other study Amor et al. (2021) evaluated the use of different oxidants such as H_2O_2, PMS and PS in the generation of hydroxyl and sulfate radicals to promote the degradation of an elderberry wastewater in UV-A LEDs presence and transition metal activators, Fe and Co. The authors verified that both AOPs radicals, hydroxyl and sulfate, are feasible processes for elderberry wastewater treatment, with almost complete degradation of the organic matter (99% of TOC removal), with UV-A LED/H_2O_2 (with multi-step additions)/Fe^{2+} and with PMS (single addition)/Co^{2+} processes. When the authors reduced the concentration of catalyst Fe^{2+} (50 mg/L to 25 mg/L) only 75% of TOC was removed. On the other hand, PMS (single step addition)/Co^{2+} process maintains the 99% reduction of TOC removal, even when the Co^{2+} concentration decreased from 50 to 25 mg/L. Based on these results the Co^{2+} concentration was optimized achieving the following optimal operational conditions: [PMS] = 45 mM; $[Co^{2+}]$ = 7.5 mg/L; pH = 3 and reaction time = 120 min. In addition, PMS/Co^{2+} process allows to increase the biodegradability (BOD_5/COD) ratio from 0.30 to 0.53. As the main conclusions of the work, the authors refer that multi-step additions of oxidants promote, in general, higher TOC removals comparatively to single additions. The efficiency of the three oxidants used they can be ranked in the following order: PMS > H_2O_2 > PS. The PMS, without UV radiation and combined with Co^{2+}, reaches a TOC removal of 99%. Analogous results were obtained with H_2O_2, but it was necessary to add UV radiation to promote the iron regeneration.

Ferreira et al. (2020) reported the results of a pre-treatment of non-biodegradable elderberry agro-industrial wastewater at pilot plant scale by different oxidative processes (solar photo-Fenton, solar electrochemistry and ozonation). The authors did an economical approach for improving biodegradability for a subsequent lower-cost biological treatment. Solar photo-Fenton, anodic oxidation, solar-assisted anodic oxidation, electro-Fenton and solar photoelectro-Fenton (SPEF) processes were successfully tested with a range of operation costs between 0.11 and 0.22 €/m^3. SPEF process (20 mg/L of Fe^{2+}) was the fastest (20 min) to attain biodegradability ($COD_b/COD = 0.30$) and it showed the lower associated operation costs 0.11 €/m. In Table II.3.19 the studies of both processes are presented as the comparison between them.

Table II.3.19. Application of S-AOP and Fenton process to treat eledreberry wastewaters.

Process	Tested Conditions	Optimal Conditions	Results	Reference
Fenton	COD_0=680 mg/L [H_2O_2]=[10-250] mmol/L [Fe^{2+}]=[5-50] mmol/L [H_2O_2]: [Fe^{2+}]=[2-5] pH=[3, 6.7] t=4 h	pH=3 [H_2O_2]:[Fe^{2+}] = 5 [Fe^{2+}]=20 mM t= 4 h 6.41 g_{H2O2}/g_{COD} 1.89 g_{Fe2+}/g_{COD}	COD, TSS and color removal of about 78%, 90% and 63%, respectively, and a BOD_5/COD improvement of 600%, from 0.05 to 0.3	Amaral-Silva et al. 2016c
PMS	COD=1320 mg/L [PMS]=60 mM [Co^{2+}] =[5-10] mg/L t=120 min ph=3±0.4	[PMS] = 45 mM [Co^{2+}] = 7.5 mg/L pH = 3 t=120 min 5.41 g_{PMS}/g_{COD} 0.006 g_{Co2+}/g_{COD}	~96% of COD and 99% TOC removed, increase of the BOD_5/COD ratio from 0.30 to 0.53	Amor et al. 2021

Regarding Table II.3.19, it is possible to verify that to remove a gram of COD it is necessary a higher amount of oxidant and catalyst in the case of Fenton process compared to S-AOP. However, there is clearly a lack of studies regarding elderberry wastewater treatment to take global conclusions about the efficiency of both processes.

II.3.6. Conclusions

The main objective of this work is to critically survey the studies carried out for the treatment of agro-industrial effluents using the Fenton process and S-AOP and try to understand whether S-AOP could be viable alternatives for these cumbersome streams treatment. S-AOP is a process with conditions very similar to the Fenton's, still presenting some advantages both in what regards the reactants handling and in the wider pH range in which it can work.

The first conclusion is that there is a huge lack of studies involving S-AOP process for the treatment of agro industrial effluents (when compared to Fenton's process) and thus it becomes more difficult to clearly conclude whether it is beneficial in relation to the Fenton peroxidation. However, in relation to POME and OMW effluents, the studies point to very competitive results. In fact, S-AOP was able to reach similar COD removals when compared to Fenton with less reactants loading and without the need to adjust the effluent pH to ~3. However, further studies must be performed to definitively compare the performance of S-AOP regarding other agro-industrial streams.

Still, there is plenty of room to totally understand and optimize S-AOP technologies. A major point is the activation strategy that may involve radiation, light and photocatalysts.

Moreover, an important aspect while developing a new chemical oxidation process for wastewater treatment relates with the toxic impact of the by-products resultant from the partial decomposition of the parent compounds. In fact, the contaminants total mineralization is not usually achieved, thus it is relevant to infer about the environmental and human health impact of the intermediary compounds. Thus, even if the legal limits for the treated effluent discharge are accomplished some environmental issue may persist. In this sense, ecotoxicological analysis should be performed, which is not usually reported in literature.

Another aspect that must be considered to promote the process full-scale application is its efficiency and stability during long term operation at real treatment conditions.

Besides, economic analysis must be performed to evaluate the treatment costs for both types of treatment. Thus, pilot-scale studies must be performed in order to conclude about the suitability of S-AOPs for agro-industrial wastewaters treatment.

II.4.References

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III. Agro-Industrial Wastewater Treatment Tecnhologies

III. Agro-Industrial Wastewater Treatment Technologies

The treatment of olive mill wastewater is a problem that still does not have an effective solution. To minimize this problem, there has been an improvement in the olive oil production process, moving from three-phase processes in oil mills to two-phase processes, and integrating the later with the oil extraction industry with n-hexane. This improvement does not totally solve the olive mill wastewater problem on its own, it only releases the olive mills from the environmental burden and concentrates the problem in the oil extraction industry.

In this chapter it was proposed a treatment of a real effluent from an olive oil extraction industry, using the Fenton´s process integrated with coagulation. Ion exchange (IE) appears as a complement to the Fenton process, allowing, on the one hand, to remove the iron excess present in the sludge, as well as reduce the COD of the real olive oil industry extraction wastewater (OOEIW) from the Fenton process.

Another approach was taken with the aim of reducing iron sludge, with low-cost catalysts for heterogenous Fenton´s process. These catalysts are wastes rich in iron and other materials naturally present in nature, namely Red Mud (RM), the volcanic rocks of the Azores (VRA) and the volcanic rocks of the Canaries (VRC), to treat a mixture of five phenolic compounds usually present in OMW (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic and Trans-cinnamic acids).

S-AOP are compared with advanced oxidation processes (namely Fenton’s peroxidation) as a depuration alternative. Synthetic olive mill wastewaters were submitted to homogeneous and heterogeneous S-AOPs using iron sulfate and solid catalysts (red mud and Fe-Ce-O) as the source of iron (III).

Finally, the performance of different AOPs in the same multiphasic reactor were evaluated to minimize real oil extraction effluent environmental impact.

To verify the suitability of the proposed methodologies on the treatment of other agro-wastewaters, the depuration of SW was also evaluated. The conventional technologies cannot face against antibiotics and other persistent compounds due to their recalcitrant character. As alternative to the traditional processes, an efficient treatment of SW in a short period of time was assessed. Fenton process was optimized and combined with other methodologies such as biofiltration and/or coagulation. Bearing in mind that the amount of dissolved iron in Fenton’s treated effluent is a major drawback, coagulation and biofiltration processes were assessed as post-treatment steps.

III.1. Olive Oil Extraction Industry Wastewater Treatment by Coagulation and Fenton´s Process

It is based on the publication: Domingues, E., Gomes, J., Castro-Silva, S., Martins, R.C. (2021) Olive Oil Extraction industry wastewater treatment by coagulation and Fento´s Process. Journal of Water Process Engineering. 39, 101818.

III.1.1. Introduction

The olive oil production represents a very important and constantly growing economic sector for the Mediterranean Basin, being the EU responsible for 64% of the worldwide production (IOOC, 2020). The optimum climate conditions and centuries of knowledge led to Spain, Italy, Greece and Portugal covering for 99% of the EU production, representing around 2.0 million tons a year (Espadas-Aldana et al., 2019; IOOC, 2020).

There are three main olive oil production processes: press, two-phase and three-phase separation. The pressing process is the most traditional, being substituted by the other methods due to the lower production efficiency and great labor costs (Messineo et al., 2020). The two-phase and three-phase, as can be seen in Figure III.1.1, continuous methods are then the most common, with a nowadays tendency of countries to update their facilities to a two-phase process due to the huge volumes of hot water added in the centrifugation/decantation step of the three-phase process, up to 6 m^3 per ton of olive oil produced (Esteves et al., 2019; Messineo, 2020). From the two-phase method, a solid waste with around 60% of moisture is formed, which can be further used in a drying/extraction process for recovery of the remaining olive oil, forming a new olive oil extraction industry wastewater (OOEIW). Despite the improvement towards water usage, the problematic involving the olive mill wastewater (OMW) is yet not totally solved, and a full characterization and study of the treatment of this new effluent are still not available (Jeguirim et al., 2020).

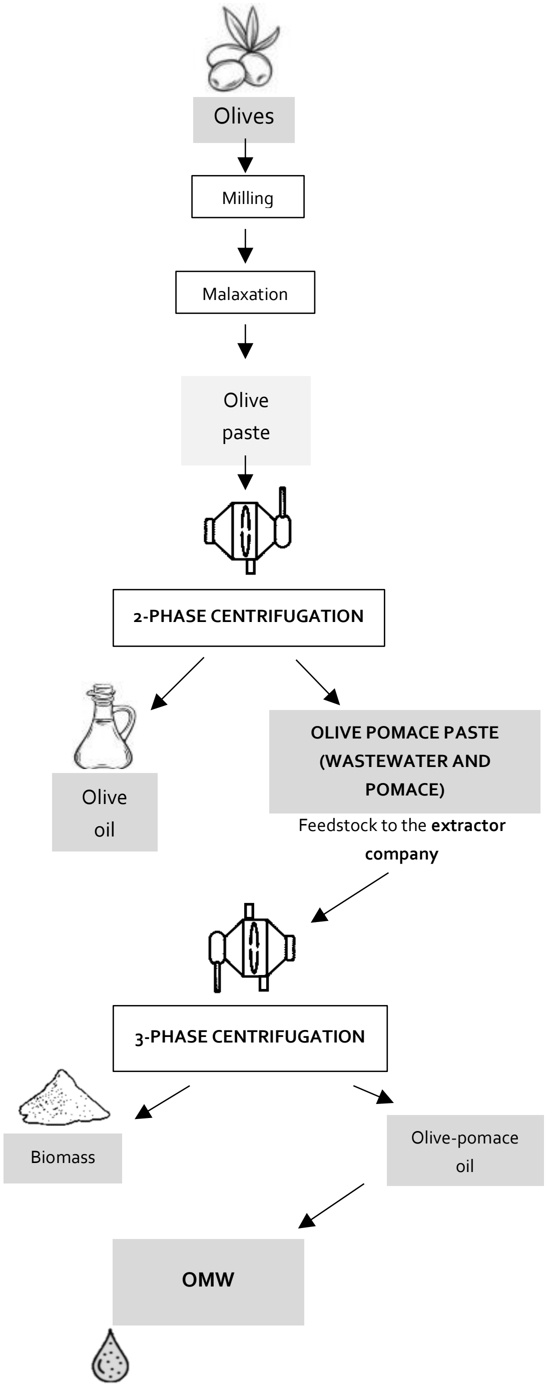

Figure III.1.1. Two-phase and three-phase process for olive mill production.

The OMWs are complex effluents with great variability associated with the different characteristics of the olive cultivation and processing, but overall, is slightly acid (pH~5) and have a high organic and phenolic content (Pavlidou et al., 2014). The phenolic substances are natural antioxidants with high added value, but at the same time have a high antibacterial activity and phytotoxicity, which hinder the application of OMWs as soil amendment for agricultural purposes (Bertin et al., 2011; Annab et al., 2019; Khdair et al., 2019).

Different technologies have been applied for the treatment of the traditional OMW, focusing mostly on the removal of the phenolic compounds and COD, and the increase of its biodegradability. Biological processes are not usually applied directly to the effluent due to its high toxicity, thus, a prior treatment to remove polyphenols or multiple dilutions are needed, which imply higher costs and complexity. Nevertheless, composting, aerobic treatment and, more frequently, anaerobic digestion have been explored (Ayed et al., 2019; Lee et al., 2019; Genethliou et al., 2020). Filtration methods, such as ultrafiltration, nanofiltration and reverse osmosis are able to achieve a considerable decrease of COD, but also have severe fouling problems, a low flow operation and high associated costs (Ochando-Pulido et al., 2013, 2014; Rikmann et al. 2014; Stoller et al., 2016; Ioannou-Ttofa et al., 2017; Zekler et al., 2020).

Successful wastewater treatment includes, but is not limited to, reductions in BOD and suspended solids by up to 85%, reduction of Ammonia, Nitrogen and Phosphorous of over 50% and over 99% reduction of coliforms, pathogenic bacteria and viruses (Zekker et al., 2019).

Advanced oxidation processes (AOPs) are specially promising and extensively researched treatment methods for different industrial effluents. They are based upon the formation of highly oxidative species, more importantly hydroxyl radicals ($^{\bullet}OH$), which can efficiently degrade a wide range of compounds. Different AOPs have been employed for OMW treatment, such as photocatalysis (Stoller et al., 2017; Al-Bsoul et al., 2020), ozonation (Martins et al., 2016), peroxone (Khani et al., 2019). The Fenton process is another AOP which has been the target of an increasing number of studies, involving H_2O_2 and an iron source, which are responsible for the peroxide activation at low pH (2-4), needing no energy input for this purpose and occurring at room temperature and pressure (Martins et al., 2016; Esteves et al., 2019; Iboukhoulef et al., 2019).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\cdot} \qquad \text{III.1}$$

Other reactions (Equations III.2 and III.33) are involved in Fenton's process global mechanism.

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-} \qquad \text{III.2}$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad \text{III.3}$$

As said, olive oil process resultant effluents are very difficult to be efficiently treated, thus, the use of pre-treatment processes is commonly applied to enhance and facilitate the effluent degradation. Coagulation and flocculation are very used methods applied in different highly organic loaded effluents, capable of disturbing colloidal formations and promote the aggregation of small particles, leading to their precipitation and consequently reducing the organic content and turbidity of the solution (Lourenço et al., 2017; Ai et al., 2020). It is a simple design and operation process with low energy requirement, with different coagulants/flocculants available, such as aluminum and iron based compounds, anionic and cationic polymers (e.g PDADMAC, PAA, PAH) and its positive results over OMW have already been proven (Lourenço et al., 2017; Esteves et al., 2019; Lee et al., 2019). The key parameters of this process are mainly the stirring velocity, which has been vastly explored, and the pH and coagulant/flocculant loading, that are intrinsically dependent of the type and characteristics of the applied chemical and its compatibility with the solution (Amaral-Silva et al., 2017; Ai et al., 2020).

Nowadays, olive mills are going to a greener operation pathway. That way, the olive oil extraction procedure is going towards two phase decantation due to lowest water demand. The solid waste produced is then sent to refined oil extraction units where further oil is extracted through drying and solid/liquid extraction processes. This way, although the olive mills are theoretically waste free plants, at the refined oil extraction units, a highly pollutant effluent is generated from the wastes leaching and during the processing. This effluent, OOEIW, is challenging, and its management is crucial to safeguard the environment.

To the best of our knowledge the treatment of this kind of effluent provided from refined oil extraction industry was never investigated using such approach. Therefore, this study aims to optimize Fenton´s process and coagulation for the removal of the organic load of this wastewater. Moreover, the optimized conditions were integrated in order to achieve a treatment capable to reduce the toxicity over bacteria *Aliivibrio fischeri* as well as improving biodegradability so that further biological treatment may be implemented. Some studies have already been developed using similar methodologies, even if using olive mill wastewaters and not effluents coming from olive oil mill wastes extraction industries. However, these works validate the approach proposed in this work for a novel effluent. Peres and Lucas (2009) integrated the Fenton process and coagulation / flocculation with lime, to treat a conventional OMW and 99.3% of COD was removed. Also, Yazdanbakhsh et al. (2015) studied a combination of coagulation, acid cracking and Fenton-like, to treat OMW. Once again, through the combination of these processes, its efficiency in removing phenols and COD was proven, as well as in improving on the biodegradability of the effluent. Thus, a similar approach will be evaluated in this new type of wastewater.

III.1.2. Material and methods

III.1.2.1. Effluent´s characterization

The effluent was collected from a refined olive oil extraction plant located in Portugal. This industrial unit receives wet olive mills wastes that are used for refined oil extraction (with n-hexane) through a sequence of drying and liquid/solid extraction. However, while the wastes are stored waiting for being processed, dark color and highly charged liquid leaches, besides, during the wastes processing before extraction a wastewater is produced. Since currently no treatment approach is available, these effluents are collected and stored in tanks. Samples were collected from the tank and stored in 25 L plastic containers to be processed in the laboratory. To simplify the text, the effluent will be referred as OOEIW.

In Table III.1. are present the most important parameters of the effluent, namely the chemical oxygen demand (COD), pH, total phenol concentration (TPh), total solids (TS), total suspended solids (TSS) and total volatile solids (TVS).

Table III.1. Physico-chemical characterization of OOEIW.

Parameter	**Value**
pH	4.8
COD	50.4 g/ L
BOD_5	8 g/ L
Total Suspended Solids	0.6 g/L
Total Volatile Solids	15.3 g/L
Total Solids	27.4 g/L
Total polyphenols	4.3 g/L
Biodegradability (BOD_5/COD)	16 %

III.1.2.2. Coagulation

Polydiallyldimethylammonium chloride (PDADMAC), a highly charged cationic polymer, was applied for effluent coagulation. In a typical coagulation procedure, the amount of a 0.1% PDADMAC solution to achieve the established coagulant concentration was mixed to 200 mL of wastewater in a three phase process: fast stirring (140 ± 5 rpm) during 3 min, slow stirring (30 ± 5 rpm) during 15 min for solids agglomeration and 30 min of sedimentation, being taken samples of the supernatants (Amaral-Silva et al., 2017; Vuppala et al., 2019;). Different concentrations of PDADMAC (5-100 mg/L) and pHs (3-11) were tested. The phased coagulant additions were applied in order to optimize the process. The phased coagulation addition was performed in two times. The first one destabilizes the sample and the second one allows a better aggregation of destabilized particles. This kind of addition can enhance the removal of solids from the liquid phase.

III.1.2.3. Fenton´s reaction

The Fenton's process was performed in 0.5 L and 1.0 L glass reactors, under continuous magnetic stirring (700 rpm) to achieve a homogeneous mixture. In each reaction, the OOEIW was mixed with a certain amount of $FeSO_4$, representing the desired iron load, pH 3.4. The solution was then mixed during 5 min to assure total homogeneity, and the addition of 33% w/v H_2O_2 represented the start of the reaction. The process occurred during 60 min and the raise of pH to 12 by addition of NaOH was applied to quench the remaining H_2O_2 and stop the reaction. Samples were taken during reaction to further analysis. Both the peroxide (1 – 28 g/L) and iron (0.1 – 3.0 g/L) loads were investigated in this study to analyze and optimize their effects over the effluent treatment (Vilardi et al., 2018; Domingues et al., 2019; Vilardi et al., 2020).

III.1.2.4. Analytical Methods

The pH measurements were done using a Crison micropH 2002 equipment.

The chemical oxygen demand (COD) was measured as a representative of the organic matter present in the samples. This parameter was determined by standard method 5220D (Greenberg et al., 1985). Samples of the Fenton's reaction were measured after precipitation to avoid iron particles interference. Each glass vial was filled with a solution containing 1.2 mL of a digestion solution ($K_2Cr_2O_7$), 2.8 mL of acidic solution (H_2SO_4 and Ag_2SO_4) and 1.0 mL of the sample. Each solution was tested in duplicate and with a control using distilled water. The vials were placed in ECO25 – Velp Scientifica thermoreactors for 2 h at 150 °C. After cooled down, sample's absorbances were measured at 605 nm in a WTW photolab S6 photometer and COD values were obtained using a calibration curve prepared using potassium hydrogen phthalate, within the range 100-4500 mgO_2/L.

The biochemical oxygen demand (BOD_5) was obtained by measuring the dissolved oxygen (DO), comparing it at the start and after 5 days of incubation using microorganisms obtained from a garden soil. Measurements were conducted using a CONSORT C863 Multi-Parameter Analyzer and the suspension were kept at 20 °C, following the Standard Methods (Greenberg et al., 1985; Martins et al., 2010b)

Total phenol concentration (TPh) was measured using Folin-Ciocalteau colorimetrical method, using a T60 PGinstruments photometer, previously described in Martins et al. (2009). The final TPh value is reported as mg/L GA eq., as gallic acid's standard solutions were used to obtain the calibration curve.

Total solids (TS) were obtained by drying samples at 105 °C until constant weight. Total suspended solids were obtained by filtering a certain volume of the effluent and consequently dried at 105 °C and weighted. Total volatile solids were calculated by calcination of the effluent's sample at 550 °C. These procedures were followed according to the Standard Method 1684 (EPA, 2001).

The coagulant and solutions zeta potentials were determined by electrophoretic light scattering using a Malvern Zetasizer Nano ZS, model ZEN3600 (Malvern Instruments Ltd, UK).

The luminesce inhibition of *Allivibrio fischeri* bacteria was used to determine the ecotoxicity of samples. A bacteria suspension was inoculated in the samples at 15 °C in a LUMISTherm (Dr. Lange (HACH)) and, after 15 min of incubation, the luminescence was directly measured in a LUMIStox 300 (Dr. Lange, HACH) and compared with a blank control, consisting in NaCl solution (2%) with the bacteria. Tests were conducted in duplicate and the solutions pH were previously corrected to a 6.5-7.5 range.

III.1.3. Results and Discussion

III.1.3.1. Coagulation

In order to lower the organic load and the high solids content of OOEIW (Table III.1.1), before the Fenton process, several experiments were carried out. First, the effluent pH was changed in order to verify its influence on the sedimentation of the organic load and the zeta potential was evaluated, Table III.1.2. By observing the values of the zeta potential, it can be concluded that it is an anionic effluent. Moreover, its anionic charge increases with increasing pH (Table III.1.2). Therefore, the choice of a cationic coagulant is essential to neutralize the dielectric layer. PDADMAC was chosen due to its high molecular weight and its positive charge. This polyelectrolyte was used by Zagklis et al. (2012) in a previous study for the coagulation/flocculation of an industrial paint wastewater with good results.

In the next step for the various pH studied, a small amount of PDADAMAC (5 mg/L) was added to evaluate its improvement in the removal of COD. The results are presented in Figure III.1.2.

Table III.1.2. OOEIW zeta potential.

pH	Potential Zeta (mV)
3	-4.88
4.8	-7.22
12	-10.7

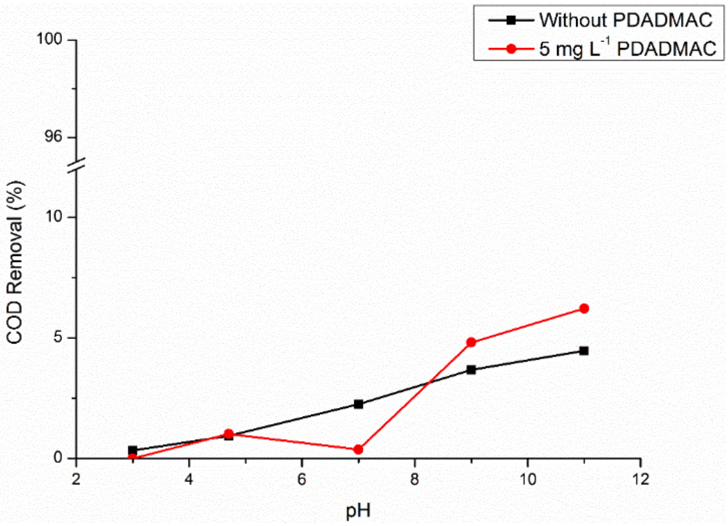

Figure III.1.2. pH effect on effluent of COD removal without and with 5 mg/L of PDADMAC. (The error between experiments is smaller than 5%).

As can be seen from the results in Figure III.1.2., the higher pH promotes greater COD removal. Adding the PDADMAC coagulant, the effect is even more noticeable in the higher pH range (9-12), achieving a further 2% reduction with the use of the coagulant. This is closely linked with the increase of anionic charge of effluent with the pH increase, since a great potential difference enhances the charge neutralization and the solid liquid separation.

Based on the previous results and considering the use of PDADMAC an advantage, in this section higher loads of PDADMAC at pH 9 were studied, as can be seen in Figure III.1.3. The choice of pH 9 results from the fact that higher pH's enhance the polyelectrolyte effect and it is more economically viable than the choice of pH 12 that would entail higher loads of reactants.

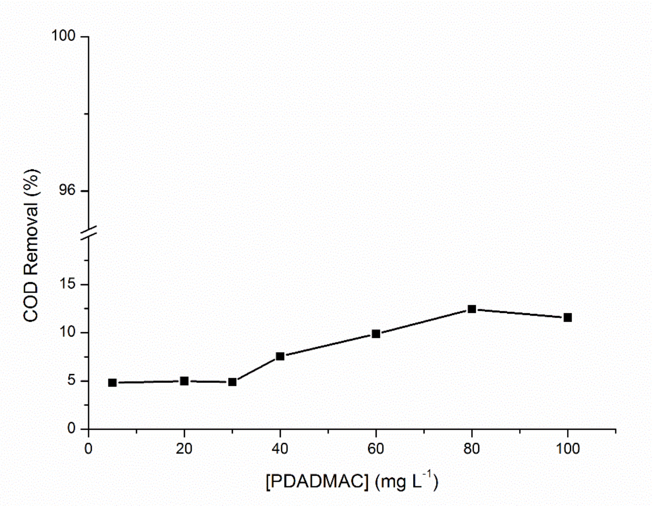

Figure III.1.3. Coagulation effect on COD removal with different loads of PDADMAC. (The error between experiments is smaller than 5%).

The highest percentage of COD removed is achieved with a load of 80 mg/L of PDADMAC, about 12.5%. For PDADMAC at concentrations higher than 80 mg/L, the COD removal decreased instead of increasing. This decrease is attributed to the polyelectrolyte itself, which, as an organic compound, contributes to the COD contained in the samples (Iakovides et al. 2014).

In order to decrease the coagulant load while maintaining the COD removal, tests were performed with a phased addition of coagulant strategy (Figure III.1.4). A maximum total load of 40 mg/L of PDADAMAC was stipulated and different combinations of coagulant addition were made.

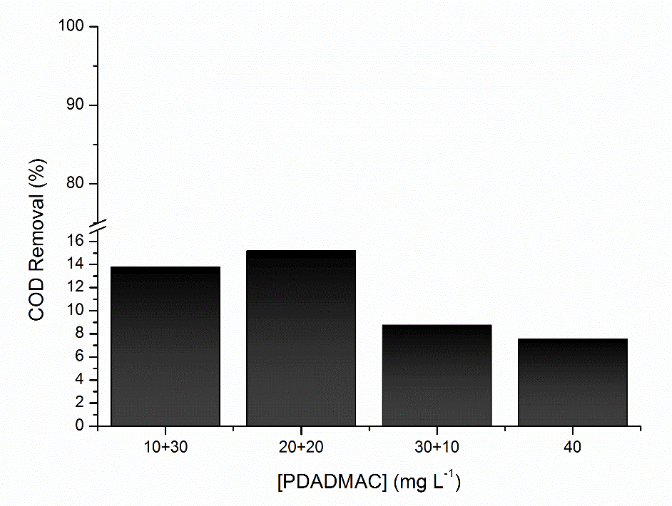

Figure III.1.4. Coagulation effect on COD removal with phased addition of PDADMAC up to a maximum load of 40 mg/L. (The error between experiments is smaller than 5%).

Looking at the results in Figure III.1.4, a combination of 20 mg/L plus 20 mg/L allows a COD reduction of 15%, a value greater than 12.5% of the load in a single phase of 80 mg/L.

Considering the economic variable and the percentage of COD removal, the next tests will have as an ideal condition, the phased addition of 20 plus 20 mg/L of PDADMAC.

III.1.3.2. Fenton´s process

Fenton´s process results from the decomposition of hydrogen peroxide into hydroxyl radicals in the presence of iron ions. The hydroxyl radicals have a high oxidizing power which allows the degradation of organic matter (Walling 1975). Despite being a very efficient technology in the treatment of various effluents, it also has a disadvantage that must be considered that is the need for removing the dissolved iron from the treated effluent. In fact, the required amount of catalyst is usually much higher than the legal threshold of iron allowed for an effluent discharge to the natural water courses (Cao et al., 2009). The study of the iron and the hydrogen peroxide dosage is extremely important in the Fenton reaction. These two parameters mostly determine the efficiency of the process in terms of organic matter degradation and the associated cost. Therefore, it is very important to optimize the iron load, considering that there is enough catalyst that allows the formation of hydroxyl radicals but not using it in excess to avoid a large formation of iron sludge.

Based on this, a study of the influence of the initial concentration of iron on the final COD value was made, which was determined by performing a series of experiments with iron concentrations of 0.1 to 3 g/L and maintaining the concentration of H_2O_2 (4 g/L) during 60 min at pH 3 (Figure III.1.5).

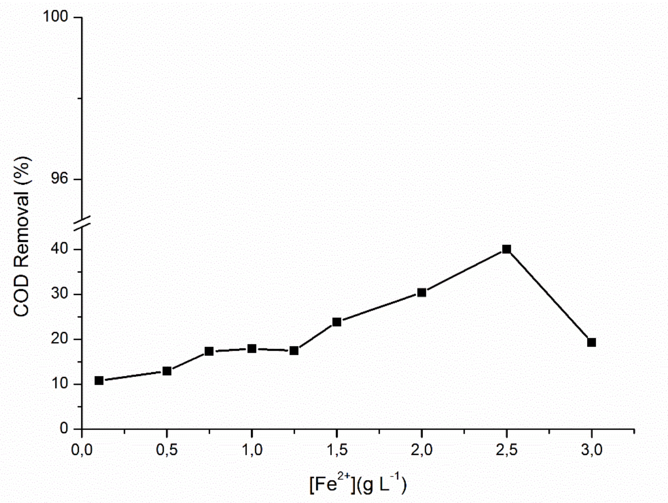

Figure III.1.5. Iron load effect on Fenton´s reaction for OOEIW after coagulation ($[H_2O_2]$ = 4 g/L, t = 60 min, pH = 3). (The error between experiments is smaller than 5%).

The results show that for a load of 2.5 g/L of iron it was managed to obtain the greatest removal of COD, around 40%. Iron values above 2.5 g/L markedly worsen COD removal. Usually the degradation efficiency of organic pollutants increases with the increasing of Fe^{2+} concentration

(Wang et al., 2014; Li et al., 2018) up to a certain limit. Excessive iron not only causes serious loss of iron species and increases the operational costs but also enhances the scavenging effect of ·OH by Fe^{2+} (Hsueh et al., 2005; Panizza and Cerisola, 2009), which has a negative effect on the degradation of organic pollutants. Besides that, a high load of iron can also become a secondary source of contamination for the environment (Nie et al, 2008; Pang et al. 2010).

The choice of the hydrogen peroxide dosage is related to the organic load of the effluent. The greater the organic load of the effluent, the greater the amount of hydrogen peroxide needed to treat this effluent. However, like the iron charge, the hydrogen peroxide concentration also has a limit, the excessive hydrogen peroxide load not only increases the operational costs, but also enhances the scavenging effect of $HO^{\bullet}$ by H_2O_2 (Borràs et al., 2010; Hu et al., 2018) leading to a negative effect on the degradation of organic pollutants. It is therefore essential to determine experimentally the appropriate hydrogen peroxide dosage to treat this OOEIW (Figure III.1.6).

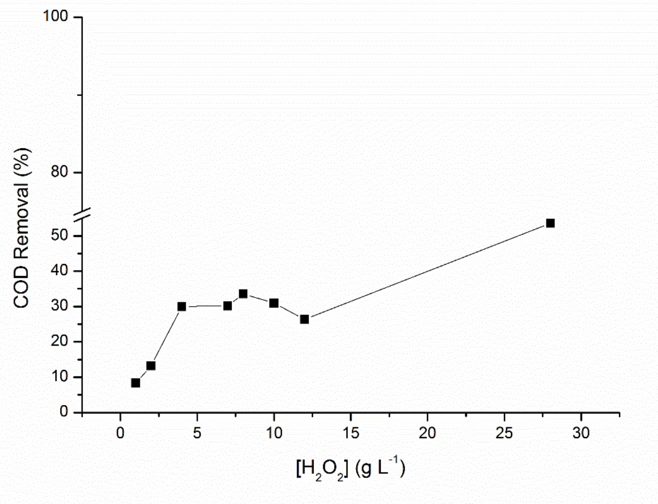

Figure III.1.6. Hydrogen peroxide load effect on Fenton´s reaction for OOEIW after coagulation ($[Fe^{2+}]$ = 2 g/L, t = 60 min, pH = 3). (The error between experiments is smaller than 5%).

In Figure III.1.6 different loads of hydrogen peroxide were studied, keeping the iron load constant (2 g/L) at pH 3, during 60 min. The choice of the 2 g/L iron load instead of the best 2.5 g/L result (Figure III.1.5) had to do with the fact that this reaction is extremely exothermic and a smaller amount of iron allowed to study a wider range of hydrogen peroxide concentration without overheating the reactor. As can be seen in Figure III.1.6, the increase in the charge of hydrogen peroxide allows to increase the removal of COD, the scavenging effect is not being identified here. This can be explained because by excessively increasing in the hydrogen peroxide charge, one may no longer be destroying the organic charge of the effluent, but it is certainly diluting it, which allows the effect of the dilution to hide the effect scavenging. With a load of 28 g/L it was possible to degrade about 53% of the organic matter, while with a load about 2 times below, the percentage of COD removal was about 30%, which is in accordance with the justification dilution effect and not the formation of further hydroxyl radicals. In conclusion, the best condition of the Fenton process, 2 g/L of iron and 4 g/L of H_2O_2 (after coagulation) can remove 30% of COD by itself and overall (including coagulation) it is possible to remove about 45% of COD.

Considering all the results, presented in Figure III.1.5 and III.1.6, the ratio between H_2O_2/Fe^{2+} must be carefully analyzed in order to avoid the scavenging effect and minimize operating costs. When the effect of the ratio was evaluated for similar proportions between different reagent loads, the results were different. For example, with a load of 8 g/L of hydrogen peroxide and 2 g/L of iron the removal of COD is 33.5%, while for a load of 4 g/L of hydrogen peroxide and 1 g/Lof iron the removal of COD corresponds to about 18%, although the ratio $[H_2O_2]/[Fe^{2+}]$ is in both cases 2. This means that more than the ratio, the amount of reagent used is important, since it is an effluent with a very high organic load and more aggressive operating conditions (higher reactants loads) are required for achieving interesting organic matter removals.

III.1.3.3. Effect of Fenton's process on the treated effluents biodegradability / toxicity

The combination of coagulation and the Fenton process does not allow leading to a treated effluent with the characteristics to be discharged into water courses. However, it may be enough to achieve such biodegradability to be referred for a further biological treatment. This integration would allow reducing the treatment costs since the biological processes are conventional wastewater treatments. The direct application of activated sludges is impossible for the management of such wastewater due to its biorefractory nature. The biodegradability of the treated effluent was evaluated considering the BOD_5/ COD ratio, being considered an easily biodegradable effluent when the value is equal to or greater than 40% (Scott and Ollis 1995). The initial effluents are not biodegradable as seen by the low BOD_5/COD. Figure III.1.7 shows the main characteristics of the treated solutions for the best operational conditions.

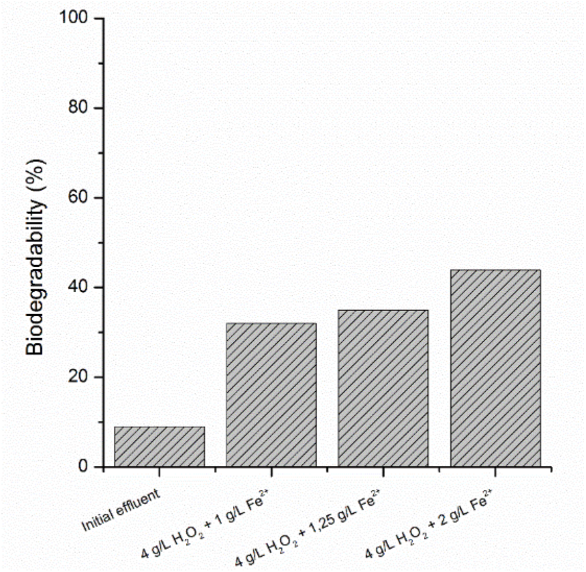

Figure III.1.7. Biodegradability of the treated effluent for best conditions in terms of COD removal. (The error between experiments is smaller than 5%).

The initial effliuent, OOEIW, has a very low biodegradability impossible to be treated by the conventional wastewater treatment plants. Clearly, biodegradability increased with the application of integrated coagulation and Fenton processes. However, only in the conditions of 4 g/L of H_2O_2 and 2 g/L of Fe^{2+} was possible to reach a ratio higher than 40%, which indicates a treated effluent fully biodegradable. As can be seen, fixing the hydrogen peroxide, the biodegradability increases with the iron load, since more hydroxyl radical will be generated promoting the decrease of refractory compounds content leading to the formation of more biodegradable substances.

Toxicity was assessed based on the luminescence inhibition, using bacteria *A. fischeri*. This bacterium was chosen because it is one of the most indicated in the literature for preliminary toxicity tests due to the resistance under adverse conditions (Miralles-Cuevas et al., 2017). In Figure III.1.8 can be found the results of luminescence inhibition for the initial effluent, for the effluent after coagulation process and for the treated effluent after coagulation and Fenton's process (4 g/L H_2O_2 and 2 g/L Fe^{2+}).

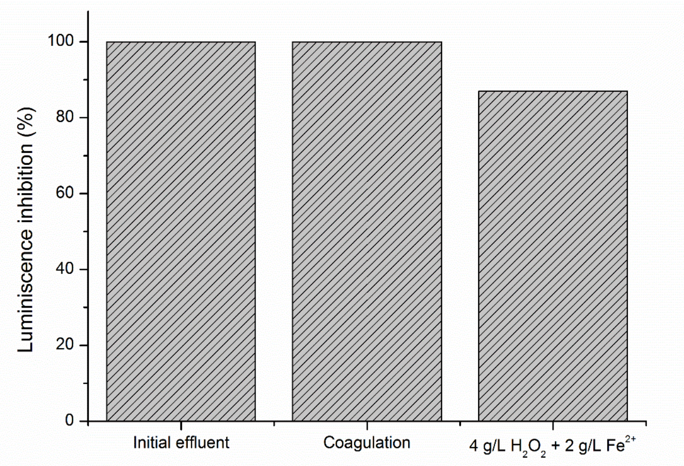

Figure III.1.8. Toxicity of the treated effluent for best conditions in terms of COD removal. (The error between experiments is smaller than 5%).

As can be seen from the results of Figure III.1.8, the initial effluent leads to 100% inhibition of luminescence. The same result is obtained for the effluent after the coagulation process. It can then be concluded that in terms of luminescence inhibition, the coagulation process has no benefit. This is related with the toxicity of the compounds present in the effluent that cannot be removed by the separation processes. However, when the Fenton process is applied, the luminescence inhibition decreases to 87%. Toxicity results from the balance between the eliminated compounds and those generated by oxidation in the Fenton process. In some studies, with synthetic effluent, it appears that the toxicity of the effluent after the Fenton process is superior to the toxicity of the initial effluent (Martins et al., 2010a, Domingues et al, 2019). This means that for this real effluent, the compounds eliminated are more toxic than the by-products generated. Probably to decrease significantly the toxicity regarding to *A. fischeri* it will be needed to strongly increase the oxidant amount (Esteves et al., 2019). However, it will represent a highly impact in terms of treatment cost.

III.1.3.4. Fenton´s process costs

The impact of the treatments applied in terms of operation costs is important to evaluate since it can dictate the process feasibility. The conventional wastewater treatments usually based on activated sludges are considered as low cost. However, the low biodegradability of this effluent does not allow its direct application. The use of advanced oxidation processes such as Fenton’s reagent is required. These approaches are more expensive due to the reactant’s requirements. On this way, it is important to establish a balance between operation costs and treatment efficiency. In fact, for the future it is possible to consider that the treatment efficiency will be more important than the operation costs due to the legal impositions for a proper wastewater management. Therefore, to establish a provisional estimative of costs for treating this effluent the Fenton´s process operation costs were evaluated.

The main cost in the Fenton´s process relates to the cost of the reagents, both for hydrogen peroxide and for the iron catalyst. Table III.3 shows the cost of each of the reagents to treat 1 m^3 of the studied OMW at the best conditions regarding COD removal (4 g/L H_2O_2 and 2 g/L Fe^{2+}). The prices for hydrogen peroxide and iron source provide from the Portuguese industry.

Table III.1.3. Costs of reagents to treat 1 m^3 OMW.

Reagents	€/kg	€/m^3 of treated effluent by Fenton´s process
H_2O_2	0.6	4.8
$FeSO_4$	0.25	1.35

As can be seen, the usage of the reagents on the Fenton's process for wastewater treatment represents about 6.15 €/m^3. Considering, the COD removal obtained through the Fenton's process this operation cost represents 0.41 €/$kgCOD_{removed}$. According to Amaral-Silva et al. (2016) to threat another type of olive oil production wastewater a cost of 0.62 €/$kgCOD_{removed}$ was required. However, in that study was considered also the coagulant and pH correction agents (Amaral-Silva et al., 2016). Besides this, the Fenton´s process encompasses the needs to account the removal of the sludge produced during this process that also entails management.

III.1.4. Conclusions

OOEIW is a complicated wastewater to treat, with a high organic load and high toxicity. Achieving a suitable treatment is crucial for that industry survival. To the best of our knowledge, this is the first work dealing with such cumbersome wastewater. In this study, two technologies were combined to make the effluent able to apply for a biological process. First, 40 mg/L of coagulant (phased addition: 20 + 20 mg/L) were used, which allowed 15% of COD removal. In a second stage, the conditions of the Fenton´s process were optimized and with 4 g/L of hydrogen peroxide and 2 g/L of iron, 30% COD removal was achieved.

Overall, with the combination of the two processes, coagulation and Fenton, a reduction of about 45% in COD was achieved, the toxicity of the effluent was reduced and a biodegradability of 44% was achieved, allowing the application of a biological process. In this context, coagulation followed by Fenton's process seems to be a feasible approach for this cumbersome effluent and should constitute an interesting option for the full-scale OOEIW treatment.

III.1.5. References

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III.2. Ion Exchange to Capture Iron after Real Effluent Treatment by Fenton´s Process

This chapter is based on the publication: Domingues, E., Fernandes, E., Vaz, T., Gomes, J., Castro-Silva, S., Martins, R.C., Quinta-Ferreira, R. M., Ferreira, L.M. (2022) Ion Exchange to Capture Iron after Real Effluent Treatment by Fenton's Process. Water. 14(5), 706.

III.2.1. Introduction

The future availability and quality of water has become a common agenda of different nations and institutions. As a reflection of this situation, new and optimized water treatment technology development has been the focus of the scientific community in order to overcome the water contamination problematic. Besides the need of a technology that can achieve a high efficiency of the degradation of compounds with multiple hazardous characteristics, such as toxicity and persistent behavior, the economical aspect need to be evaluated to obtain a feasible treatment alternative that can be applied at larger scales.

The advanced oxidation processes (AOPs) are a group of interesting technologies, vastly applied in water treatment, as they are based on reactions involving species with high oxidative potentials that are highly efficient and non-selective (Lucas et al., 2007). In fact, AOPs under certain conditions can transform different organic compounds into less hazardous and complex molecules, such as H_2O, CO_2, and other inorganic ions, as products of the respective oxidation reactions (Gallard and Laat, 2000). The Fenton reaction is part of the AOPs group, appearing as an attractive alternative to conventional treatment methods of effluents, in particular as it contains a high concentration of recalcitrant compounds, namely olive oil production effluents (Domingues et al., 2018).

Fenton's reagents applied in the reactions are hydrogen peroxide (H_2O_2) and an iron ions source, which are considerably simple and taken as a greatly effective method for organic pollutants oxidation, already applied in a variety of wastewaters (Lucas et al., 2007; Hussain et al., 2021). The high efficiency of the method is a result of strong hydroxyl radicals ($HO^{\cdot}$) formation and change of oxidation state of Fe^{2+} in Fe^{3+} (Santos et al, 2011). Both iron ions are coagulants, so Fenton's reaction combines both oxidation and coagulation treatments (Badawy and Ali, 2006). The operating conditions that best suit the target effluent are required to be specifically optimized to achieve optimum degradation efficiencies. Fenton's process is dependent on pH, Fenton reagents' concentration and ratio, and initial organic pollutants concentration (Domingues et al., 2021). The possibility of being performed at room temperature and the fact that the pressure conditions use innocuous and easy to handle reactants, as well as the high elimination rates reached are the main advantages of this method (Duarte et al., 2011). However, Fenton's process also has drawbacks; namely, it is typically restricted to low pHs, uses elevated H_2O_2 dosage, and the buildup of ferric sludge affects the oxidation efficiency (Wang et al., 2016; Domingues et al., 2018).

Iron is the most commonly used metal catalyst, due to its abundant availability and lower price (Hussain et al., 2021). The use of a homogeneous iron catalyst in the process leads to an elevated concentration of dissolved iron in the treated liquid post oxidation. Metals may possess toxic effects to living organisms including humans when in very high concentration (Volesky, 2021). Thus, environmental legislation establishes strict limits for metals in discharged wastewater.

The Portuguese environmental legislation (DL n.º236/98) establishes a maximum limit of 2.0 mg/L of total iron, for the release of wastewater into the natural water bodies and for public water source. Therefore, Fenton's process is usually followed by an additional separation method regarding treated water iron content, prior to the effluent's disposal (Martins et al., 2017). Metal ions are commonly removed by chemical precipitation. However, this generates severe drawback, as it leads to a large sludge volume, requiring an additional post management and disposal (Ostroski et al., 2009). Furthermore, the iron concentration in the liquid may be still high even after the precipitation step. Moreover, the catalyst recovery is not possible.

Currently, the ion exchange (IE) process is taken as a very effective method of separation dissolved compounds, due mainly to its low cost, ease of handling, small requirement of reagents, and the possible retrieval of added-value components through the formation of adsorbent/IE resin (Abdel-Ghani et al., 2007). Different materials can be applied as sorbent, such as synthetic resins with different characteristics (Marañon et al., 2007; Üstün et al., 2007; Víctor-Ortega et al., 2016a; Martins et al., 2017; Silva et al., 2020) synthetic and natural zeolites (Kim et al., 2001; Al-Anber et al., 2008) and algae (Mane and Bhosle, 2012).

To surpass the disadvantage of homogeneous Fenton's reaction producing sludge, this present study focuses on the investigation of an alternative strategy for the management and treatment of the resultant real wastewater of an olive oil extraction process (OOEIW). This strategy comprises the implementation of Fenton's process for organic degradation, followed by an iron recuperation step, applying Amberlite@HPR1100 strong-acid cationic resin. The iron load influence in the pretreated olive oil extraction wastewater (POOEIW) stream was investigated for 1–2 g/L range. The equilibrium behavior of this ion has been studied by the application of different prediction models (Langmuir, Freundlich and Temkin). Other empirical models were additionally used for the description of the sorption process dynamics in a continuous fixed-bed column when different experimental conditions were considered. The suggested IE procedure suitability and characteristics of the adsorbent post regeneration were evaluated. Moreover, the possibility of IE resin also removing organic matter from the wastewater was evaluated.

Some studies have been undertaken for iron recovery after the Fenton process and its reuse in the Fenton-like process (Víctor-Ortega et al., 2016b; García-Rodriguez et al., 2017). However, to the best of our knowledge, this is the first time such an approach has been applied to a real wastewater with a very high organic load (~50 gO_2/L). This high COD implies the use of a high load of iron which increases the complexity of IE process. The performance of the resin in the removal of COD, as well as the interference of the organic load in the removal of the iron, was explored for the first time to the best of our knowledge. In addition, which types of pollutants are more selective to the resin among the organic matter in the real effluent was investigated. Therefore, this study builds on previous studies but accounts for relevant factors that have not been discussed before.

III.2.2. Materials and methods

III.2.2.1. Ion exchange resin and chemicals

Amberlite@HPR1100 resin, provided by Sigma-Aldrich (St. Louis, MO, USA), physically and chemically characterized in Table III.2.1, was used in the IE tests.

The chemicals heptahydrate iron sulfate, hydrogen peroxide, sulphuric acid and sodium hydroxide were obtained from PanReac.

Table III.2.1. Physical characteristics of Amberlite@HPR1100.

Appereance[a]	Amber, translucent, spherical beads
Copolymer, Matrix[a]	Styrene-divinylbenzene, Gel
Functional group[a]	Sulfonic acid
Ionic Form as Shipped[a]	Na^+
Particle diameter[a] (μm)	585 ± 5
Surface area[b] (m^2/g)	0.673
Average pore diameter[b] (nm)	2.595
Pore volume[b] (cm^3/g)	0.0004
Real density[b] (g/cm^3)	1.227

[a] Information obtained by supplier.
[b] Determination by nitrogen porosity.

The real effluent comes from a refined oil extraction plant located in Center region of Portugal. Wet olive mills waste, resulting from the production of olive oil in two phase process, are used for oil extraction. While waiting for being processed, these wastes are stored and a dark color and highly charged liquid leaches, besides, during the wastes processing before extraction a wastewater is produced. The olive mill wastewater formed are collected and stored in tanks because no efficient treatment approach is available. For this study, samples collected from the tank were stored in 25 L plastic containers to later be used in the laboratory.

III.2.2.2. Fenton´s reaction

Fenton’s tests were carried out in a batch stirred reactor (0.5 L at 700 rpm) for a homogeneous mixture. The catalyst, $FeSO_4.7H_2O$, was added to the effluent and with addition of H_2SO_4 the pH was adjusted to 3 due to iron’s solubility and to ensure higher reaction rate. The solution was then mixed for 5 min to assure total homogeneity, and the addition of the required volume of 33% w/v H_2O_2 represented the start of the reaction. After reaction (60 min), the effluent goes directly to the IE process.

The conditions for the Fenton reaction were previously optimized by Domingues et al. (2021): pH 3; $[H_2O_2] = 4$ g/L; $[Fe^{2+}] = 2$ g/L and t = 60 min. Physicochemical characteristics of OOEIW after Fenton (FOOEIW) process, which will be used later in IE, are presented in Table III.2.2.

Table III.2.2. Physico-chemical characterization of OOEIW before and after Fenton´s process.

Parameter	**Before Fenton process**	**After Fenton process**
pH	4.8 ± 0.3	3-3.4
COD (g O_2/L)	50.4 ± 5	17.5 – 22.5
BOD_5 (mg O_2/L)	8000 ± 800	770 – 1100
Biodegradability (BOD_5/COD) (%)	0.16 ± 0.05	44
$[Fe^{3+}]$ (g/L)	---	~2

III.2.2.3. Batch adsorption experiments

Amberlite@HPR1100 was washed with several cycles of 1.0 M HCl, 1.0 M NaOH and water for removing solvents and other impurities, in a fixed-bed column, before being used as adsorbent. The last conditioning step consisted of contacting the resin with a HCl solution (1.5 M) to convert it to the H^+ form. The resin was regenerated, repeating the conditioned method before being referred after each operational cycle. To determine equilibrium isotherms, batch tests were performed by contacting 20 or 40 mL of iron solutions with olive oil extraction wastewater of a known concentration with different conditioned resin amounts (0.2–5.4 g) at pH 3 (characteristic pH of the Fenton reaction). The sealed flasks were continuously stirred in a thermostatic bath for 24 h at constant temperature (25 °C) until equilibrium was reached. In the end, the solid (resin) and liquid phase were separated by filtration and the amount of iron in the liquid phase, quantified. The amount of iron absorbed, qe (mg/g), by the resin was calculated by the Equation III.1.

$$q_e = (C_0 - C_e)V/m \tag{III.1}$$

where C_0 and C_e are the metal ion concentration in the beginning and equilibrium phase (mg/L), respectively, V is the amount of solution (L) and m is the mass of resin used (g).

In order to infer the role of adsorption in the real wastewater chemical oxygen demand (COD) abatement, some batch IE experiments were also performed with simulated effluents. Thus, a synthetic solution of humic acid (Sigma-Aldrich) with the same COD of the real effluent tested was mixed with iron sulphate (the same load applied in Fenton's process–2 g/L) and subjected to IE experiments at batch conditions. The same was performed but with a synthetic solution of 5 phenolic acids (trans-cinnamic, 3,4-dimethoxybenzoic, 4-hydroxybenzoic, 3,4,5-trimethoxybenzoic and 3,4-dihydroxybenzoic acid) at 100 mg/L each. These acids are known to be part of the composition of the real wastewater.

Freundlich, Langmuir, Temkin and Langmuir–Freundlich isotherm models described the equilibrium characteristics of sorption of Fe^{2+} ions by the resin Equations (III.2)–(III.5), respectively:

$$q_e = q_{max}K_L C_e/(1 + K_L C_e) \tag{III.2}$$

$$q_e = K_F C_e^{nF} \tag{III.3}$$

$$q_e = B\ln(AC_e) \tag{III.4}$$

$$q_e = Q_m(K_a C_e)^n/1 + (K_a C_e)^n \tag{III.5}$$

The maximum absorption capacity by the absorbent is q_{max} (mg/g) the Langmuir constant correlated to the energy of adsorption is K_L (L/mg) (Gupta, 2009; Abbas et al., 2014); the Freundlich constant is K_F ($mg^{1-(1/n)}L^{1/n}$ /g) and the heterogeneity of the adsorbent surface is described by n_F, the equilibrium constant suggestive of adsorption intensity (Freundlich, 1906). The Temkin model takes into consideration the effect of interactions on the adsorption process between adsorbent (resin) and adsorbate (iron) (Temkin and Pyzhev, 1940). The parameter A (L/mg) is the equilibrium binding constant, and B (J/mol) is the Temkin constant associated to the heat of adsorption.

The Langmuir–Freundlich isotherm considers both the Langmuir-type and Freundlich-type adsorption. The adsorption capacity of the technique is represented by Q_m (mg of sorbate/g sorbant), the concentration in aqueous phase at equilibrium is C_{eq} (mg/L), the affinity constant for adsorption is defined by K_a (L/mg) and the level of heterogeneity is represented by n. The Langmuir–Freundlich isotherm permits classifying the density function for heterogeneous systems using a heterogeneity index n, which is allowed to vary from 0 to 1. For a homogeneous material the value of n is 1, and for heterogeneous materials it is less than one (Umpleby et al., 2001; Turiel et al., 2003).

The Fe^{3+} removal efficiency, R, was calculated by Equation (III.8), as a function of resin dosage (m/V). This equation results from combining the solute mass balance in Equation (III.6), the efficiency definition in Equation (III.7), and Langmuir equilibrium isotherm in Equation (III.2):

$$\mathrm{VC_0} = \mathrm{VC_e} + \mathrm{mq_e} \qquad \text{III.6.}$$

$$R = (C_0 - C_e)/C_0 \qquad \text{III.7.}$$

$$C_0 - C_0(1-R) - \left[\frac{q_{max}K_LC_0(1-R)}{1+K_LC_0(1-R)}\right]\frac{m}{V} = 0 \qquad \text{III.8.}$$

III.2.2.4. Ion exchange continuous experiments

For IE experiments, a continuous packed bed column system was used, containing Amberlite@HPR1100, and a peristaltic pump (Minioplus3-Gilson) to feed the treated effluent. The IE column was made of a glass tube (120 mm height × 15 mm internal diameter).

During the whole experiment, the feed solution was continuously stirred. The flow rate was also a parameter studied (5–15 mL/min) as well as the amount of resin. The initial pH of feed solution was ~3 (the optimal pH for Fenton's process).

Different initial concentration of iron was examined in terms of absorption capacity, at the levels: 1–2 g/L.

At the exit of the column, samples were collected for iron and chemical oxygen demand (COD) analysis. The fraction of the saturated bed (FSB), is defined by Equation (III.9) and quantifies the ratio between the total mass of Fe^{3+} adsorbed in the column until the breakthrough time, t_{bp}, and the mass of iron introduced into the column until equilibrium:

$$\mathrm{FSB} = \frac{\int_0^{\mathrm{tbp}}\left(1-\frac{\mathrm{C}}{\mathrm{Ce}}\right)\mathrm{dt}}{\int_0^{\infty}\left(1-\frac{\mathrm{C}}{\mathrm{Ce}}\right)\mathrm{dt}} \qquad \text{III.9.}$$

the time required to the exit concentration, C, is denominated by tbp and is about 1% of Ce; tex is about 95% of Ce and is the time required to C, tst can be expressed by Equation (III.10):

$$\mathrm{t_{st}} = \int_0^{\infty}\left(1-\frac{\mathrm{C}}{\mathrm{Ce}}\right)\mathrm{dt} \qquad \text{III.10}$$

III.2.3. Results and Discussion

III.2.3.1. Adsorption equilibrium isotherms

The main objective of the use of ion-exchange technology is to withdraw the iron from the sludge resulting from the Fenton process. The Fenton reaction occurs at pH~3, thus, industrially it is not necessary to alkalinize the effluent after Fenton's process to promote iron precipitation. The goal is to directly send the Fenton's treated effluent to the IE process. According to Víctor-Ortega et al. (2016b), during the IE process the removal efficiency of iron ions increases with an increase in the initial pH up to a value equal to 4. At moderate pH with an initial pH on the range of 3–5 the linked H^+ is free from the active sites of the cation exchange resin, which favors the exchange of ions, thus considering the acidic environment beneficial. On the other hand, by increasing the initial pH, there will be lower IE removal efficiencies due to the precipitation of metallic hydroxides as the dominant mechanism and, consequently, lower cation exchange capacity. The pH effect was a parameter widely studied by other authors (Rao et al., 2005; Millar et al., 2015), who corroborated the benefit of a low pH in equilibrium isotherms. For a correct assessment in terms of COD and dissolved iron removal, in this work the Fenton reaction was stopped, using a NaOH solution to increase the pH to 11. Before IE the pH was again adjusted to 3, thus re-dissolving the iron.

The outcome of adsorbent dosage on Fe^{3+} and COD removal was evaluated, changing the initial concentration of iron and COD. The results are presented in Figure III.2.1.

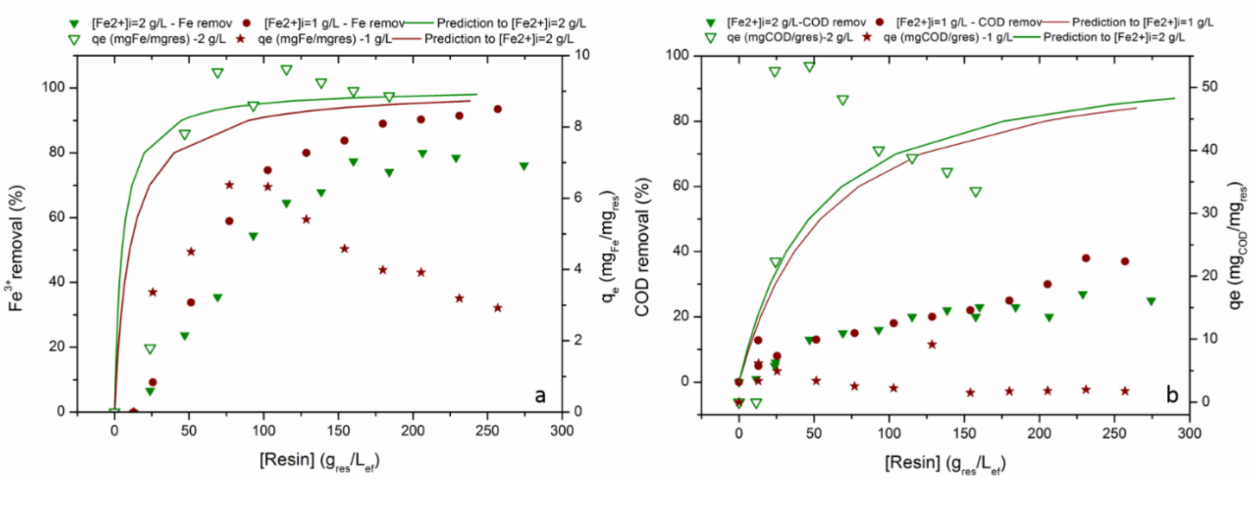

Figure III.2.1. (a) Effect of adsorbent dosage on Fe^{3+} and (b) COD removal by Amberlite@HP1100 in OOEIW pretreated by Fenton´s process.

Figure III.2.1 shows that the increase on the adsorbent load up to the approximate value of 175 g_{res}/L_{ef} improves both iron and COD removal. From this value onwards, removals are constant in the order of 90 and 80% for iron and 20 and 30% for COD, considering an initial concentration of 1 and 2 g/L of iron, respectively. These results are extremely interesting, as the effluent presents a high organic load; with IE it is possible, on the one hand, to face the great disadvantage of the Fenton's process, which is the formation of iron sludge, allowing the iron limits required in the discharge of the effluent to be met. On the other hand, the effluents COD can be further removed after the Fenton process.

From Figure III.2.1a it is still possible to evaluate the effect of iron initial concentration on IE removal efficiency. Iron concentration was evaluated between 1–2 g/L and the results showed that the adsorption of ions by the resin was strongly affected by its initial concentration. When the feed has a lower iron concentration, for the same resin load, higher iron removal is achieved. This decrease in iron removal with increasing iron initial concentration is related to IE resin saturation (Senthil et al., 2009; Víctor-Ortega et al., 2016a). Bulai and Cionca (2011) reported a loss in the iron removal effectiveness with Purolite S930-H resin from 95%, with an initial concentration of 10 mg/L to 20% for an initial concentration of 300 mg/L considering a resin concentration equal to 1 g/L.

The prediction models are based on Equation (III.8) and Langmuir model parameters, considering the initial concentrations of iron (1 and 2 g/L) and the initial concentrations of COD (23 and 20 g/L). The prediction for iron removal is closer to experimental values than the one presented for COD removal. The effluent heterogeneity certainly contributes to having an optimistic model in relation to the experimental values.

The classic Langmuir (1918), Freundlich, Temkin and Langmuir–Freundlich models were selected to describe the equilibrium experimental data for Amberlite@HPR1100 resin regarding iron and COD removal from real OOEIW after Fenton's process (Figure III.2.2).

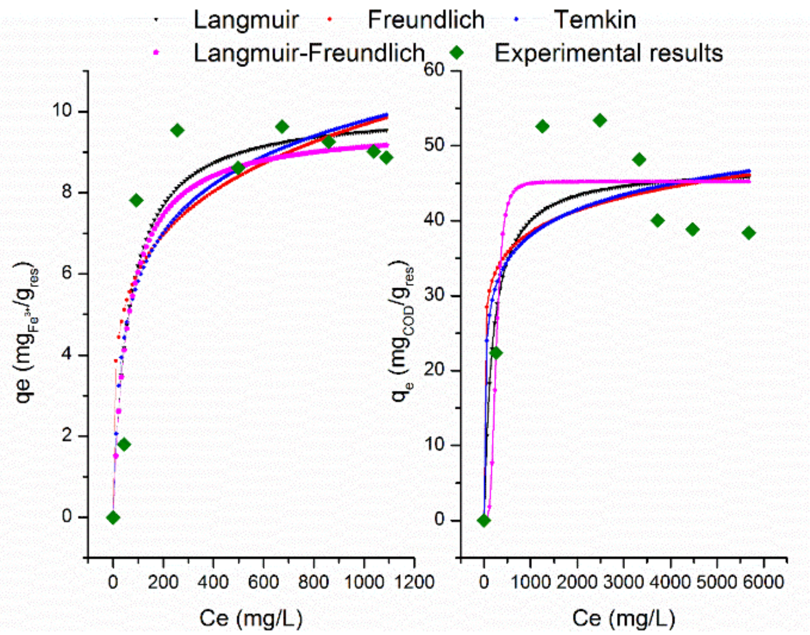

Figure III.2.2. Adsorption isotherms of COD on Amberlite@HPR1100, and fitting through Langmuir, Freundlich and Temkin models for a feed concentration of 2 g/L of iron.

Three equilibrium models Langmuir, Freundlich and Temkin, were used for the experimental data analysis. The parameters of these isotherms were predictable by the nonlinear regression method and are summarized in Table III.2.3.

Table III.2.3. Parameters values of equilibrium models.

	Langmuir			**Freundlich**			**Temkin**			**Langmuir-Freundlich**			
	K_L (L/ mg)	**q_{max}** (mg/g)	**R^2**	**K_F** ($mg^{1-1/n}$ $L^{1/n}$/g)	**n_F**	**R^2**	**A** (L/g)	**B** (J/ mol)	**R^2**	**Qm** (mg/ g)	**K_a** (L/ mg)	**n**	**R^2**
Fe^{3+}	0.02	10.09	0.87	2.37	0.20	0.77	0.30	1.71	0.81	9.66	0.02	1	0.84
COD	0.01	47.35	0.80	18.65	0.10	0.71	2.29	4.92	0.72	---	--		---

The equilibrium data for Fe^{3+} sorption onto Amberlite@HPR1100 can be well described by Langmuir and Langmuir–Freundlich isotherms considering the values of coefficients of determination (R^2), shown in Table III.2.3. The values of R^2 are around 0.80, not as high as they usually appear in the literature for synthetic mixtures, but one must note that it is a real effluent. Thus, a strong interaction and competition between the several compounds present in this cumbersome mixture will occur. This means that several compounds can compete for the active sites in the resin. From the analysis of Table III.2.3, it is also possible to observe that the maximum IE capacity (qmax) by Amberlite@HPR1100 for iron removal is 10.09 mg/g. This value is higher compared for iron adsorption onto olive stones (2.12 mg/g) (Hodaifa et al., 2013). On the other hand, Víctor-Ortega et al. (2016a) studied iron adsorption onto Dowex Marathon C, a strong-acid cation exchange resin, for olive mill effluent reclamation and, in this case the q_{max} was 23.27 mg/g, although the initial concentration of iron was in the range of 0.5–100 mg/L quite inferior to the 2 g/L in this study. With Purolite S930, having an initial iron concentration of 100 mg/L, the maximum experimental iron adsorption was near to 30 mg/g (Bulai and Cioanca, 2011).

Another parameter that is relevant to understanding the Langmuir isotherm is the factor separation R_L, which can be calculated from Equation (III.11):

$$R_L = \frac{1}{1+K_L \cdot C} \qquad \text{III.11}$$

R_L in this case is about 0.67 for an initial iron concentration of 2 g/L, which indicates favorable adsorption, and it can be observed that data fit the Langmuir isotherm model.

Regarding the Freundlich model, the value of R^2 (0.77) was found to be lower than the value of R^2 (0.87) of Langmuir isotherm. With regards the n coefficient, the value is higher than 1, which proves the favorability of the adsorption process. Considering Figure III.2.2, it can be noted that Freundlich model is able to describe the adsorption experimental data with less consistency. Pehlivan and Altun (2006) verified that Langmuir model fits better than the Freunlich model for the experimental data for adsorption of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} ions on Dowex 50 W, a strong-acid cation exchange resin. In addition, Víctor-Ortega et al. (2016a) reached the same conclusion for iron removal with Dowex Marathon C. Martins et al. (2017) concluded the same when recovering iron from a treated synthetic winery effluent with Fenton's process using Lewatite TP207.

The R^2 value for the Temkin model (0.81) is lower than that calculated for the Langmuir model (0.87) but higher than that for the Freundlich model (0.77). The parameters of the Temkin model, A and B, were presented in Table III.2.3 and the heat of sorption process, assessed by Temkin isotherm model, is 4.92 J/mol.

Regarding COD, the Langmuir model is the one that presents the best fit with an R^2 of 0.80. The Freundlich and Temkin models have a lower fit in the order of 0.70. There is no information in the literature regarding the adjustments of the models in terms of COD; however, since it is a real and complicated effluent, one can consider the adjustments quite acceptable.

As referred before, it was interesting to discover that IE also allows COD removal. In order to understand the nature of the organic matter that is adsorbed by the resin, two synthetic solutions were prepared and applied in IE. In a first step, a solution of humic acid was prepared to simulate the organic matter present in the actual treated effluent (thus with the same COD) and subsequently subjected to the IE process. It was found at those conditions, and no COD removal was possible, since no COD variation was detected after the IE process. Since it is known that OOEIW has phenolic acids in its composition, the synthetic solution prepared with five phenolic acids was subjected to the IE process. It was verified that the resin can retain a percentage of these acids (Figure III.2.3). To better understand which acids, have a higher affinity to the resin, the samples were analyzed over time by HPLC. The results are shown in Figure III.2.3.

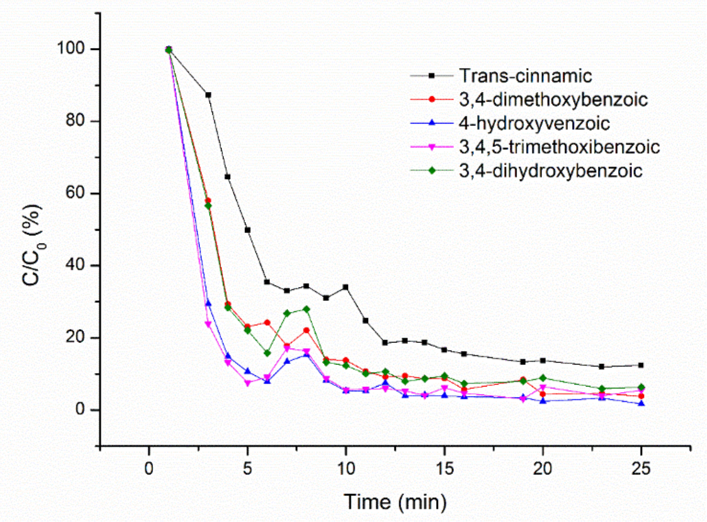

Figure III.2.3. Phenolic acids removal by resin Amberlite@HPR1100 in a batch system at pH 3.

By analyzing Figure III.2.3, one can observe that the resin can remove whichever acid, with a slightly lower affinity towards trans cinnamic acid. Thus, the COD abatement observed during IE of the real POOEIW can be partially explained by the retention of some phenolic compounds in the resin.

III.2.3.2. Analysis of Fe^{3+} sorption in continuous process

The design of a fixed-bed sorption system considers several operational variables. In this study, the superficial velocity effect of the fluid, u_0, of mass of resin, m, and of iron initial concentration, C_e, on the IE performance was investigated. The experimental breakthrough curves and key parameters were calculated and are shown in Table III.2.4. The results obtained were useful to identifying the optimal conditions for the liquid flowrate, Q, and mass, m, which leads to an effective column utilization.

Table III.2.4. Experimental conditions parameters to evaluate the process performance.

Run	Q (ml/min)	m (g)	q (mg/g)	τ (min)	t_{st} (min)	FSB
1	10 (iron solut.)	8.0	9.84	0.39	5.68	0.015
2	5	8.0	9.80	0.78	13.25	0.026
3	10	8.0	9.80	0.26	4.49	0.021
4	15	8.0	9.86	0.39	5.30	0.021
5	10	13.0	9.77	0.78	14.34	0.065
6	10	18.0	9.86	1.18	16.17	0.044
7	10	55.0	9.78	3.76	68.04	0.040
8	10	36.0	9.78	2.43	43.69	0.076

The superficial velocity effect on the iron adsorption by Amberlite@HPR1100 was studied, varying the flowrate to 5, 10 and 15 mL/min and keeping the inlet iron concentration (C0 ~2 g/L) constant at pH 3 and the mass of resin (or bed depth) at 8.0 g. Figure III.2.4a,b show the breakthrough curves for different liquid flowrates (keeping the mass of resin constant) and different resin amounts (keeping the liquid flowrate constant), respectively. Figure III.2.4c compares the results obtained when using the real wastewater after Fenton's process (iron C0 ~2 g/L) with those obtained when a synthetic solution (ultrapure water containing the same concentration of iron) was applied. In both cases, a flow rate of 10 mL/min and a resin mass of 8 g were employed. Moreover, both real and synthetic wastewater were used at pH 3. The velocity variation does not affect *FSB*, while the height of fixed-bed growths this parameter. This means that with longer columns better performance is achieved.

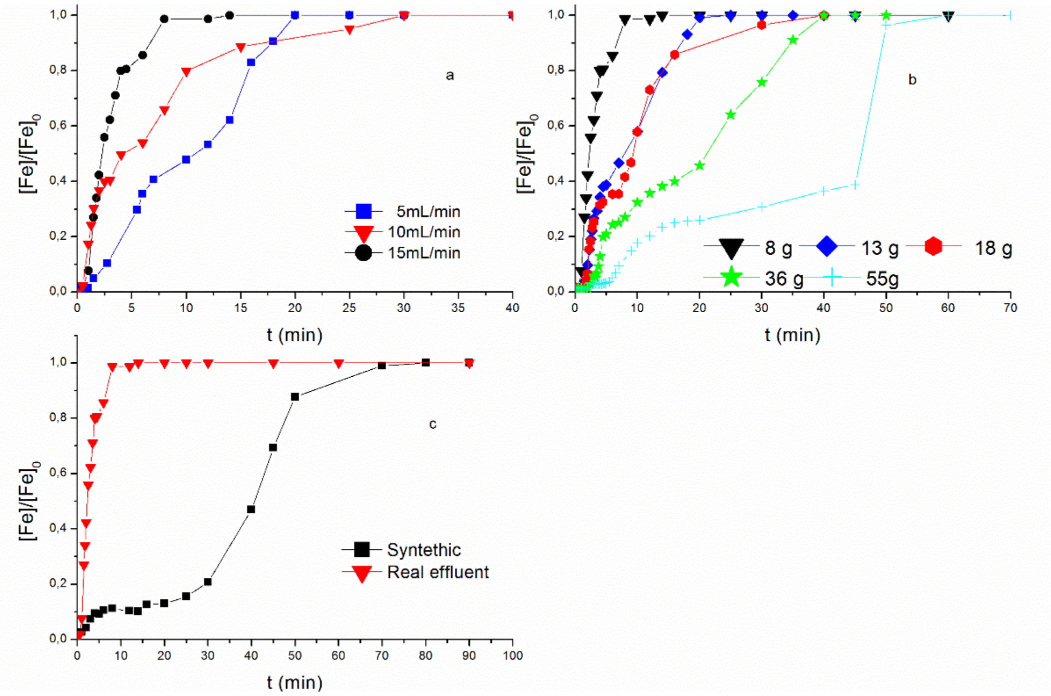

Figure III.2.4. Breakthrough curves obtained under diverse operating settings: a) Effect of the flow rate for a fixed resin mass of 8 g and feed concentration of 2 g/L of iron after a Fenton reaction with real effluent; b)

Effect of the resin amount for a fixed flow of 10 ml/min and feed concentration of 2 g/L of iron after a Fenton reaction with real effluent; c) Comparison of IE using synthetic and real effluent after Fenton reaction with a flow rate of 10 ml/min, 8 g of resin and a feed concentration of 2 g/L of iron.

The results specified in Figure III.2.4 and Table III.2.4 show that, by increasing the flow rate keeping constant resin mass, the times τ and t_{st} tend to become lower for all experiments. This is justified by the fact that higher flow rate decreases the contact time between the metal ions and the adsorbent; consequentially, the mass transfer of Fe^{3+} from the solution to the adsorbent decreases.

Figure III.2.4c shows that the resin saturates much faster when the real wastewater is applied compared to the synthetic solution only containing iron. These results reveal that the quantity of organic matter present in the stream strongly affects the IE performance. In fact, as it was concluded from the batch experiments, this resin can remove some of the effluent COD. Most likely, phenolic acids present in its composition can adsorb in the resin surface. Thus, there will be competition between organic matter and iron ions for the solid active sites. This way, the resin will saturate faster when a complex effluent is applied when compared with cases where a synthetic solution only containing iron is used. This shows the need of testing real wastewater to design this process since the results obtained when simulated streams are applied are not directly applicable to real water treatment conditions.

Simplified models, namely Yoon and Nelson, Thomas and Bohard-Adams, were fitted to the experimental breakthrough curves allowing to estimate kinetic parameter related to the uptake of Fe^{3+} ions by the tested resin during its saturation in a fixed-bed. This study can be useful for the proper design, operation and reliable scale-up of the IE process. The root mean square error (RMSE) and the coefficient of determination (R^2) were determined and are presented in Table III.2.5, and the fit is shown in Figure III.2.5. These parameters allow for validating the fit of the applied models.

Table III.2.5. Model variables for iron adsorption onto Amberlite@HPR1100.

Model	**Parameter**	**Run**							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bohard-Adams	k_{ba} (L/mg min)	0.052	0.126	0.508	0.169	0.142	0.147	0.041	0.065
	q_{ba} (mg/g)	22.85	5.24	0.46	2.11	3.79	4.15	22.82	10.94
	R^2	0.97	0.98	0.98	0.93	0.97	0.96	0.90	0.96
	RMSE	1.78	0.06	0.05	0.10	0.09	0.09	1.72	0.10
Thomas	k_{th} (mL/min mg)	0.05	0.13	0.51	0.17	0.14	0.15	0.04	0.07
	q_{th} (mg/g)	47.93	12.77	3.18	5.80	9.66	10.60	47.31	23.64
	R^2	0.97	0.98	0.98	0.93	0.97	0.96	0.90	0.96
	RMSE	1.78	0.06	0.05	0.10	0.09	0.09	1.72	0.10
Yoon and Nelson	k_{yn} (1/min)	0.10	0.25	1.02	0.34	0.28	0.29	0.08	0.13
	τ_h (min)	38.35	10.22	2.55	4.64	7.72	8.48	37.85	18.91
	R^2	0.97	0.98	0.98	0.93	0.97	0.96	0.90	0.96
	RMSE	1.78	0.06	0.05	0.10	0.09	0.09	1.72	0.10

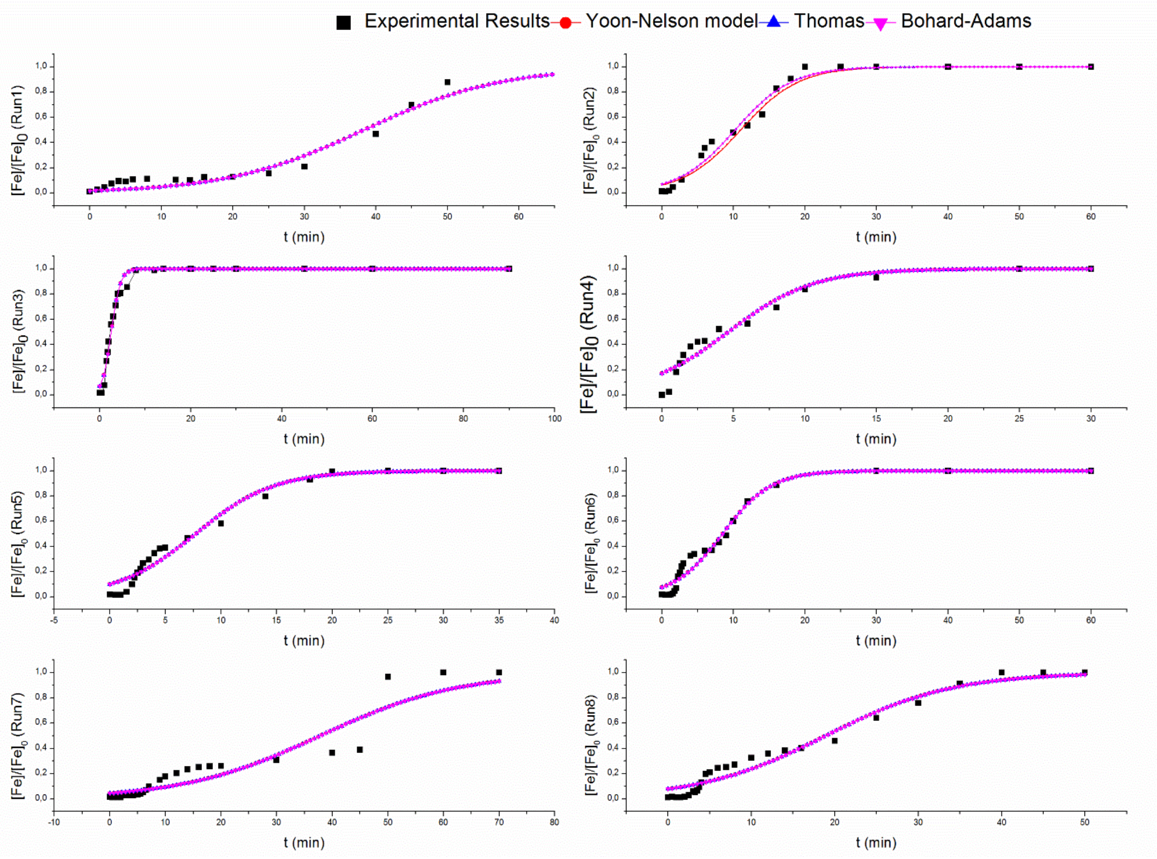

Figure III.2.5. Saturation curves predicted by the Yoon-Nelson, Thomas and Bohard-Adams models for all experiments.

The error values obtained for the three empirical models (R^2 = 0.93–0.98 and RMSE = 1.72–6.25) are acceptable and there are no significant variations between them for operating conditions studied. Figure III.2.5 represents the saturation curves predicted by the models and, as the values indicate, quite satisfactory adjustments can be observed.

III.2.3.3. Amberlite@HPR1100 regeneration

From a financial, operational and ecological point of view, the study of resin reuse is extremely important. Figure III.2.6 presents results in terms of iron and COD removal efficiency from resin reuse.

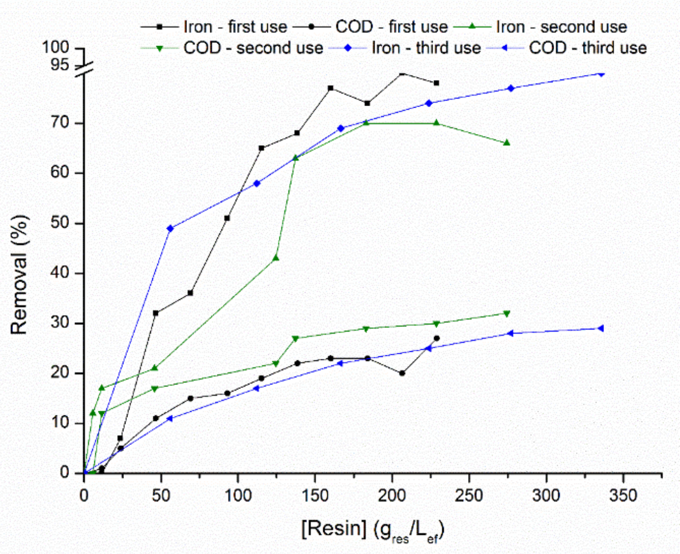

Figure III.2.6. Amberlite@HPR1100 resin reuse (Adsorption: 2 g_{Fe}/L, real effluent OOEIW).

The regeneration process—adsorption-desorption-washing—was supported for three cycles in the batch, as described in Section III.2.2.3, using several resin loads. It was observed that after three cycles, at 215 gres/Lef, the iron removal capacity of the resin decreased from ~80% to 68%. Iron desorption should be close to 100% according to proposal protocol. In an acidic medium, protons compete with iron ions and can release the adsorbed iron almost completely. Consequently, some authors have also resorted to hydrochloric acid solutions to remove iron from strong acid cation exchange resins, similar to those used in this study. Millar et al. (2015) achieved iron regeneration with efficiencies greater than 90% using 10% HCl and with 5% HCL: regeneration efficiencies of 89.6%. After 10 cycles of reuse, Víctor-Ortega et al. (2016b) reported that 100% recovery efficiencies were maintained.

The presence of organic matter in the real wastewater challenges iron adsorption since there is competition between iron ions and organic matter for the active sites. In addition, organic matter will likely challenge the resin regeneration. The desorption of these compounds can be more difficult and thus compromise the complete resin regeneration. Interestingly, COD removal was not very much affected by the regeneration process. Indeed, the third reuse of the resin leads to COD removals very similar to those obtained for the first use.

III.2.4. Conclusions

This study investigated the effectiveness of a fixed-bed IE process with a strong-acid cation exchange resin for the final iron sludge free Fenton process to treat an olive oil extraction industry wastewater.

Adsorption isotherms were studied, and analytical isotherm equations such as Langmuir, Freundlich and Temkin isotherms, which are extensively used for modeling adsorption data, were fit with acceptable values considering the complex real effluent.

Breakthrough curves proved up to 75% maximum iron adsorption capacity onto Amberlite@HPR1100 resin, for a feed concentration of 2 gFe^{3+}/L, and an efficiency for COD removal of 30% for an initial COD between 17.5–22.5 gO_2/L.

The experimental breakthrough curves were well adjusted by the Bohard-Adams, Thomas and Yoon–Nelson empirical models.

Resin reuse proved to be viable, as it maintains its capacity over the cycles. With these features, the IE process could permit iron reuse in the Fenton reactor as a catalyst, which would balance the cost-effectiveness ratio of the integral process, minimizing or even avoiding the need for acid and iron to induce the Fenton reaction.

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III.3. Screening of low-cost materials as heterogeneous catalysts for olive mill wastewater Fenton´s peroxidation

This chapter is based on the publication: Domingues, E., Rodrigues, F., Gomes, J., Quina, M.J., Castro-Silva, S., Martins, R.C. (2020) creening of low-cost materials as heterogeneous catalysts for olive mill wastewater Fenton´s peroxidation. Energy Reports, 6, 161-167.

III.3.1. Introduction

Olive mill wastewater (OMW) needs attention due to its significant impacts on the environment. Considering that about 30 million m^3 of OMW are generated annually worldwide, only ¼ of this has received appropriate treatment (McNamara et al., 2008). The impacts on the environment are significant, essentially due to its acidic properties, the high organic load (COD can reach values above 170 gO$_2$/L, containing phenolic compounds above 24 g/L and long chain fatty acids) (Chatzisymeon et al., 2013). Based on these properties and recalling that it is a seasonal effluent, when stored, oxidation and polymerization reactions (tannic acid, lignin) may occur, resulting in recalcitrant compounds, giving it a dark color and bad odors. Moreover, its low BOD$_5$ to COD ratios, when compared for example with domestic effluents, makes these streams resistant to biodegradation and, consequently, cannot be sent to treatment plants based on biological processes (Martins et al., 2014).

There are physical and thermal processes that are useful as a pre-treatment to remove suspended solids and to decrease volume. However, they are not efficient due to the high operational costs associated, nor do they contribute to the depollution of toxic compounds present in it. As an alternative, biological and chemical treatments emerge, they are applied as they reduce the organic load of the effluent. However, due to the toxic and refractory character of these effluents, biological treatments are not feasible. According to Rahmanian et al. (2014), physical-chemical treatments (neutralization, precipitation, etc.) are cheaper treatment routes, but require the integration of later treatment, which increases the processing time. On the other hand, advanced oxidation processes (AOP) show to be more effective in pollutant degradation despite the higher costs. Thus, taking into account the large organic load of the oil mill effluents as well as the presence of phenolic compounds, it is necessary to reach the legal limits for the management of these residues, and the option under study is the Fenton reaction. In this case, the literature has highlighted the possibility of achieving degradation of phenolic compounds using low-cost catalysts. The Fenton process is efficient under ambient conditions (pressure and temperature), the reaction time is relatively short compared to other existing processes, the reagents do not present any danger to the user or require the application of specific equipment (Domingues et al., 2018). Regarding the degradation of organic compounds, it is a promising technique, through the partial oxidation of phenolic compounds, resulting in a decrease in the organic load (COD). The efficiency of the reaction is essentially dependent on certain parameters such as the pH of the medium (values between 2.5 and 4.5), and the oxidant/catalyst ratio (H_2O_2/Fe^{2+}), which is important to optimize the quantities of reagents to obtain the highest degree of degradability and a smaller amount of residual hydrogen peroxide (Peres et al., 2004). As an alternative to the homogeneous systems, there is the possibility of carrying out the reaction using a solid catalyst (heterogeneous process) that remains in suspension at the end., In this way, there is no longer a limitation for the removal of solubilized iron, mediated by additional separation processes and, therefore, it becomes a less complex operation (Rossi et al., 2014). Another interesting aspect is the possible non-acidification of the medium to ensure the solubilization of the catalyst, but it may continue to be an important parameter to guarantee the optimization of the reaction, through OMW effluents. In this method, the solid catalyst must be rich in iron or other materials with similar catalytic properties, to promote the oxidative activity of H_2O_2 (via hydroxyl radicals) to degrade each organic pollutant.

In this work, the behavior of the Fenton reaction with the use of catalysts such as Red Mud (RM), volcanic rocks from the Canaries (VRC) and the Azores (VRA) will be studied. According to the studies presented by Domingues et al. (2019) and Martins et al. (2013), these have high iron content and without the need for modifications, showing a priori reagents with the potential to be applied in the Fenton process. Thus, the focus is given on concepts such as environmental impact and circular economy, based on the use of waste from the metallurgical industry and availability in nature, as a catalyst.

III.3.2. Materials and Methods

III.3.2.1. Catalysts and reagents

RM was provided by a Greek aluminum producer, was washed with water, dried at 105 °C for 24 h, and ground until a powder was obtained. RM was previously characterized by Domingues et al. (2019). VRC and VRA were collected from Canaries and Azores Island and were characterized in the works (Martins et al., 2013; Gomes et al., 2018). Hydrogen peroxide (33% w/V) was purchased from Panreac.

The synthetic OMW initial concentration was obtained through the mixture of 100 mg/L of each phenolic acid (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic and (5) Trans-cinnamic).

III.3.2.2. Experimental procedure

Fenton's reactions were carried out in a batch spherical reactor, under ambient temperature and pressure conditions, the pH of the medium was readjusted to 3, and the reaction was carried out for 60 min. A catalyst load of 1 g/L and an amount of oxidizer (H_2O_2) of 100 mg/L were applied. The oxidant was fully introduced at the beginning of the reaction or in several aliquots over time. The reactor was agitated with magnetic stirring at 300 rpm. The required amount of catalyst is added 10 min before starting the experiments to test the adsorption of the pollutants. In the Fenton experiments, the reaction started when H_2O_2 was introduced. Samples taken periodically were filtered using 1 μm glass fiber membranes to remove the catalyst particles and then a few drops of $Na_2S_2O_3$ (0.1 N) were added to remove the remaining H_2O_2, stopping the reaction.

III.3.2.3. Analytical techniques

The concentration of the individual phenolic acids was obtained by HPLC (Shimadzu) analysis using a C18 (SiliaChrom) column at 40 °C. The mobile phase (0.5 mL/min) consists of a 50:50 mixture of methanol and acidified water (0.1% orthophosphoric acid). The determination occurred at 255 nm.

The total phenolic content of the effluent was determined by the Folin–Ciocalteau method and, since the calibration curve was based upon standard solutions of gallic acid, the polyphenolic content (TPh) was expressed as mg/L of equivalent gallic acid. The detailed procedure is described elsewhere (Martins et al., 2008).

Hydrogen peroxide concentration along the reaction was followed spectrophotometrically (PG Instruments T60 spectrophotometer) using the potassium titanium (IV) method.

III.3.3. Results and discussion

III.3.3.1. Catalysts characterization

In the heterogeneous Fenton process, three solid catalysts were used, namely RM, VRA, and VRC. These materials are attractive due to their physical and chemical properties, the high iron content, and because it is possible to be used as solid catalysts. In this way, they have the potential to be used in the Fenton process, avoiding the application of a homogeneous catalyst that requires a subsequent separation stage. On the other hand, these materials can be considered low-cost catalysts, since come from industrial residues, from which they can be reused and reintegrated in other process cycles (in the case of RM) or reused in nature, as in the case of VRA and VRC.

RM consists of elements such as Fe, Al, Ca, Ti, Si, and Na and is composed of significant fractions of Fe_2O_3 (hematite) and AlOOH (boehmite) (Domingues et al., 2019). The presence of hematite shows that RM is a source of Fe (III) and not of Fe (II).

The VRA composed mostly of Al, Fe, Ca, Mg, and O, accounts for a fraction of Fe in about 55.8% (w/w), which is higher than for the other elements. On the other hand, X-ray diffraction showed intense peaks corresponding to silicate compounds (Gomes et al., 2018).

Concerning the VRC, from the study presented by Martins et al. (2013), this solid catalyst presents traces of elements such as Fe, Na, Ca, Mg, while the former represents the highest fraction (6.45%). In this case, complexes such as hematite, pyroxene (single chain inosilicates), quartz, and feldspar were detected.

Another relevant characteristic regarding catalytic materials is related to its specific area (or BET surface area) since it determines the area available for the reactions to occur. According to the literature, these materials register the values of 0.6, 28.3, and 3.59 m^2/g, for RM, VRA, and VRC, respectively.

III.3.3.2. Effect of [H_2O_2] injection mode

The optimization of H_2O_2 charge is key due to the potential scavenging effect of this reagent when in excess (Lucas et al., 2009). One way to control this parameter may be to gradually introduce it in the reaction medium. The catalyst used to perform these tests was RM, based in the conditions optimized previously (pH = 3, [H_2O_2] = 100 mg/L and [catalyst] = 1 g/L) (Domingues et al., 2019). In all tests, except the first in which the amount of total hydrogen peroxide is injected, half the amount of oxidant is injected at the initial moment (t = 0 min) and then the other half is divided according to the number of injections (totality at 0 min for 1x; at 15 and 30 min for 2x; at 10, 15 and 30 min for 3x; and at 5, 10, 15 and 30 min in the case of 4x) (Figure III.3.1a).

Figure III.3.1b shows the effect of the hydrogen peroxide injection mode on the removal of phenolic compounds present in the simulated effluent, measured by the Folin–Ciocalteau method (in the form of total phenolic content). Figure III.3.1a there is less residual H_2O_2 amount when H_2O_2 (100 mg/L) is totally injected at the beginning of the reaction. This behavior is possibly due to its rate of decomposition (which is proportional to the amount of reagent) being higher at the beginning of the reaction than during the process.

However, there are inconstant moments in the amount of residual H_2O_2, suggesting that it is consumed and formed during the reaction. In fact, studies show that oxidation reactions involving unsaturated carbon bonds can lead to the formation of H_2O_2. This fact was verified by Martins et al. (2014) in the case of ozonation, with the possibility of such a process also occurring in the case of the Fenton reaction. It is also verified, when comparing the profile of one injection (1x) with the profile of 2x, 3x, and 4x injections, that in these cases there are higher residual oxidant values. This suggests that the addition spread over the process leads to the accumulation of H_2O_2, affecting efficiency. The results in Figure III.3.1b show that for only a single injection of H_2O_2 (at the beginning of the reaction), there is a higher removal of phenolic compounds (100%) present in the simulated effluent. On the other hand, in the case in which 3 and 4 injections are performed, the lowest value is reached in the phenolic content removal (approximately 55%) after 60 min of reaction. The kinetics of removal is faster at the beginning of the process, hence there are higher rates of removal with just one injection. In a more detailed analysis, phenolic acids were individually identified and quantified through HPLC analysis.

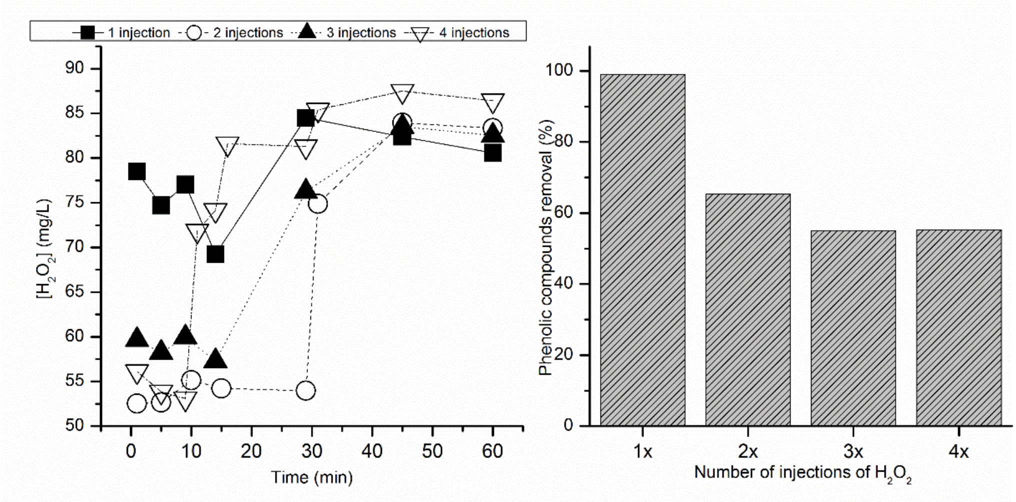

Figure III.3.1. a) Evolution of residual hydrogen peroxide, with different injections, over 60 min of reaction b) Total degradation of phenolic content.

In Figure III.3.2, the final removal of each phenolic acid present in the simulated effluent is observed when hydrogen peroxide was introduced in different injections.

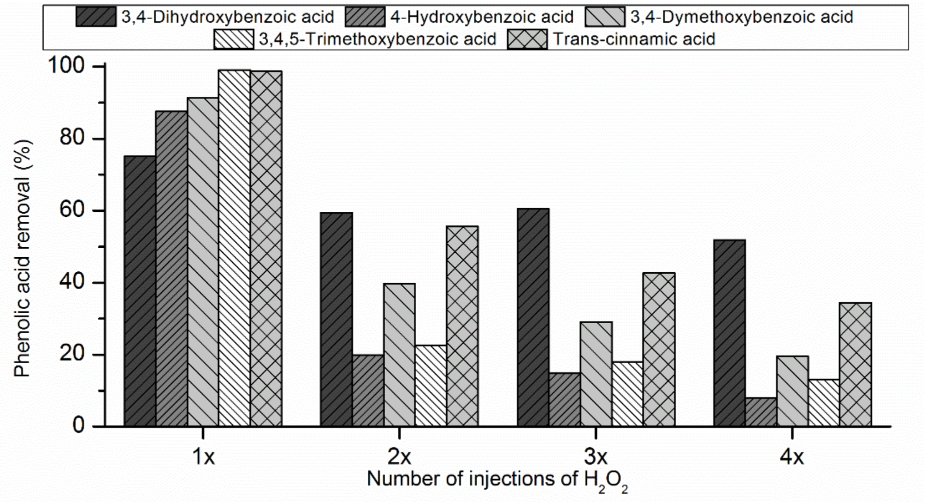

Figure III.3.2. Degradation of phenolic acids, for the different injections of H_2O_2, with $[H_2O_2]$ = 100 mg/L, pH = 3, [catalyst] =1 g/L.

HPLC analyzes show higher degradation rates of phenolic acids when H_2O_2 is fully injected at the beginning of the reaction, corroborating the conclusions obtained when the total phenolic content was measured. More specifically, after 60 min, removals of 75.1% of 3,4-dihydroxybenzoic acid, 87.6% of 4-hydroxybenzoic acid, 91.4% of 3,4-dimethoxybenzoic acid, 99.1% of 3,4,5-trimethoxybenzoic acid and 98.7% trans-cinnamic acid were obtained. Therefore, it is possible to state that the total injection at the beginning of the reaction shows more promising results. It should be noted that, in general, the acid that achieves the greatest degradation is trans-cinnamic acid while the most difficult to remove is 4-hydroxybenzoic acid. In fact, while the first has a very reactive double bond outside the benzene ring in its ortho position, the second has only one -OH functional group, which makes it less apt to be attacked by hydroxyl radicals. Hydroxyl radicals have an electrophilic character and therefore are more prone to attack an isolated oleophilic (unsaturated) double bond in the benzenic ring. This explains the greater degradation typically achieved by trans-cinnamic acid. As previously mentioned, the molecular structure of the 4-hydroxybenzoic compound, has only one functional group -OH in the 4th position of the benzene ring. In this way, this represents a limitation to the electrophilic attack by the hydroxyl radicals since they are more preferred by the 3rd positions during the oxidation process.

III.3.3.3. Screening of low-cost catalysts

The cost of the catalyst is also an important variable in the economy of a process. In this sense, the application of natural materials or residues from other processes can be interesting alternatives to industrially synthesized catalysts. In fact, the production of catalysts entails large energetic costs associated to drying and calcination of the materials. In this sense, a residue RM and two types of volcanic stones were selected: VRA and VRC.

It is also relevant to evaluate the efficiency of the process in removing phenolic content and organic matter using VRA and VRC compared to RM. According to the previous results, it was decided to make only one injection of hydrogen peroxide (at the beginning of the reaction). All catalysts were tested using a load of 1 g/L.

Figure III.3.3a shows the comparison of the performance of the different catalysts in the Fenton reaction with respect to the evolution of the amount of residual hydrogen peroxide. Figure III.3.3b compares the removal of the total phenolic content after 60 min of Fenton's reaction using the different catalysts.

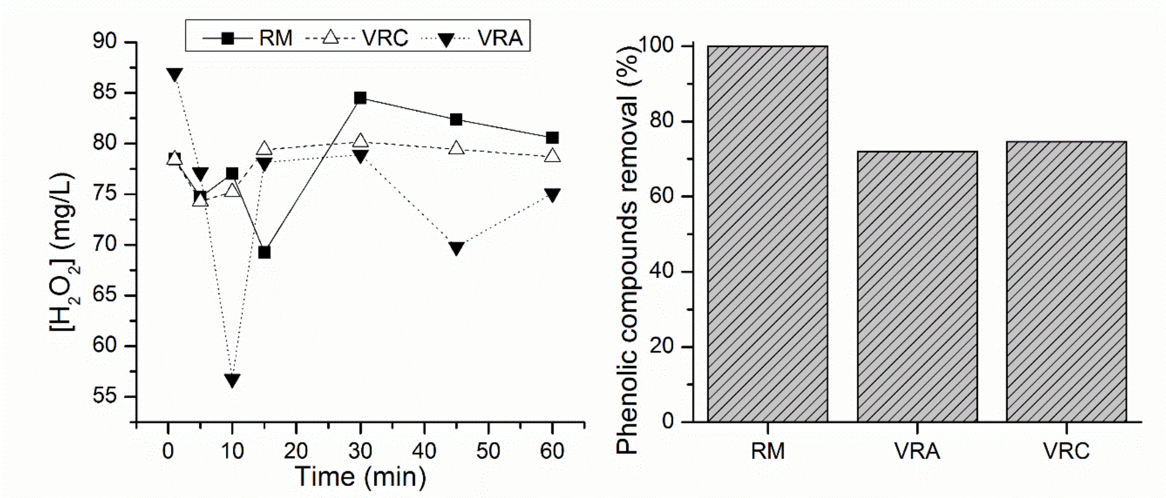

Figure III.3.3. a) Evolution of the residual amount of H_2O_2, over time, for RM, VRA and VRC. b) Total degradation of phenolic content, for RM, VRA and VRC, for pH = 3, [Catalyst] = 1 g/L and $[H_2O_2]$ = 100 mg/L.

The amount of residual H_2O_2 is less when using the VRA, and in the first 10 min of reaction, the consumption of H_2O_2 is highest. This can be explained by the larger BET surface area and, thus, greater availability of active sites on the catalyst surface. This phenomenon is reflected in a higher rate of decomposition of hydrogen peroxide in hydroxyl radicals or in species with less oxidative power (for example, hydroperoxyl radicals - $HO_2^{\cdot}$). RM, on the other hand, shows fluctuations over time, but less abrupt consumption of hydrogen peroxide than VRA. At the end of 60 min, it ends with a higher residual amount compared to the other catalysts. As previously mentioned, it has a smaller BET surface area, which is proportional to the number of active sites available for H_2O_2 decomposition. Comparing the residual H_2O_2 profile over the reaction time for the 3 catalysts, with SBET, it is possible to affirm a relationship between this parameter and the residual amount of oxidant, that is, the higher this value, the lower the residual amount obtained.

III.3.4. Conclusions

In this work, a synthetic OMW was studied based on five phenolic acids usually present in the real OMW (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic, and (5) Trans-cinnamic). This effluent was treated by the Fenton process using three low-cost catalysts: RM, VRA, and VRC. It was concluded that:

-At the end of 60 min the removal of phenolic content reaches 100% for RM, while in the case of VRA and VRC this value is 72.0% and 74.6%, respectively;

-The 3 catalysts show a shifting behavior, revealing that there is formation and decomposition of H_2O_2 throughout the process.

-The degradation rate of phenolic compounds was not directly related to the increase in the BET surface area of the catalyst.

The study of the effect of hydrogen peroxide injection mode was also evaluated using RM in the following conditions: pH = 3, $[H_2O_2]$ = 100 mg/L and [catalyst] = 1 g/L). It was concluded that less residual oxidant amount is obtained when the totality of H_2O_2 (100 mg/L) is injected at the beginning of the reaction, while a greater removal of phenolic compounds (100%) was observed in this case.

The use of wastes and/or natural materials avoids the need for synthesizing catalysts that entails larger energetic costs related with the thermal treatment of such materials. Thus, globally the wastewater treatment cost will decrease while contributing to a circular economy.

III.3.5. References

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III.4. Effect Catalytic Efficiency of Red Mud for the Degradation of Olive Mill Wastewater through Heterogeneous Fenton´s Process

It is based on the publication: Domingues, E., Assunção, N., Gomes, J., Lopes, D.V., Frade, J.R., Quina, M.J., Quinta-Ferreira, M. M., Martins, R.C. (2019) Catalytic Efficiency of Red Mud for the Degradation of Olive Mill Wastewater through Heterogeneous Fenton's Process. Water. 11(6), 1183.

III.4.1. Introduction

Agro-industries, such as olive mills, are a relevant economic sector in the Mediterranean Sea area. This region has an important role in the production of olive oil as it accounts for almost 95% of the worldwide production (Eroglu et al., 2006). These countries suffer from severe drought periods and water shortening, and olive oil production plants are high water demand. Moreover, during their operation high amounts of polluted streams are generated. Olive mill wastewater (OMW) is an effluent resulting from the production of olive oil. Fresh OMW is considered phytotoxic mainly because it contains phenolic compounds (Pinho et al.,2017). These substances are prejudicial for biological processes resulting in an antimicrobial activity in OMW treatment. OMW can be characterized by high pollutant load (g/L): chemical oxygen demand (COD) 45–180, biochemical oxygen demand (BOD_5) 25–100, total solids 24–120, mineral solids 5–15, total phenolics 2–15, fat 0.5–1.0 and pH 4.0–5.2 (Vlyssides et al., 2004). The treatment of those effluents is a priority to environmental preservation and water recovery (Domingues et al., 2018). The most common treatments are based on biological reactors, but they are not efficient when applied to OMW due to the presence of toxic compounds (Guido et al., 2006; Saadi et al., 2007). The high organic load makes these streams hard to manage, as well as the fulfillment of the legal thresholds for their discharge to the environment (Azbar et al., 2004). A method widely used to manage OMW is the disposal in artificial evaporating ponds. This method is environmentally risky for aquifers besides promoting bad odors, and therefore, should not be used near housing areas (Saez et al, 1992). The traditional physical-chemical treatments, namely flocculation, coagulation, filtration, only solve part of the problem since the contaminants are not destroyed but rather phase changed. Oxidation (chemical or biological) treatment is necessary to complete the treatment of the effluent. They are usually applied as a combination of processes (Beltran et al., 1999; Domingues et al., 2018). It is documented that the advanced oxidation processes show potential to treat this type of effluents. Among them, Fenton´s reagent is usually identified as promising for industrial applications (Cañizares et al., 2007; Amaral-Silva et al., 2016; Amaral-Silva et al., 2017).

Fenton’s process is based on the generation of very reactive free radicals, specifically hydroxyl radicals. It has a high capability of mineralizing almost every organic compound. Fenton´s technology is easy to handle, and the chemicals used (iron and hydrogen peroxide) are commonly available and safe. The optimal conditions for treating OMW occurs in acidic medium at pH values between 2.5 and 4.5 (Peres et al., 2004). The main disadvantage of this process is sludge formation (Martins et al., 2017; Reis et al., 2018). In fact, the use of a homogeneous catalyst (iron salts) implies its removal from solution at the end of the treatment. Typically, this is achieved by increasing pH of the treated effluent to promote iron hydroxides precipitation. To overcome this issue, research is being focused on the development of suitable solid catalysts that can be easily removed from the liquid bulk and reused (Rossi et al., 2012; Martins et al, 2013; Shi et al., 2018). Another important disadvantage of this process is related to the formation of a high concentration of ions in the treated wastewater, which could interfere on the reaction efficiency and increase conductivity (Qiang et al., 2003). Moreover, the process is highly dependent upon H_2O_2 concentration and is only efficient at low pH-levels (Neyens et al., 2003).

The use of iron-rich residues as catalysts in this process can be an interesting environmental approach (Martins et al., 2010). In this work, a low-cost catalyst, red mud, was innovatively applied in the Fenton process with the objective of reducing the operation costs and reusing a waste that is currently produced in large quantities. Red mud is the iron-rich waste formed during aluminum oxide production by the bauxite leaching process (Bayer process). The production of this waste is about 1 to 1.5 tons per ton of alumina which globally rises to 66 million tons of annual production (Oliveira et al., 2011). Though the main constituents of red mud are non-hazardous iron and aluminium oxides or oxy-hydroxides, red mud is characterized by high alkalinity and also contains traces of potentially pollutant components. Since the most common destination of this waste is landfilling, which requires large areas, this management approach may be an environmental problem to soils and groundwater due to the leaching of hazardous components.

Additional motivation for this work was the intended valorization of red mud, bearing in mind the need of following a path towards a circular economy of industrial wastes. Thus, red mud should be envisaged as raw material, based on the potential applicability of the main iron and aluminium-based constituents, and also significant fractions of other valuable components such as rare earth oxides. Therefore, the applicability of this waste as a catalyst in Fenton or other oxidation processes can contribute to a sustainable future (Costa et al., 2010; Dias et al., 2016).

The advanced oxidation processes such as Fenton process normally can be a suitable methodology for the abatement of chemical pollutants, such as phenolic acids. However, the presence of reactive oxidative species can promote the degradation of the initial pollutants through partial oxidation instead towards total mineralization pathways. Therefore, to consider wastewater reclamation, the treated solutions should be evaluated in terms of toxicity regarding aquatic species. In fact, Gomes et al. (2019) verified that parabens degradation through catalytic ozonation promotes the production of by-products slightly more toxic than the corresponding dilution of parabens mixture. In this way, the treated solution at the optimal dose of red mud and hydrogen peroxide was evaluated regarding toxicity. This result was compared with the one obtained for the samples coming from Fenton's process using different red mud loads since the heavy metals leaching from the waste can contribute to the treated wastewater toxicity. The toxicity tests performed cover different trophic levels and thus, a bacterium, *Aliivibrio fischeri*, a clam, *Corbicula fluminea* and a plant *Lepidium sativum* were selected as non-target species.

In this context, the aim of the present research was to analyze the efficiency of red mud as a solid low-cost catalyst in Fenton's process for OMW treatment. A simulated solution containing phenolic acids typically found in actual OMW was selected as model effluent. The effect of the operating conditions was evaluated and the impact of the treatment over the ecotoxic characteristics of the wastewater was assessed considering a wide range of species. Dias et al. (2016) used red mud as a support for a carbon coating and then as a catalyst for the photo-Fenton degradation of Reactive black 5. The activity of red mud reduced with H_2 at high temperatures was verified on the oxidation of methylene blue dye using heterogeneous Fenton with interesting results (Costa et al., 2010). To the best of the authors' knowledge, the direct application of red mud as a catalyst in heterogeneous Fenton's process was never optimized. Moreover, in this work, a complex mixture of pollutants mimicking the phenolic character of OMW was tested which is not usual in the literature.

III.4.2. Material and Methods

III.4.2.1. Reagents and synthetic OMW preparation

The simulated OMW was prepared by dissolving 100 mg/L of each of the following phenolic acids in ultrapure water: Trans-cinnamic, 3,4-dimethoxybenzoic, 4-hydroxybenzoic, 3,4,5-trimethoxybenzoic and 3,4-dihydroxybenzoic acid. All phenolic acids were purchased from Sigma-Aldrich. This mixture mimics the phenolic fraction of real OMW. The solution was used straight after preparation.

Methanol and orthophosphoric acid (sigma-aldrich) were used for HPLC analysis. Sodium thiosulphate and tert-butanol (sigma-aldrich) were employed to quench hydrogen peroxide and hydroxyl radicals, respectively.

III.4.2.2. Red Mud characterization

RM was kindly supplied by a Greek aluminium producer. It was grounded to powder after drying at 105 °C for 24 h.

The red mud was characterized morphologically by scanning electron microscopy (SEM) with a Hitachi SU-70 microscope.

Particle size distribution was performed with a Coulter LS 230 (0.040–2000 μm).

The specific surface area by the Brunauer-Emmett-Teller (BET) method was studied with a Micromeritics Germini 2380. X-ray diffraction was used to ascertain the crystallography of the powder with a PANalyticalXPert PRO diffractometer ($2\theta = 10–80°$, CuKα radiation), where a PanalyticalHighScorePlus 4.1 (PDF-4) was used for phase identification.

The determination of RM pH of zero-point charge (pHzpc) was performed according to the method described by Rivera-Ultrilla et al. (Rivera-Ultrilla et al., 2001).

III.4.2.3. Fenton experiments

Fenton’s experiments were carried out in a glass spherical reactor (500 mL stirred with magnetic agitation at 300 rpm). The volume of 500 mL of the synthetic OMW was initially loaded. pH was previously corrected to 3 using H_2SO_4. The required amount of dried red mud is added, and the reaction started when hydrogen peroxide (33% w/V, Panreac) was introduced. Aluminum foil was used to cover the reactor and avoid light interference. Samples taken periodically were filtered using 1 μm glass fiber membranes to remove the catalyst particles and then a few drops of $Na_2S_2O_3$ (0.1 N) were added to remove the remaining hydrogen peroxide and stop the reaction. For the samples used for toxicity assessment, hydrogen peroxide was quenched by increasing pH after filtration (Ltaïef et al., 2018). To test if the degradation reaction involved the production of hydroxyl radicals, some spiked experiments with tert-butanol (a hydroxyl radical scavenger) were performed.

III.4.2.4. Analytical Techniques

The concentration of the individual phenolic acids was obtained by HPLC (Shimadzu) analysis using a C18 (SiliaChrom) column at 40 °C. The mobile phase (0.5 mL/min) consists of a 50:50

mixture of methanol and acidified water (0.1% orthophosphoric acid). The determination occurred at 255 nm.

Total organic carbon (TOC) was measured at the beginning and end of each experiment using a TOC analyzer (TOC-V-CPN model, Shimadzu).

Iron dissolved at the end of the reaction was evaluated by atomic absorption (Perkin-Elmer 3300) to assess the leaching of the catalyst throughout the process.

Hydrogen peroxide concentration along the reaction was followed spectrophotometrically (PG Instruments T60 spectrophotometer) using the potassium titanium (IV) method as described elsewhere (Seller et al., 1980).

III.4.2.5. Toxicity Assessment

The toxicity of the initial phenolic mixture was compared with the one of the treated samples after Fenton's process. To minimize the impact of pH on the toxicity evaluation, since the Fenton's process works at acidic conditions, it was necessary to correct the sample pH to values within the range of 6.5–7.5. This correction was performed by adding drops of a solution of either sodium hydroxide or sulfuric acid.

To evaluate the toxicity of the samples towards a sensitive species, *A. fischeri* bacteria, was used. The luminescence inhibition of treated solutions was performed in comparison with a blank, where bacteria were placed in a 2% NaCl solution, which is the ideal medium. The inhibition of luminescence due to treated and untreated samples was measured after 15 and 30 min of incubation (15 °C) using a LUMIStox 300 apparatus (Dr. Lange).

Asian clams, *C. fluminea* were collected from a well-established population place from a canal in Mira, Portugal (N40°25′06.90″/W8°44′13.18″). Clams were collected from the canal by a sieving sediment bag (5-mm mesh). Clams with the shell length in the range of 15–30 mm were selected, placed in field water and transported to the laboratory, where they were gradually acclimated to the test conditions. After two weeks of acclimation with dechlorinated tap water in laboratory bottles, 10 clams were placed in contact with 500 mL of liquid to perform toxicity tests. Two replicates of treated solutions for each condition were used along with two blank controls (10 clams in contact with dechlorinated water). The test vessels were kept under 16 h^{Light}; 8 h^{Dark} photoperiod cycle at constant temperature 20 ± 2 °C and air stream for continuous aeration to minimize the impact of dissolved oxygen (Rosa et al., 2015). The clams' mortality was assessed every 24 h during 72 h based on the evidence of animal's siphoning activity and/or their resistance to valve opening when gently forced with a blunt dissection needle (Gomes et al., 2014).

The phytotoxicity test with *L. sativum* allows the determination of germination index (GI) which will then be classified according to Trautmann et al. (1997) criteria. GI is the product of relative radicle growth (RRG) by the relative seed germination (RSG) as in Equations (III.12) – (III.14). In this test, the volume of treated and untreated samples was 5 mL to wet a filter paper in a Petri dish. Following this, 10 seeds of cress were evenly spread above the wet filter paper. As a blank, 5 mL of ultrapure water was used instead of the samples. Then the Petri dishes were placed in the oven for 48 h at a constant temperature of 27 °C and at dark conditions. The number of germinated seeds and the radicle growth length were recorded. These experiments were performed in duplicate.

$$\mathrm{GI}(\%) = \frac{\mathrm{RRG}\ (\%) \times \mathrm{RSG}\ (\%)}{100} \qquad \text{III.12}$$

$$\mathrm{RRG}\ (\%) = \frac{L_{R,T}}{L_{R,B}} \times 100 \qquad \text{III.13}$$

$$\mathrm{RSG}\ (\%) = \frac{N_{SG,T}}{N_{SG,B}} \times 100 \qquad \text{III.14}$$

where $L_{R,T}$ and $L_{R,B}$ correspond to the average radicle length for each sample and blank, respectively; $N_{SG,T}$ and $N_{SG,B}$ are the arithmetic means of the number of seeds germinated for each sample and blank with ultrapure water, respectively.

III.4.3. Results and Discussion

III.4.3.1. Red Mud Characterization

SEM images of RM are shown in Figure III.4.1a,b, with individual particles extending from the nanometer to sub-micrometer range, and tending to form agglomerates with sizes in the range 1–10 µm. Elemental analysis provided by SEM-EDS (Figure III.4.1c) showed that Fe, Al, Ca, Ti, Si and Na are present in the waste. The agglomerates found in SEM are confirmed by the volumetric particle size distribution (Figure III.4.1d) which shows a median size (D_{50}) of 0.58 µm. Note also that 10% of particles have particle diameter below 0.17 µm (D_{10}) and 90% of particles show a diameter lower than 2.86 µm (D_{90}).

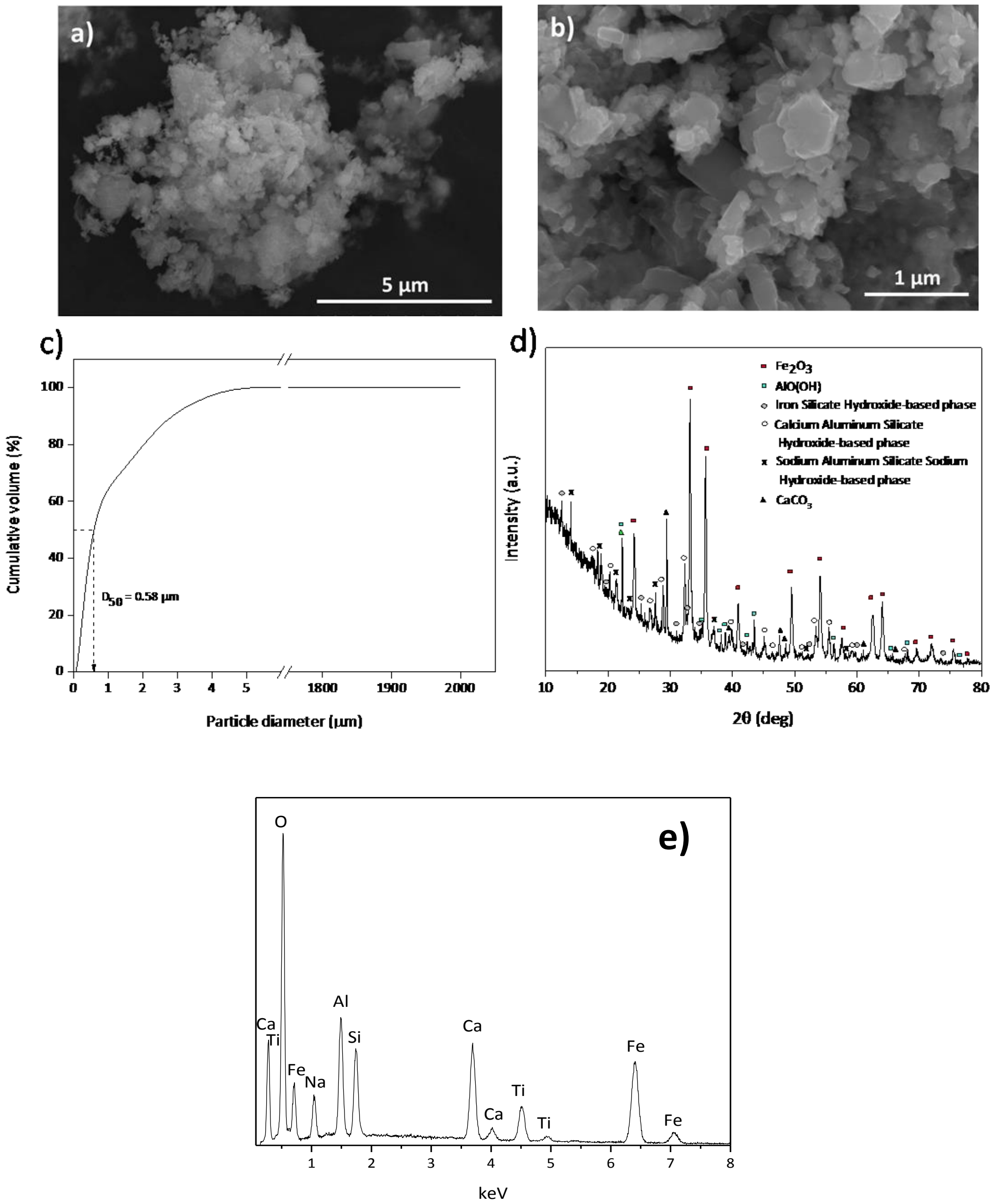

Figure III.4.1. (a,b) Scanning electron microscopy (SEM) of the red mud powder; (c) EDS spectrograph; (d) Cumulative volume (%) of red mud particles; (e) XRD pattern of red mud.

The BET specific surface area was S = 0.6 m^2/g and pore volume 0.02 cm^3/g. These results confirm agglomeration by estimating an average particle size down to $d = 6/(S\rho) \approx 0.14$ µm, based on the actual results of specific surface area and a typical density of about 4 g/cm^3, in the expected range of prevailing phases, such as hematite (5.26 g/cm^3) and boehmite (3.06 g/cm^3). Thus, a significant fraction of particles in the nanometric range (<100 nm) is expected, probably resulting from the highly alkaline leaching conditions of the Bayer process (Khairul et al., 2019).

XRD studies (Figure III.4.1e) shows that the prevailing phases in the red mud waste are hematite (Fe_2O_3) and boehmite (AlOOH), combined with significant fractions of silicate or aluminosilicate phases, calcite and other (not shown) minor phases such as SiO_2, TiO_2, and $Al(OH)_3$.

The material pHzpc was of 13.0 ± 0.1. This characterization of the red mud used in the present study is, in general, in agreement with the literature (Khairul et al., 2019), except for expected differences related to the starting raw material (bauxite) and operating conditions of the Bayer process.

III.4.3.2. Fenton´s process

Initially, the capacity of RM to adsorb the contaminants on its surface was evaluated (Figure III.4.2). The phenolic acids were contacted with 1 g/L RM during 1 h at pH 3.4 (natural pH of the phenolic mixture prepared). According to Figure III.4.2, it is shown that RM has a negligible ability to adsorb phenolic acids. In fact, only 3,4-dihydroxybenzoic acid was partially adsorbed (less than 10% of its initial concentration). In this sense, it is concluded that the adsorption of contaminants on the surface of the solid catalyst will not be the primary mechanism for their degradation. This low adsorption capacity can be related, not only with the small BET surface and low pore volume as above mentioned, but also the low affinity of the adsorbent to the phenolic acids in the conditions of the test. Moreover, the RM zero-point charge pH is 13, thus at the reaction conditions, it should be positively charged. This can explain the low phenolic acids adsorption at its surface as observed in Figure III.4.2.

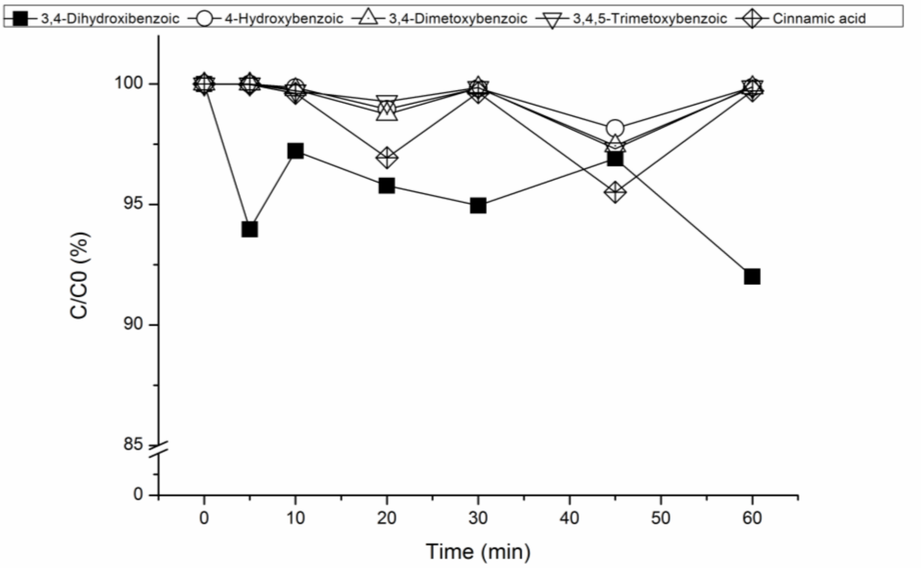

Figure III.4.2. Study of the adsorption capacity of red mud (RM) (pH = 3.4; RM = 1 g/L).

In order to evaluate the ability of the catalyst RM to produce hydroxyl radicals by decomposing hydrogen peroxide (Fenton-like reactions), experiments using 50 mg/L of hydrogen peroxide and 1 g/L of RM were performed. Figure III.4.3 shows the normalized concentration of each phenolic acid along the experimental time. As shown above, the adsorption on red mud alone was not capable to promote significant phenolic acids removal. Therefore, the decline of the contaminants that can occur in the presence of hydrogen peroxide should be related to the hydroxyl radicals production due to Fenton's reaction. In fact, when tert-butanol was used, an efficiency reduction was observed (data not shown), proving the relevance of $^{\bullet}HO$ on the process.

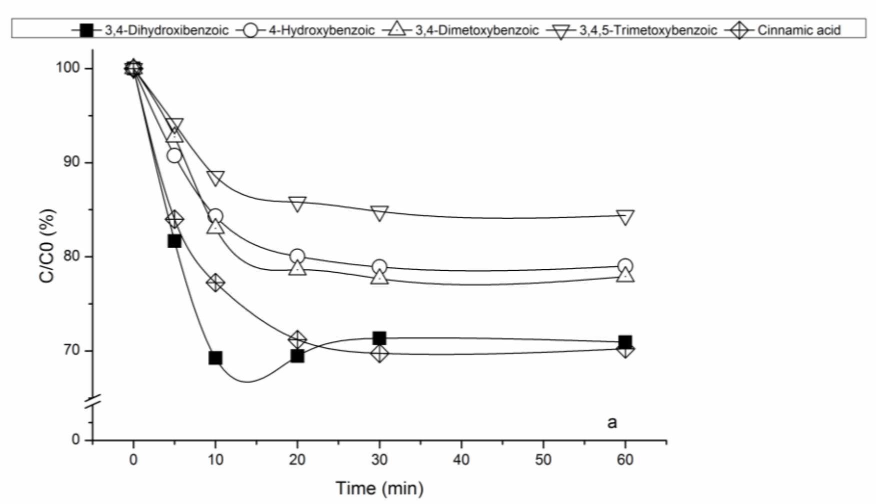

Figure III.4.3. Normalized concentration of phenolic acids throughout the process of Fenton [H_2O_2] = 50 mg/L; RM = 1 g/L; pH = 3.4).

Under the mentioned conditions, the rate of degradation of the phenolic acids was initially high and reached a maximum of 30% in the case of the cinnamic and 3,4-dihydroxybenzoic acids. The cinnamic acid has an unsaturated bond outside the benzene ring, which makes it highly reactive. On the other hand, 3,4-dihydroxybenzoic acid has two hydroxide groups which unprotect the benzene ring making it readily reactive with hydroxyl radicals. In fact, at the beginning of the reaction, a high amount of hydrogen peroxide and iron (II) should be available to react and produce hydroxyl radical, according to Equation (III. 15) (Domingues et al., 2018).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\cdot} \qquad \text{III.15}$$

Furthermore, the hydrogen peroxide can be in excess and react with the hydroxyl radicals produced to further production of water Equation (III.16) or decompose Equation (III.17). The hydroperoxyl radical produced according to Equation (III.16) can present a synergistic effect for phenolic acids degradation due to the presence of the saturated bonds such as benzenic rings

(Gomes et al., 2017). However, this radical presents lower oxidant power when compared with the hydroxyl radical.

$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet}$ III.16

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ III.17

The catalyst load is a key parameter in the optimization of the treatment process, especially regarding Fenton's reaction. In fact, the increase of the catalyst amount leads to a higher number of active sites for the reaction which will favor the production of hydroxyl radical able to decompose pollutants. However, when the catalyst load exceeds the optimal value, it can act as radical scavenger, reducing the production of reactive oxidant species and leading to the decrease of the effluent decontamination efficiency.

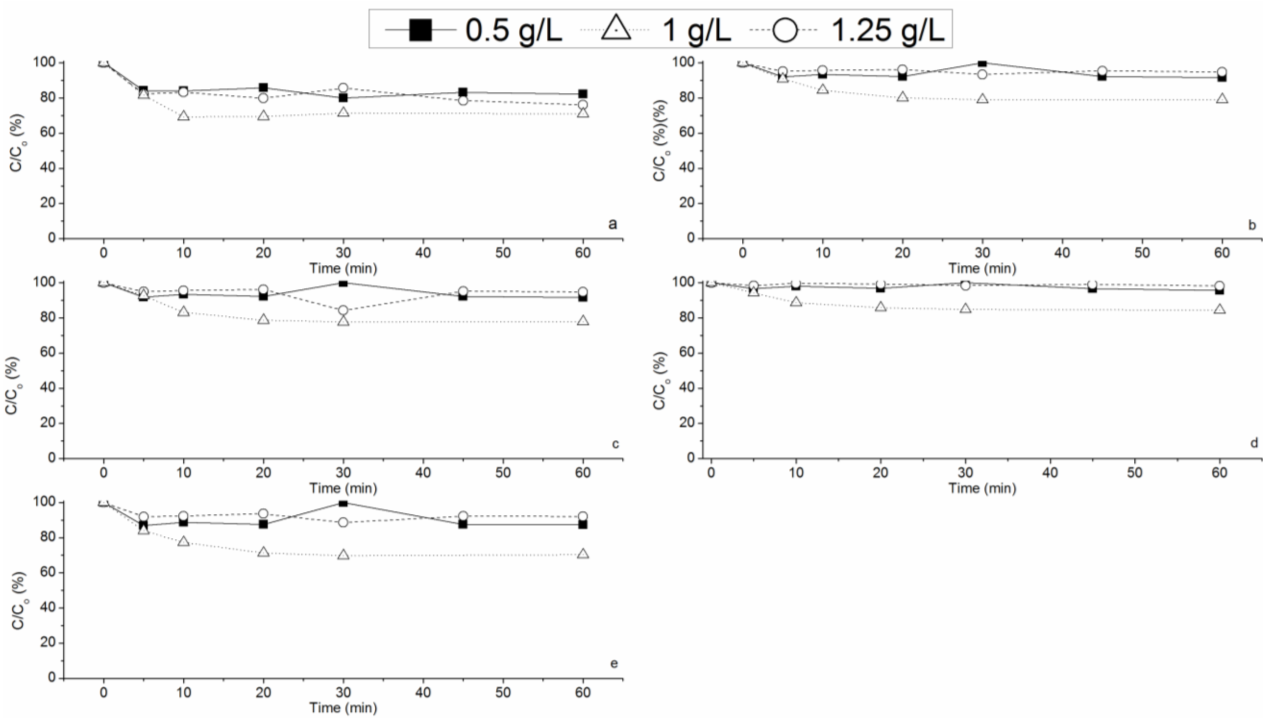

Figure III.4.4. Effect of the catalyst load on the acid degradation (a) 3,4-dihydroxybenzoic acid, (b) 4-hydroxybenzoic acid, (c) 3,4-dimethoxybenzoic acid, (d) 3,4,5-trimethoxybenzoic acid and (e) cinnamic acid. (H_2O_2 = 50 mg/L; pH = 3.4).

Figure III.4.4 shows the effect of the catalyst loading on the degradation of each phenolic acid studied for 60 min at the pH of the phenolic acid mixture (about 3.4). Initial hydrogen peroxide concentration of 50 mg/L was used and the RM load within the range of 0.5–1.25 g/L was evaluated.

Increasing the catalyst load from 0.5 to 1 g/L improved the efficiency of the process. This effect is due to the presence of more active sites to promote the production of hydroxyl radical.

However, above this value (1.25 g/L), the degree of degradation decreases, reaching the same level as the one obtained with 0.5 g/L of RM. Thus, above 1 g/L of catalyst load, the scavenger effect prevails. Therefore, the next tests were carried out using 1 g/L of RM.

Hydrogen peroxide is a key parameter in the efficiency of Fenton´s peroxidation. On the other hand, it can constitute a large part of the operational costs of the process. In this sense, the optimization of the quantity used must be carefully carried out. Above the optimum concentration, hydrogen peroxide can scavenge hydroxyl radicals leading to the reduction of the process efficiency (Domingues et al., 2018).

The concentration of H_2O_2 was evaluated within the range of 25–125 mg/L, pH 3.4, and using 1 g/L of RM (selected in the previous section). Figure III.4.5 shows the normalized concentration of each phenolic acid for 60 min of the reaction, at different concentrations of hydrogen peroxide.

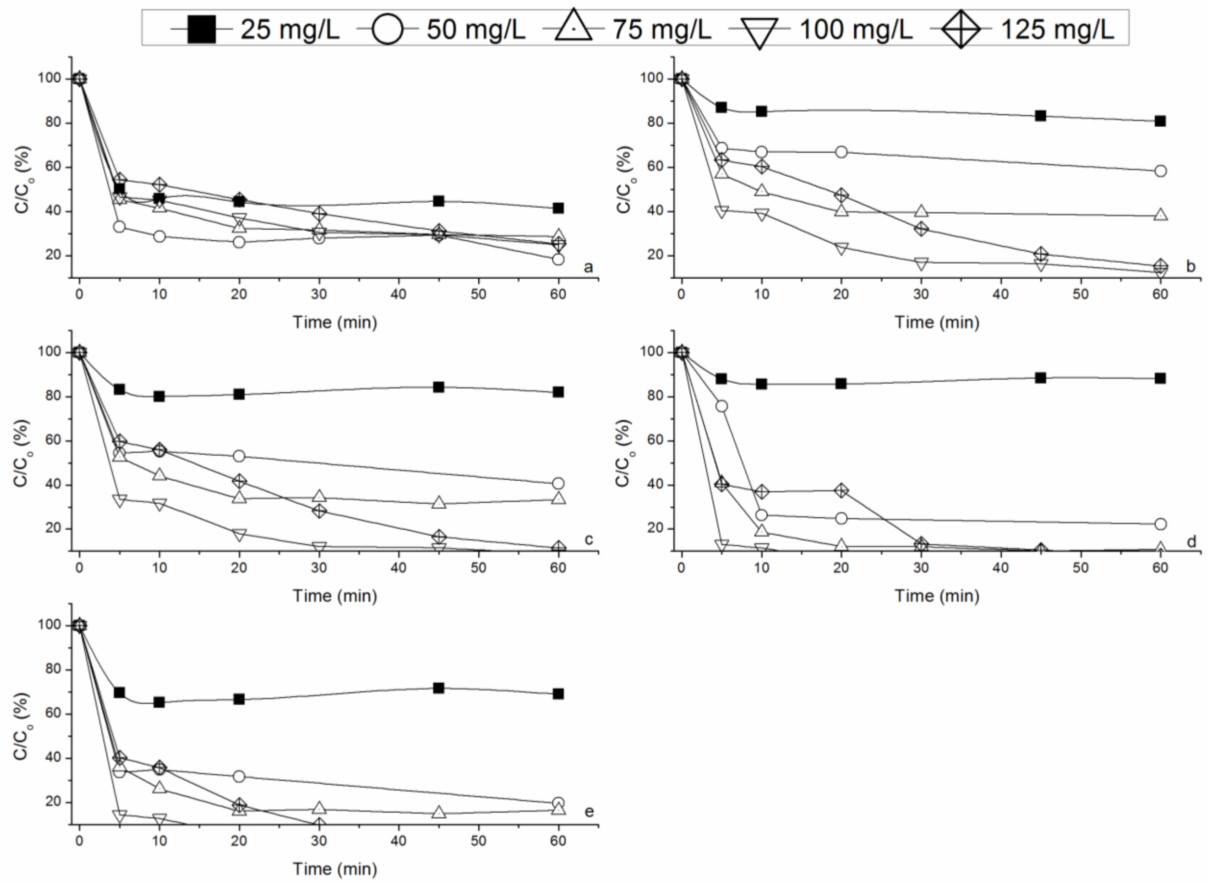

Figure III.4.5. Effect of the concentration of hydrogen peroxide on the degradation of (a) 3,4-dihydroxybenzoic acids, (b) 4-hydroxybenzoic acid, (c) 3,4-dimethoxybenzoic acid, (d) 3,4,5-trimethoxybenzoic acid and (e) cinnamic acid. (RM = 1 g/L; pH = 3.4).

For all the phenolic acids, it was found that increasing the concentration of hydrogen peroxide from 25 mg/L until 100 mg/L improves their degradation rate. The increase in efficiency is less evident for cinnamic acid. Indeed, the unsaturated bond outside the benzenic ring makes this acid a very reactive species, whatever the conditions of heterogeneous Fenton's process operation. Approximately 25 mg/L of H_2O_2 seems to be a low concentration for the degradation of phenolic acids. The increase to 50 mg/L enhances significantly the degradation rate of phenolic acids. Nevertheless, a load of 125 mg/L leads to the scavenger effect due to the hydrogen peroxide excess according to the reaction in Equation (III.17). The literature refers that the excessive amount of H_2O_2 in Fenton's process promotes its auto decomposition to produce water and oxygen (Ramirez et al., 2007). According to Equation (III.16), H_2O_2 may react with hydroxyl radicals leading to hydroxyperoxyl radicals, which have a lower oxidation capacity than the former, leading to lower degradation rates.

Besides the degradation of phenolic acids during Fenton's process, the degree of mineralization achieved by this treatment process was also evaluated through TOC analysis. In fact, the complete degradation of the initial phenolic compounds does not necessarily mean that the production of carbon dioxide and water (mineralization) occurs. Instead, partial oxidation may happen. Therefore, TOC analysis allows understanding if the reaction of degradation occurs mainly towards partial oxidation or mineralization pathway. TOC removal was analyzed for the same conditions of the previous section, which means using different amounts of hydrogen peroxide and 1 g/L of red mud. As can be seen in Figure III.4.5, with the exception of the case where 25 mg/L of H_2O_2 were applied, high degradation of almost all phenolic acids was achieved. However, TOC removal indicates that the preferential way was partial oxidation since the mineralization level achieved is low. In terms of TOC reduction, the efficiency as a function of H_2O_2 load followed this order (efficiency between brackets): 25 mg/L and 125 mg/L (5.1%) < 50 mg/L (10%) < 100 mg/L (25%). Accordingly, it is possible to conclude the best condition applied on the Fenton's process was 1 g/L of red mud and 100 mg/L of H_2O_2. The lowest hydrogen peroxide load (25 mg/L) presents a low reduction of phenolic acids concentration and a small TOC reduction. On the other hand, the highest load (125 mg/L) was able to remove almost all phenolic acids which were not mineralized, but in turn, produced several by-products through partial oxidation. Thus, for this excess level of H_2O_2, the radical scavenger effect was more evident regarding mineralization.

III.4.3.3. Toxicity assessment

Since total mineralization of the wastewater was not achieved, it is necessary to demonstrate if the by-products resulting from phenolic acids partial degradation are more or less toxic than those from the initial mixture. Moreover, while Fenton's process usually applies hydrogen peroxide in excess at the end of the reaction, it can still be present in solution and can affect toxicity. Therefore, the use of a wide range of species for the toxicity assessment will allow the assessment of the impact of the raw and treated sample over different trophic levels. In this way, the toxicity tests selected a bacteria (*A. fischeri*), a clam (*C. fluminea*) and a plant (*L. sativum*). *A. fischeri* was included since the literature indicates this species as the most commonly used for preliminary toxicity tests (Miralles-Cuevas et al., 2017). The Asian clam is an invasive species with high dispersal capacity due to its high resistance to adverse conditions (Rosa et al., 2014). These characteristics make this species an important indicator in terms of toxicity for aquatic species. Finally, the *L. sativum* (garden cress) was selected due to its resistance capacity, and as an indicator of the potential impact if water recovery is aimed for agriculture purposes. According to the oxidation experiments, the best conditions for the phenolic acids degradation through Fenton's process are 1 g/L of red mud coupled with 100 mg/L of hydrogen peroxide. The toxicity was evaluated to the sample obtained after 60 min of heterogeneous Fenton at those conditions and compared with the initial mixture of phenolic acids. Moreover, to attest the effect of red mud amount applied as a catalyst over toxicity, two different loads (0.5 g/L and 1.5 g/L) were considered. In fact, the leaching of metals from red mud can be problematic in terms of toxicity for aquatic species (Gomes et al., 2019). For these two concentrations of red mud, the same amount of hydrogen peroxide (100 mg/L) was used. Figure III.4.6 presents the luminescence inhibition of bacteria after 30 min of exposure (a), the mortality of clams (b), and germination index of cress (c) for the different samples.

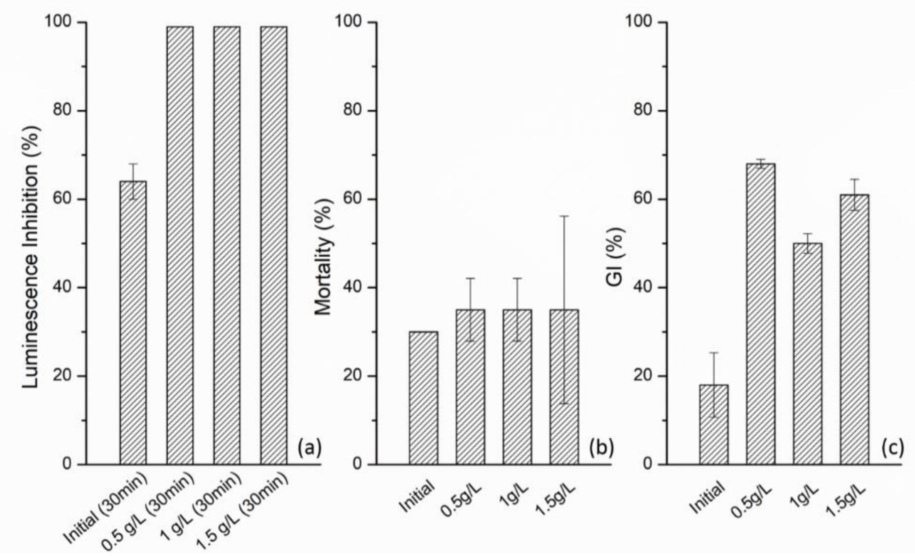

Figure III.4.6. Luminescence inhibition of *A. fischeri* (a), mortality of *C. fluminea* (b) and germination index of *L. sativum* (c) for the initial phenolic acids mixture and different RM concentration (0.5, 1 and 1.5 g/L) (pH 3.4; concentration of H_2O_2 = 100 mg/L).

Figure III.4.6a shows that the luminescence inhibition of *A. fischeri* after 30 min of exposure to treated solutions was approximately 100%. These results reveal no difference independently of the amount of RM applied during Fenton's process, whereas the initial mixture of phenolic acids induces a lower luminescence inhibition of about 64%. As previously mentioned, the presence of H_2O_2 in excess can be the reason for this behaviour. In fact, the hydrogen peroxide concentration is high after 60 min of Fenton's process. For the 0.5 g/L, 1 g/L and 1.5 g/L at the end of reaction, the hydrogen peroxide concentration was 120 mg/L, 60 mg/L and 80 mg/L, respectively. The luminescence inhibition of 100 mg/L of hydrogen peroxide without red mud was measured for comparative purposes. This concentration promotes 100% of luminescence inhibition. Therefore, the toxicity of the treated solutions over *A. fischeri* should be highly related to H_2O_2 residual concentration.

C. fluminea mortality seems to present the same behaviour as bacteria. The treated solutions after 72 h of contact revealed to be more toxic than the initial mixture of phenolic compounds. However, the difference was not so high. The initial mixture of phenolic acids leads to 30% of mortality while treated solutions promoted 35% of mortality. This can be due to the clams higher resistance when compared to bacteria. This low difference seems to indicate that H_2O_2 does not have a significant impact over *C. fluminea*. Moreover, the amount of RM applied also does not affect the toxicity of the treated samples over clams. Therefore, the small increase of treated samples toxicity towards *C. fluminea* can be due to the by-products formed in the oxidation process. In fact, Gomes et al. (2019) verified for parabens degradation when the 4-hydroxybenzoic acid (by-product from parabens oxidation) concentration decreases, it promotes the formation of hydroquinone, which is more toxic than the 4-hydroxybenzoic acid. In this way, the formation of these by-products can be more toxic than the initial mixture, even if a very low concentration is produced.

L. sativum seems to be the most sensitive species tested to the initial phenolic mixture since the germination index for the raw effluent was about 19%. According to the Trautmann and Krasny (1997) criteria, this value should be considered as severe toxicity. This shows that the direct application of OMW in agricultural fields should be monitored to avoid negative impact over plants. On the other hand, the GI increased for the treated solutions reaching the classification of moderate toxicity. *L. sativum* has been used in traditional medicine for diseases treatment due to its capacity to work as an antioxidant (Yadav et al., 2010). In turn, hydrogen peroxide is seen as an oxidative stress agent resulting in dead cells (Hwang and Yen, 2008). Al-Shedi et al. (2016) verified that the *L. sativum* seed extract has a protective effect over human liver cells at the presence of hydrogen peroxide. Compared to our study, the presence of more hydrogen peroxide results in a higher germination index. In fact, the use of 0.5 g/L of RM in Fenton's process results in a final H_2O_2 concentration of 120 mg/L and the GI was about 68%. The highest RM dose leads to a final concentration of H_2O_2 of 80 mg/L and the GI was 61%. Therefore, it is possible to conclude that the GI is highly related to the residual hydrogen peroxide concentration. Nevertheless, increasing pH of the final treated water may be a suitable methodology to overcome this issue since H_2O_2 decomposition is promoted in these conditions. Thus, Fenton's process using RM can be a suitable solution for OMW decontamination.

III.4.4. Conclusions

A simulated olive mill wastewater was treated by a heterogeneous Fenton's process. An industrial waste from the alumina industry (red mud-RM) was used as a heterogeneous source of iron. The effect of hydrogen peroxide and the RM load on the process efficiency were evaluated. The excessive amount of RM on the Fenton's process seems to inhibit the degradation rate. Similarly, high amounts of H_2O_2 enable the degradation of phenolic acids mixture until a certain point above which it shows a radical scavenger effect. The best operating conditions were 1 g/L of RM and 100 mg/L of hydrogen peroxide which led to 100% of phenolic acids removal and 25% of mineralization in 60 min. The toxicity assessment reveals that bacteria are very sensitive to the resulting solution mainly due to the presence of high concentrations of residual H_2O_2. However, this effect may be overcome with a suitable hydrogen peroxide removal process. On the other hand, for clams and garden cress, the treated solutions do not present high toxicity when compared with the raw phenolic mixture. Therefore, the application of red mud (a waste) as a heterogeneous source on the Fenton´s process seems to be a suitable option working towards a circular economy.

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III.5. Persulfate Process Activated by Homogeneous and Heterogeneous Catalysts for Synthetic Olive Mill Wastewater Treatment

It is based on the publication: Domingues, E., Silva, M.J., Vaz, T., Gomes, J., Martins, R. C. (2021). Persulfate Process Activated by Homogeneous and Heterogeneous Catalysts for Synthetic Olive Mill Wastewater Treatment. Water, 13(21), 3010.

III.5.1. Introduction

The discharge of industrial wastewaters into water resources, without any type of treatment, is an unfortunate reality. This limits access to quality water. A problematic industry is olive oil production. This industry generates a large amount of contaminated liquid effluent that is highly difficult to treat. Olive mill wastewater (OMW) is a serious environmental problem, produced in olive mills either by the discontinuous press method or by the continuous centrifugation method for olive oil extraction and olive washing processes. However, it is worthy to mention that the European Union (EU) does not have specific legislation with regard to OMW treatment, leaving it to Member States to establish their own legislation.

During olive oil production, large quantities of olive mill wastewaters and residues—olive pomace (OP)—are generated. OP is currently sent to extraction units, where olive oil extraction industry wastewaters (OOEIWs) are also produced. OMW is a dark, odorous, turbid and highly polluted wastewater due to the wide variety of contaminants it contains (Alver et al., 2015). According to its age and the production process, the color of OMW varies from dark red to black. This dark colored wastewater, with very large contents of organic matter, recalcitrant/toxic components such as phenolic compounds (polyphenols, tannins), sugars, proteins, and a considerable salt concentration, is a substantial pollutant and is environmentally hazardous (Gürsoy and Arslan, 2015; Ochando-Pulido et al., 2017; Flores et al., 2018; Ochando-Pulido and Martinez-Ferez, 2018). Given the lack of technologies capable of treating these wastewaters due to their characteristics, the most common practice is to proceed with their disposal in ponds; the paste resulting from this process is discharged into the soil. However, these wastewaters are a source of phenolic compounds and, given their toxicity to both aquatic and human life, they are considered an environmental problem.

Fenton’s process, an advanced oxidation process (AOP) is specified in the literature as interesting alternative for agro-industrial wastewater treatment (Lucas and Peres,2009; Amor et al., 2019). However, Sulfate Radical based Advanced Oxidation Processes (S-AOPs) have been the subject of recent investigations to overcome some of the disadvantages of Fenton's process (Rodríguez et al., 2020). S-AOPs can be applied to remove or degrade resistant pollutants, such as antibiotic-resistant microorganisms, drugs, and non-biodegradable organic matter (Qiu et al., 2020). The sulfate radicals ($SO_4^{\cdot-}$) bind with the pollutants by removing hydrogen from the saturated carbon and adding it in the double bonds or by electron transfer, causing partial or total mineralization of the organic matter (Genç et al., 2020).

The use of S-AOPs has some advantages over the Fenton method, such as:

Sulfate radicals have a higher stability and thus a longer life span than the hydroxyl radical $HO^{\cdot}$, which is the radical formed in the Fenton process;
The oxidant agent necessary to generate $SO_4^{\cdot-}$ is solid at room temperature, which facilitates its transport and storage;
The range of pH values of the S-AOP is wider than the one used in the Fenton process;
Sulfate radicals have a bigger solubility in aqueous solution than HO;
The hydroxyl radicals react through unselective multi-step pathways, which limits the process efficiency (Brienza and Katsoyiannis, 2017; Ioannidi et al., 2020; Gormez et al., 2020).
However, some authors have reported that although sulfate radicals have a greater stability and have an oxidation potential similar to hydroxyl radicals, the reaction rate between SO_4^{-} and organic matter is slower than the one observed between $HO^{\cdot}$ and organic compounds (Waclawek et al, 20147; Giannakis et al., 2021). Nevertheless, other authors have found that the reaction between the organic matter and the sulfate radicals is faster than the one with hydroxyl radicals (Brienza and Katsoyiannis, 2017). The oxidation efficiency of free sulfate radical ($SO_4^{\cdot-}$) is made clear by its oxidation potential ($E_0 = 2.6$ V), which is the third highest after fluorine ($E_0 = 3.6$ V) and $HO^{\cdot}$ ($E_0 = 2.8$ V) (Usman et al., 2020).

Sulfate radicals are generated through the activation of an oxidant agent, like persulfate (PS, $S_2O_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^{-}). Regarding the activation of PS and PMS through catalytic processes, the most common is the use of Fe (II), as shown in Equations (III.18-III.19). It is important to note that during the activation process, in addition to the formation of sulfate radicals, other radicals can be formed, as described in Equations (III.18)–(III.22) (Manos et al., 2020; Qiu et al., 2020; Xiao et al., 2020).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + Fe^{3+} \tag{III.18}$$

$$HSO_5^{-} + Fe^{2+} \rightarrow SO_4^{\cdot-} + OH^{-} + Fe^{3+} \tag{III.19}$$

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + HO^{\cdot} + H^{+} \tag{III.20}$$

$$HSO_5^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + HO^{\cdot} \qquad \text{III.21}$$

$$HSO_5^- + Fe^{3+} \rightarrow Fe^{2+} + SO_5^{\bullet -} + H^+ \qquad \text{III.22}$$

The activation of PS and PMS can be carried out in homogeneous or heterogeneous systems. In homogeneous systems, there is less resistance to mass transfer, and consequently, the reaction rate is faster. Nevertheless, some unwanted side reactions take place, and ferrous sludge is formed. Heterogeneous systems emerged with the aim of eliminating the disadvantages of homogeneous systems, namely the formation of iron sludge (Manos et al., 2020; Xiao et al., 2020). Persulfate decontamination technologies, whether using radical driven processes or direct electron transfer, have proven to be very powerful processes for the treatment of a wide range of pollutants, namely halogenated olefins, BTEXs (benzene, toluene, ethylbenzene and xylenes), perfluorinated chemical products, phenols, pharmaceutical products, inorganics, and pesticides (Lee et al., 2020).

The use of iron-rich residues as catalysts in this process can be an interesting environmental approach. Red mud (RM) is a low-cost catalyst, and it was innovatively applied in the Fenton process with the objective of reducing the operation costs and reusing a waste that is currently produced in large quantities. RM is the iron-rich waste formed during aluminum oxide production by the bauxite leaching process (Bayer process) (Domingues et al., 2019). In another perspective, Fe-Ce-O was studied because ceria-based iron catalysts have shown good performance in enhancing the removal of organic compounds, reducing toxicity, and improving biodegradability in the depuration of phenolic wastewaters with the ozonation process (Martins et al., 2009).

Bearing all this in mind, the objective of the present work is to evaluate the applicability of S-AOPs in the treatment of synthetic olive oil wastewater. More specifically, the applicability of metal-activated persulfate as a source of radical sulfates is analyzed. Homogeneous S-AOPs are compared with the heterogeneous process. Moreover, the results are compared with Fenton’s peroxidation, considering the pollutants’ abatement but also the toxic impact of the treated samples.

To the best of our knowledge, the degradation of synthetic OMW has not been carried out by PS oxidation through the application of iron as an activator. In the present study, the degradation of synthetic OMW by PS oxidation, using homogeneous (Iron (II) Sulfate Heptahydrate) is studied for the first time. Moreover, new solid catalysts (RM and Fe-Ce-O) were also innovatively tested as activators of PS.

III.5.2. Materials and Methods

III.5.2.1. Reagents

The synthetic OMW consists of a solution of five phenolic compounds (Trans-cinnamic acid, 3,4-Dihydroxybenzoic, 4-Hydroxybenzoic, 3,4,5-Trimethoxybenzoic, and 3,4-Dimethoxybenzoic) dissolved in ultrapure water, with a concentration of 100 mg/L each. All phenolic acids were purchased from Sigma-Aldrich (Velp Scientifica, Taufkirchen, Germany).

III.5.2.2. Catalysts

The Red Mud was supplied by a Greek aluminum producer, and it was prepared for used in accordance with Domingues et al. (2019): grounded and sieved (diameter < 0.105 μm) after drying at 105 °C for 24 h. RM elemental composition was determined by atomic absorption. First, the solid sample was digested (HCl, 6 M). The insoluble compounds were separated by vacuum filtration, and the filtrate was transferred to a 100 mL flask to which ultrapure water was added until the volume was adjusted. The solution was then characterized by atomic absorption to determine its content in metal elements.

Fe-Ce-O is a solid prepared in the laboratory, according to (Martins et al., 2010a), composed of a molar ratio Fe/Ce equal to 70/30. The catalyst precursors were $Fe(NO_3)_3{\cdot}9H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ (Panreac, Barcelona). After co-precipitation, the solution was filtered and washed 5 times with ultrapure water, and the resulting precipitate was dried at 105 °C for 3 h. Then, the sample was calcined for 3 h at 300 °C, and finally it was ground manually and sieved (diameter < 0.105 μm).

It should be noted that Fe-Ce-O 70/30 was selected as a heterogeneous iron-based catalyst for this study due to its good performance in the Fenton process (Martins et al., 2010b). In addition, the choice of calcification temperature was also based on the results obtained in a previous work (Rossi et al., 2012) when applying Fe-Ce-O 70/30 in the Fenton process.

III.5.2.3. S-AOP experiments

The S-AOP experiments took place in a 500 mL spherical reactor made of glass. To this reactor, 250 mL of synthetic OMW was added and subjected to a stirring of 300–500 rpm in homogeneous catalysis, and 800–1000 rpm in heterogeneous catalysis, by magnetic agitation. Then, the catalyst was added, followed by pH correction, by pouring drops of a NaOH and a H_2SO_4 solution. The reaction was then started through the addition of the oxidant agent (PS). To stop the reaction, after 30 min, the pH was changed to 7 by pouring drops of NaOH and

H_2SO_4. Then, the solution was centrifuged at 4000 rpm in a Nahita centrifuge model 2655 for 5 min, and finally it was filtered through a 0.45 µm cellulose acetate filter.

After the reaction stopped, the efficiency of the treatment applied was analyzed in terms of the reduction of the chemical oxygen demand (COD), biological oxygen demand (BOD_5), total organic carbon (TOC), and the concentration of phenolic compounds. The experimental procedure described above, from the formulation of the OMW to the analysis of the efficiency of the process, is outlined in Figure III.5.1.

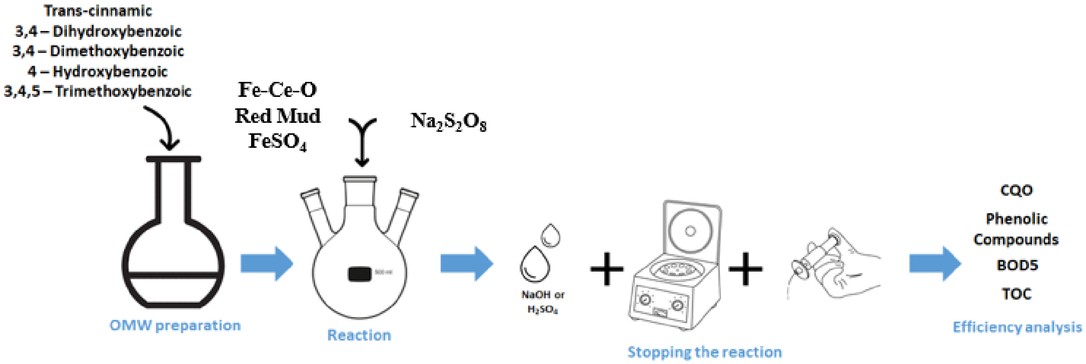

Figure III.5.1. Outline of the experimental procedures.

III.5.2.4. Analytical techniques

To analyze the COD, the 5220 D method was applied (Baird et al., 2017). For the application of this method, samples of the treated OMW were diluted by a factor of 10. Then, 2.5 mL of the diluted OMW was introduced into the digestion vessels along with 1.5 mL of the digestion solution and 3.5 mL of the acid solution. Afterwards, the vessels were introduced in the ECO 25 (Velp Scientifica, Taufkirchen, Germany) digester at 150 °C for 2 h. Finally, the vessels were cooled slowly to room temperature over 1 h. After cooling, the absorbance of the samples was read in the PhotoLab S6 (WTW) filter photometer at 445 nm. All samples were analyzed at least in duplicate.

The phenolic content was obtained throughout the Folin–Ciocalteu method (Lamuela-Raventós, 2017). For the application of this method, 20 µL of the treated OMW was placed in cuvettes with 1.58 mL of distilled water, 100 µL of the Folin–Ciocalteu (Panreac, Darmstadt, Barcelona) reagent, and 300 µL of a saturated solution of sodium carbonate (Na_2CO_3). After 2 h in the dark, the absorbance of the samples was read in the T60 UV/VIS (PG Instruments, Leicestershire, UK) spectrophotometer at 765 nm. All samples were analyzed in duplicate.

To analyze the TOC, the 5310 B method was applied (Baird et al., 2017). For the application of this method, the sample had to be homogenized and diluted, as necessary. The sample was then injected, and the inorganic and organic carbon were measured via a nondispersive infrared analyzer. This analysis was carried out in an SSM-5000A (Shimadzu, Tochigi, Japan).

The respirometry (BOD_5) measurement is a pressure measurement. If oxygen is consumed in a closed vessel at a constant temperature, a negative pressure develops. If a gas is released, an overpressure develops. The OxiTop® measuring head measures and stores this pressure for the whole duration of a measurement once started. The OxiTop® OC 110 controller collects the pressure values from the measuring heads and processes them.

HPLC was applied to evaluate the individual degradation of the five phenolic acids present in OMW and identify intermediate compounds. HPLC was applied according to Domingues et al. (2020), and a C18 column (SiliaChrom) at 40 °C was used. The mobile phase had a flow rate of 0.5 mL/min and consisted of a 50/50 mixture of methanol and acidified water, with 1% orthophosphoric acid. The peak determination occurred at 255 nm.

The purpose of atomic adsorption was to characterize the RM as well as to identify and quantify metal leaching during heterogeneous catalysis. The analyses were performed according to the 3111 B method, in accordance with Baird et al. (2017). For the application of this method, standard solutions of the metals were prepared according to the method mentioned above. The samples for the leaching analysis were prepared according to the 3030 C method. For this method, ContrAA 300 (Analytik Jena Gmbh, Jena, Germany) equipment was used.

III.5.2.5. Toxicity

To assess the toxicity of treated wastewater, the sensitivity of species such as bacteria *Aliivibrio fischeri* and *Lepidium sativum* was analyzed, as described by Domingues et al. (2019) and Baird et al. (2017).

Regarding the toxicity studies carried out on *A. fischeri*, the luminescence inhibition was analyzed and compared with a blank, according to the 8050 method described by Baird et al. (2017) The blank consists of a solution with 2% NaCl that is suitable for the growth of bacteria.

The inhibition effect was measured after 15 and 30 min of contact of the bacteria with the treated and untreated wastewater, using a Lumistox 300 (Dr. Lange) luminometer. Before starting the tests, all samples had their pH corrected to a value between 6.5 and 7.5.

The toxicity tests with *L. sativum* consisted of the introduction of 10 seeds evenly separated in filters placed in Petri dishes. Afterwards, the filters were wet with 5 mL of treated and untreated wastewater and with distilled water (blank). Then the Petri dishes were placed in an oven at 27 °C for 48 h. These experiments were carried out in duplicate, and before starting the tests, all samples had their pH corrected to a value between 6.5 and 7.5. These tests allowed us to determine the germination index (GI), according to Trautmann and Krasny (2017).

III.5.3. Results and discussion

III.5.3.1. Synthetic OMW characterization

The characterization of the synthetic OMW was made based on the following parameters: pH, chemical oxygen demand (COD), total organic carbon (TOC), and phenolic compounds (Table III.5.1).

Table III.5.1. Synthetic OMW characterization.

Parameter	**COD (mg/L)**	**TOC (mg/L)**	**Phenolic Compounds (mg/L)**	**pH**
Value	800 ± 64	284 ± 23	300 ± 24	3.5 ± 0.2

III.5.3.2. Homogeneous catalysis

The performance of the S-AOPs based on iron-activated persulfate, in homogeneous catalysis and using iron sulfate as a catalyst, was optimized and analyzed in terms of the results obtained regarding the removal of organic matter and toxicity.

Before optimizing the operating conditions of homogeneous catalysis, the need for persulfate activation was investigated. Thus, an experiment involving the addition of persulfate (600 mg/L) to the effluent at pH 5 was tested. At these conditions, it was possible to obtain a COD removal of 4.08 ± 0.44% after 60 min of reaction. These results evidence the need for persulfate activation. In fact, Chueca et al. (2017a) attained up to 87% of COD removal in the treatment of synthetic wastewater from the wine industry with iron activated persulfate. In this context, the need for persulfate activation is clear. At homogeneous conditions, iron sulfate was selected as the iron source for persulfate activation.

To optimize the operating conditions of the homogenous process, pH, persulfate load, and iron concentration were selected as operation variables. Regarding the pH tests, the initial concentrations of iron and persulfate (PS) were kept constant and equal to 200 mg/L and 600 mg/L, respectively. pH ranged within 3–11. Figure III.5.2 represents the pH influence on COD and phenolic compound removal after 30 min of reaction.

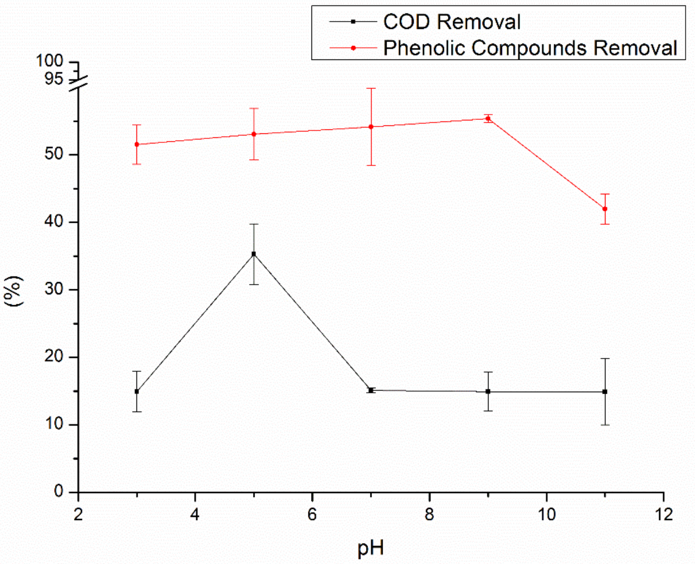

Figure III.5.2. pH influence on COD removal and phenolic compound removal (30 min of reaction, $[Fe^{2+}]$ = 200 mg/L and [PS] = 600 mg/L).

By analyzing Figure III.5.2, it is concluded that a pH value of 5 makes it possible to obtain a maximum COD removal of approximately 35%, while the remaining tested pH values allowed a COD removal of approximately 15%. However, it also can be observed that the pH value does not have a significant influence on the removal of phenolic compounds (around 50%). The exception is pH 11, which slightly decreases the removal efficiency of these compounds.

The low COD removal obtained for a pH of 3 can be justified by the scavenger effect that H+ causes on the sulfate radical. On the other hand, the low COD removal at alkaline conditions may be caused by the formation of $HO^{\cdot}$, which, although having an oxidation redox similar to sulfate radicals, has a shorter life span (Ghanbari and Moradi, 2017; Hoa et al., 2021) which may make it less available for reaction.

Bearing in mind COD and phenolic content removal, a pH of 5 was selected as the optimal value. The result obtained agrees with that obtained by Chueca et al. (2017a,b), which, among the few studies found, focused on the treatment of wastewaters from the agro–food industry by iron-activated PS. Although the result obtained was as expected, the discrepancy between the efficiency of COD removal between pH 5 and the remaining values was unexpected, since it was reported by Ioannidi et al. (2020) that the S-AOP has a wide operating range of pH values.

With the pH tests, it was also found that, with the course of the reaction, regardless of the initial pH, the pH of the medium decreased. This can be justified by the reaction of the sulfate radical with OH^{-} and the consequent formation of H^{+}, as represented in Equation (III.5.9) and mentioned by Fan et al. [33].

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + HO^{\cdot} + H^{+} \qquad \text{III.23}$$

To test the effect of the persulfate, the initial concentrations of iron and the pH value were kept constant and equal to 200 mg/L and 5, respectively. The persulfate load was analyzed within the range of 400–800 mg/L. Figure III.5.3a–d represent the PS load influence on COD and phenolic compound removal, respectively.

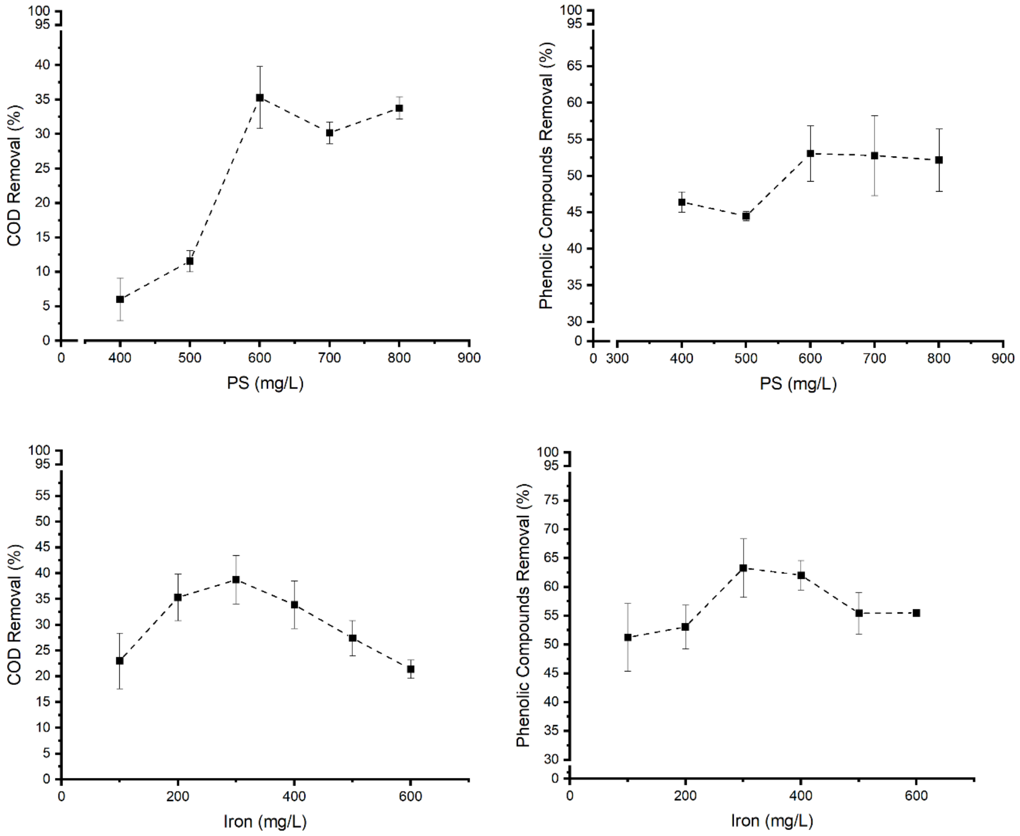

Figure III.5.3. Persulfate and iron load influence on COD removal and phenolic compound removal. (a) Persulfate COD removal, (b)iron phenolic compound removal, (c) Persulfate phenolic compound removal (d) iron COD removal.

Through Figure III.5.3a, it is concluded that a persulfate concentration of 600 mg/L allowed us to obtain a maximum COD removal of approximately 35%. From 400 to 600 mg/L, there was an increase in the COD removal efficiency, and from this point onwards an increase in the PS concentration led to a plateau, with COD removal barely changing. A PS concentration of 600 mg/L also allowed the maximum phenolic compound removal, approximately 53% (Figure III.5.3b). After this, the phenolic content removal did not significantly change with the increasing concentration of the oxidant. It was expected that the increase in PS concentration would result in a scavenger effect, that is, a decrease in removal efficiency. However, this was not the case, perhaps because, as mentioned by Xiao et al. (2020), the PS scavenger effect is not very noticeable, and the PS load may not have increased enough to detect this phenomenon.

Iron load tests (Figure III.5.3c,d) were performed keeping the initial concentrations of persulfate and the pH value constant at 600 mg/L and 5, respectively. Iron load was evaluated within the range of 100–600 mg/L.

From Figure III.5.3c,d, it is concluded that the optimal concentration of iron is 300 mg/L, as this load results in the more pronounced removal of COD and phenolic compounds: 39% and 63%, respectively. COD and phenolic content removal increased with an increase in the iron load from 100 to 300 mg/L. From this point onwards, an increase in the catalyst load resulted in a decrease in the removal efficiency of the process.

III.5.3.3. Toxicity assessment

In order to evaluate the effect of the treatment on the wastewater toxicity, the treated samples' GI was compared with the initial effluent. For the toxicity assessment with *L. sativum*, samples from the reactions that operated with a PS concentration of 500, 600, and 700 mg/L were analyzed. The results of these experiments are presented in Table III.5.2.

Table III.5.2. Germination index results for *L. sativum*, for different conditions of process.

Type of effluent	**Synthetic Effluent**	**400 mg/L**	**500 mg/L**	**600 mg/L**	**700 mg/L**	**800 mg/L**
GI (%)*	30.6 ± 3.2	---	46.1 ± 11.5	39.9 ± 11.5	29.7 ± 16.6	---
GI (%)**	30.6 ± 3.2	47.3 ± 19.3	42.7 ± 15.1	39.2 ± 10.0	33.8 ± 0.5	43.6 ± 1.0
GI (%)***	30.6 ± 3.2	39.9 ± 11.5	33.1 ± 6.9	34.1 ± 0.4	---	---

* Germination index results for *L. sativum* for a PS concentration of 500, 600, and 700 mg/L; Iron = 200 mg/L; pH 5. ** Influence of the PS load without iron on *L. sativum* growth. *** Germination index results for *L. sativum* for an iron concentration of 200, 300, and 400 mg/L.

From the analysis of Table III.5.2, it can be observed that the treated samples have a higher or equal GI than that of the untreated wastewater. In this scenario, in accordance with Trautmann and Krasny (2017), the treated sample with a PS load of 500 mg/L showed a strong inhibition towards plant growth, the sample with a PS load of 600 mg/L showed a severe inhibition, and the sample with a PS load of 700 mg/L showed a severe inhibition.

Considering the decrease in GI with the increase in the PS load, the individual influence of the PS load on the toxicity of *L. sativum* was also analyzed. For this, ultrapure water with different PS concentrations was used in the germination tests. These results are shown in Table III.5.2. It seems that all samples have a higher GI than the untreated wastewater. Thus, considering the PS load and the organic matter concentration present in the sample, it seems that the toxic effect of persulfate introduced in the solution is less than that of the phenolic compounds present in the wastewater. It is also concluded that an increase in PS load results in a slight decrease of the GI, that is, an increase in the toxic effect. Among all samples, only the two with the lowest PS load (400 and 500 mg/L) are classified, according to Trautmann and Krasny (2017), as having strong inhibition, whereas the rest are classified as having a severe inhibition.

By comparing the results of Table III.5.2, it is possible to conclude that the increase in PS concentration does not justify the decrease in GI and, consequently, the increase in toxicity. Thus, intermediate and/or secondary compound formation during the oxidation treatment are also a reason for the toxic character of the treated samples.

To evaluate the effect of iron load on the treated wastewater's toxic character, toxicity tests were carried out on *L. sativum* using the samples of the reactions that operated with an iron load of 200, 300, and 400 mg/L. Results are shown in Table III.5.2. It can be observed that the treated samples have a higher—but similar—GI than that of the untreated wastewater. In this scenario, in accordance with Trautmann and Krasny (2017), all samples show a strong inhibition towards plant growth.

III.5.3.4. Homegeneous S-AOP Performance under the Optimal Operating Conditions

From the experiments described above, it can be concluded that the optimal conditions involve the use of 600 mg/L of PS and 300 mg/L of iron. This means an optimal mass ratio between the PS load and the iron load of two, which is equivalent to use a molar ratio of 0.58. This conclusion does not line up with the recommendation of Rodriguez et al. (2012) and Xiao et al. (2017) which is the use of a molar ratio between the PS load and the iron load of one. This phenomenon can be justified by the occurrence of secondary reactions that consume iron (II), as in the case of the reaction between iron and dissolved oxygen (Xiao et al., 2017).

Knowing the optimal ratio between the reagents, the influence of the increased loads of reactants was analyzed, keeping this ratio constant. For these tests, the initial pH value was kept constant at five, and the following pairs of values were used for the concentration of PS and iron, respectively, in mg/L: (600; 300), (1200; 600), (1800; 900), (2400; 1200). Figure III.5.4 shows the influence of these loads on COD and phenolic compound removal.

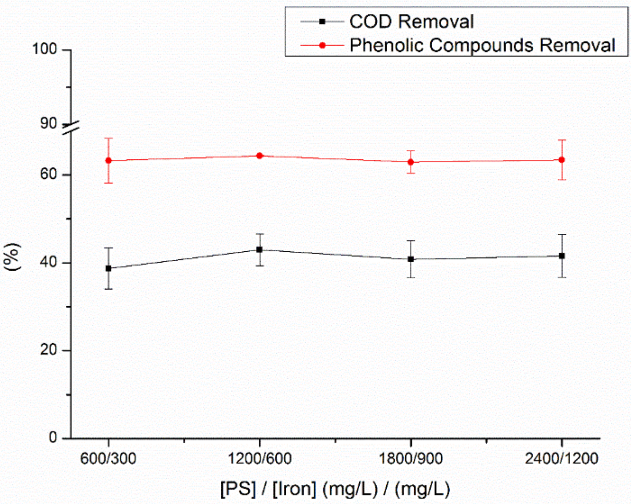

Figure III.5.4. Persulfate and iron load influence on COD removal and phenolic compound removal. (30 min of reaction at pH 5).

From the analysis of Figure III.5.4, it is possible to conclude that an increase in the loads of persulfate and of iron, maintaining the proportion between them, does not result in a significant increase in the removal of COD or the removal of phenolic compounds. Therefore, it can be said that the optimum concentration of reagents to be introduced is 600 mg/L of PS and 300 mg/L of iron, as previously discussed.

As in previous experiments, the toxicity of treated wastewater was analyzed. In this case, for the tests with L. sativum, samples of the reactions that operated with the pairs of values (600; 300) and (1200; 600) were evaluated, and the results are shown in Table III.5.3.

Table III.5.3. GI results for *L. sativum*, for a persulfate an iron load of (600; 300) and (1200; 600) mg/L.

Type of effluent	**Synthetic Effluent**	**(600; 300) mg/L**	**(1200; 600) mg/L**
Germination Index (%)	30.6 ± 3.2	33.1 ± 6.9	32.8 ± 1.6

From the analysis of the Table III.5.3, it can be observed that the treated samples have a similar GI to that of the untreated wastewater, which may be caused by the formation of intermediate compounds with a higher or similar toxicity to the original compounds present in the OMW. In this scenario, in accordance with Trautmann and Krasny (2017), all samples showed a strong inhibition towards plant growth.

As mentioned above, a pH value of 5, an iron concentration of 300 mg/L, and a PS concentration of 600 mg/L are the optimal parameters for the treatment process under analysis. Under these conditions, it is possible to achieve a COD removal of 38.74 ± 4.7%, a removal of phenolic compounds of 63.19 ± 5.1%, and a removal of TOC of 36.98 ± 7.2%. Thus, the treated wastewater under the best operating conditions has, approximately, a COD load of 520 ± 40 mg/L, a TOC load of 179.3 ± 20.5 mg/L, and a concentration of phenolic compounds of 129 ± 18 mg/L.

Therefore, considering the environmental limit values (ELVs) for the discharge of OMW in water resources, as represented in Table III.5.4, the effluent resulting from the treatment process cannot be discharged.

Table III.5.4. ELV for OMW discharge (Adapted from Halalsheh et al., 2021).

Parameter	**Portugal**	**Spain**	**Greece**	**Italy**
COD (mg/L)	150	160–500	45–180	160
BOD_5 (mg/L)	40	40–300	15–60	40
Phenolic Compounds (mg/L)	0.5	0.5–1	0.005–0.5	0.5
pH	6–9	5.5–9.5	6–9	5.5–9.5

In addition, under the optimal operating conditions, the treated OMW still has high levels of toxicity for *A. fischeri* (bacteria). After 15 min of contact with the solution, the luminescent activity of the bacteria was inhibited by 64.82 ± 2.85% and, after 30 min, by 69.16 ± 3.20%. For the same contact times, the untreated wastewater inhibited microbial activity by 60.38 ± 0.31% and 61.29 ± 0.54%, respectively. Regarding the toxic effect on the species L. sativum (plant), as mentioned before, the untreated OMW showed a GI of 30.6 ± 3.2%, while the treated wastewater had a GI of 33.1 ± 6.9%. All the values mentioned above are shown in Table III.5.5.

Table III.5.5. Luminescence inhibition and germination index results for bacteria and *L. sativum*, respectively, for the untreated OMW and the treated wastewater under the optimal conditions.

Type of Solution	***Bacteria A. fischeri***		***L. sativum***
	Inhibition (15 min)	**Inhibition (30 min)**	**GI**
Untreated OMW	60.38 ± 0.31%	61.29 ± 0.54%	30.6 ± 3.2%
Treated OMW	64.82 ± 2.85%	69.16 ± 3.20%	33.1 ± 6.9%

The performance of the process under the optimum conditions was further analyzed considering the individual degradation of each of the five phenolic compounds present in the OMW. This analysis was performed based on the variation of the peak area, obtained using high performance liquid chromatography (HPLC), over time. The results of this analysis are shown in Figure III.5.5.

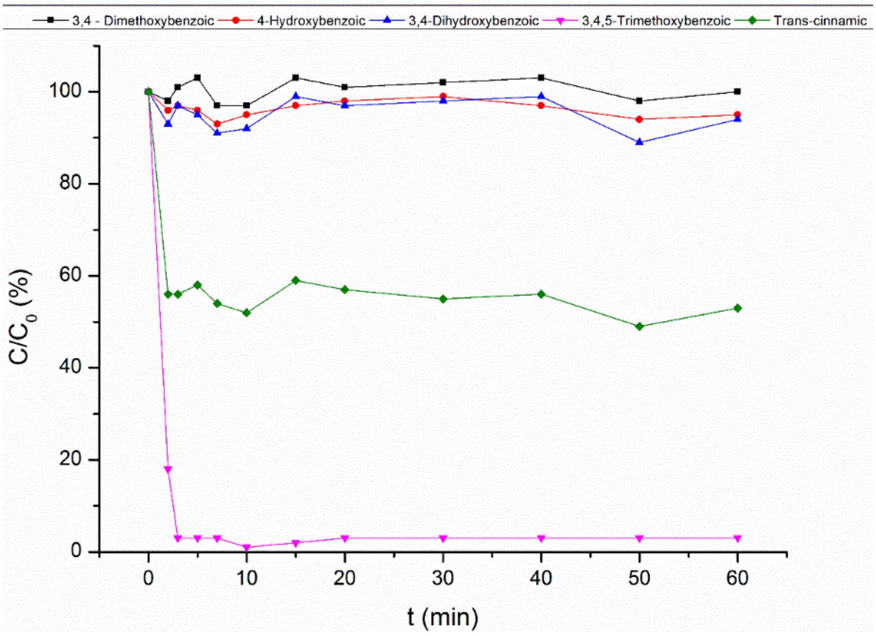

Figure III.5.5. Individual degradation of the five phenolic compounds by the optimized S-AOP.

The analysis of Figure III.5.5 shows that the S-AOP can fully degrade the 3,4,5-trimethoxybenzoic compound and can degrade the trans-cinnamic compound by 50%, but cannot degrade the remaining three compounds. Such behavior may be due to the higher selectivity of sulfate radicals towards certain organic compounds when compared to that of the hydroxyl radicals, as mentioned by Brienza et al. (2017). It should be noted that, although only two of the five phenolic compounds present in the OWM were degraded, these were the most complex compounds in the mixture in terms of chemical structure, as they were the ones with the most or the longest substitutes. It is also noted that the compounds were degraded in the first 5 min of the reaction, suggesting that this is a process of rapid and selective degradation.

Based on the HPLC results, it was also found that, along the reaction, other peaks appear in the chromatogram in addition to those used in the formulation of synthetic OMW. These peaks were formed during the reaction, and that they did not exist in the initial samples, which allows us to conclude that they are representative of intermediate compounds. Based on the database of the equipment used, it was found that these peaks may correspond to hydroquinone and 2-phenylhydroquinone, as mentioned by Santos et al. (2004) and Enguita and Leitão (2013), which may suggest that the toxicity of wastewater does not decrease with the treatment, although there is a reduction in the content of organic matter.

III.5.3.5. Comparison with Fenton´s process

As the Fenton process is an advanced oxidation process very much studied for the abatement of agro-industrial wastewaters, with an operation comparable to S-AOP, the performance of both technologies was analyzed.

Rossi (2014) studied the applicability of the Fenton process in the treatment of synthetic wastewater like the one used in this work. It is possible to verify that, to achieve a removal of COD and phenolic compounds using the Fenton process (Table III.5.6) similar to that achieved using the S-AOP, it is necessary to introduce 100 mg/L of Fe^{2+} and 830 mg/L of H_2O_2. It should be noted that these are not the optimal conditions for the Fenton process analyzed in the cited study.

Table III.5.6. Comparison between the Fenton process and the SRbAOP, in a homogeneous system.

Process	Process Conditions	Results	Reference
Fenton	$[Fe^{2+}]$=100 mg/L $[H_2O_2]$=830 mg/L pH=3	~40% COD removal ~85% phenolic compounds removal	Rossi, 2014
Fenton	$[Fe^{2+}]$= 25 or 50 mg/L $[H_2O_2]$=3 or 2 g/L pH=3	~40% TOC removal ~100% phenolic compounds removal	Esteves et al., 2018
S-AOP	$[Fe^{2+}]$=300 mg/L $[S_2O_8^{-2}]$=600 mg/L pH=5	~40% COD removal ~37% TOC removal ~63% phenolic compounds removal	This work
Fenton	H_2O_2/Fe^{2+} = 15 H_2O_2/COD = 1.75 pH=3.5 T=30ºC	70% COD removal	Lucas and Peres, 2009

Esteves et al. (2018) also studied the applicability of the Fenton process in the treatment of a smilar synthetic effluent. It is possible to verify that, to achieve the same TOC removal efficiency as in the S-AOP with the Fenton process, it is necessary to introduce, in the system, 3 g/L of H_2O_2 and 25 mg/L of iron or 2 g/L of H_2O_2 and 50 mg/L of iron (Table III.5.6). It should be noted that these are not the optimal conditions for the Fenton process analyzed in the cited study.

Lucas and Peres (2009) studied the effect of pH, temperature, H_2O_2/Fe^{2+} molar ratio, and H_2O_2/COD weight ratio for Fenton's peroxidation of OMW (collected in Portugal and diluted to an initial COD ~2 g/L). The authors verified that the best operating conditions (pH 3.5, 30 °C, H_2O_2/Fe^{2+} = 15, and H_2O_2/COD = 1.75) led to 70% COD removal. This was a real effluent diluted to achieve twice the COD of the synthetic effluent studied in this work.

From the analysis of Table III.5.6, it appears, according to Rossi et al. (2014) and Esteves et al. (2018), that for the same treatment efficacy, the Fenton process produces less sludge, since it uses a lesser amount of catalyst. However, it requires a greater amount of oxidizing agent, which may increase the operating costs.

III.5.3.6. Heterogeneous catalysis

In this section, the performance of S-AOP based on metal-activated persulfate, in heterogeneous catalysis, using red mud and Fe-Ce-O as a catalyst, is optimized and analyzed in terms of the results obtained regarding the removal of organic matter and toxicity.

For a correct analysis of the treatment process using heterogeneous catalysis, it is essential to know the physical and chemical characteristics of the selected catalysts. The characterization of the Fe-Ce-O and the red mud was previously described by Rossi et al. (2012) and Domingues et al. (2019), respectively. Table III.5.7 summarizes the characterization of these catalysts in terms of their surface area, pore size, chemical composition, and particle size and Table III.5.8 presents the RM chemical characterization.

Table III.5.7. Red mud and Fe-Ce-O characterization.

Catalyst	**Surface Area (m^2/g)**	**Porosity**	**Chemical Composition**
Fe–Ce–O	188	0.58	Fe/Ce 70/30 (mol/mol)
Red Mud	0.6	–	*

As previously mentioned, the red mud and the Fe-Ce-O were sieved, so the catalyst particles used had a diameter of <0.105 µm.

Table III.5.8. Red mud chemical composition.

Chemical Element	**$m_{chemical\ elementl}/m_{red\ mud}$**
Copper	43 ppm
Iron	5.9 %
Zinc	17 ppm
Nickel	726 ppm
Chromium	862 ppm
Lead	53 ppm
Manganese	175 ppm
Magnesium	943 ppm
Calcium	3.4 %
Sodium	1.9 %
Potassium	0.29 %

Two iron catalysts (RM and Fe-Ce-O) were tested regarding their ability to activate persulfate. In both scenarios, the initial pH value and the PS load were kept constant and equal to 5 and 600 mg/L, respectively, and the catalyst load was optimized; see Figure III.5.6.

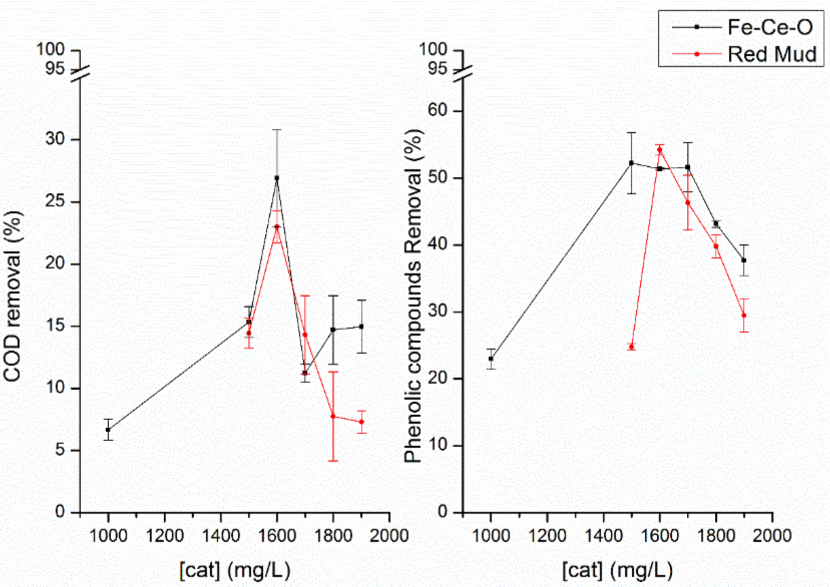

Figure III.5.6. Catalyst load influence on COD removal and phenolic compound removal. (30 min of reaction, pH 5, and (PS) = 600 mg/L).

Regarding the red mud tests, the following red mud loads analyzed were 1500, 1600, 1700, 1800, and 1900 mg/L; for Fe-Ce-O tests, the loads were 1000, 1500, 1600, 1700, 1800, and 1900 mg/L. The effects of heterogeneous S-AOPs were studied in terms of COD and phenolic compound removal.

From the analysis of Figure III.5.6, it is possible to conclude that a red mud load of 1600 mg/L makes it possible to obtain the maximum COD and phenolic compound removal, of approximately 23% and 55%, respectively. From this point forward, an increase of the red mud load results in a decrease of the process efficiency.

A load of 1600 mg/L of Fe-Ce-O allows for the maximization of the COD and phenolic compound removal, achieving, approximately, 27% and 55% COD and phenolic compound removal, respectively. It is also verified that an increase in Fe-Ce-O load from 1000 to 1600 mg/L results in a COD removal increase, and from this point onward, an increase in the catalyst load induces a decrease in the COD removal.

In order to evaluate the toxic impact of the treated wastewater, *A. fischeri* luminescence inhibition provoked by treated samples at the optimal conditions was compared to the untreated simulated OMW (Table III.5.9).

Table III.5.9. Luminescence inhibition results for bacteria and GI for *L. sativum* for the untreated OMW and the treated wastewater with red mud and Fe-Ce-O (30 min of reaction, pH 5, [PS] = 600 mg/L and [cat] = 1600 mg/L).

Type of Solution	**Bacteria *A. fischeri***		***L. sativum***
	Inhibition (15 min)	**Inhibition (30 min)**	**GI**
Untreated OMW	60.38 ± 0.31%	61.29 ± 0.54%	30.6 ± 3.2 %
Treated OMW (red mud)	61.25 ± 1.64%	65.49 ± 1.59%	0.8 ± 1.2 %
Treated OMW (Fe-Ce-O)	88.97±6.16%	95.13±5.63%	23.4 ± 1.4%

Treated wastewater has a toxicity towards the bacteria comparable to the untreated OMW. In Table III.5.9, it can be observed that the treated samples have a lower GI than that of the untreated wastewater. As the results from the toxicity tests for the treated samples may be influenced by the presence of metals leached from the catalysts, the amount of iron dissolved in the effluent after the reaction was evaluated. This is also an important issue regarding the catalyst’s stability and reutilization. For red mud, under optimal operating conditions, iron leaching of 13.08 ± 4.99 mg/L was observed, which means that, for every milligram of catalyst introduced in the system, 0.008 ± 0.003 mg of iron are leached. Regarding Fe-Ce-O, at the optimal conditions, an iron leaching of 42.32 ± 2.51 mg/L was observed, which means that, for every milligram of catalyst added, there is a leaching of 0.027 ± 0.002 mg of iron.

There are several studies in the literature focusing on the toxicity of phenolic wastewater in different oxidation treatments, such as ozonation and photocatalytic treatment. After the photocatalytic treatment of wastewaters containing different aromatic compounds, the early intermediates were more toxic and less biodegradable than the original pollutants (Santos et al., 2004). Those authors reported that an improvement in the BOD/TOC ratio and in toxicity were observed only when mineralization of at least 80% of the initial TOC was reached. Some studies (Suarez-Ojeda et al., 2008; Liotta et al.,2009; Moussavi et al., 2009) have shown that major intermediates of phenol oxidation in AOPs can be categorized as readily biodegradable compounds (acetic, fumaric, propionic, formic, and succinic acids), nonbiodegradable compounds but without inhibitory or toxic effect over the biomass (maleic, oxalic, and malonic acids), toxic compounds (p-benzoquinone and hydroquinone), and finally inhibitory compounds (catechol) for biodegradation (Suarez-Ojeda et al., 2008). These results may agree with what happens with persulfate. The mineralization is not very high under the conditions studied, and in addition the reaction time was only 30 min. Thus, in line with what has been reported for other oxidation processes, in our case, toxic intermediates (such as hydroquinone) could also be formed. The analytic techniques applied only allowed us to identify hydroquinone, but surely other toxic intermediates (unidentified) were produced. The amount and type of intermediates formed are surely dependent on the conditions applied (such as the type of catalysts). So, even if hydroquinone was not identified in the heterogeneous oxidation, other toxic intermediates that were not identified were produced. This may explain the lack of variation of toxicity during those processes.

Considering the RM chemical composition, in Table III.5.8, the optimal RM load corresponds to 94.4 mg/L. Therefore, the molar ratio between PS and iron is 1.85, which does not follow the recommendation by Xiao et al. (2020) and Rodriguez et al. (2012); the conclusions of these authors also do not apply to systems activated by Fe (II). According to Wu et al. (2016), who studied the activation of PS by Fe (III), a molar ratio of two between PS and iron is more appropriate for these systems, which is close to the value reached in this work.

Considering the Fe-Ce-O composition present in Table III.5.7., the introduction of the optimal Fe-Ce-O load results in an input of iron, into the system, of 480 mg/L. Thus, the molar ratio between PS and iron is 0.36, which does not follow the recommendations of Wu et al. (2016), in iron (III)-activated PS systems, a molar ratio of two between the PS and iron should be adopted. Therefore, the system may be suffering from a lack of PS.

Finally, the performance of heterogeneous S-AOP was compared with the Fenton process using the same catalysts. The comparison with the literature results is given in Table III.5.10.

Table III.5.10. Comparison between the Fenton process and the SRbAOP, using red mud as the catalyst.

Process	**Process Conditions**	**Results**	**Reference**
Fenton	[red mud]=1000 mg/L $[H_2O_2]$=25 mg/L pH=3	~5% TOC removal 25% TOC removal can be achieved with 100 mg/L of H_2O_2 For 100 mg/L of H_2O_2: GI ~50% Bacterial inhibition = 100%	Domingues et al. 2019
S-AOP	[red mud]=1600 mg/L $[Fe^{3+}]$=100 mg/L $[S_2O_8^{2-}]$=600 mg/L pH=5	~23% COD removal ~1% TOC removal ~55% phenolic compounds removal GI = 0.8 ± 1.2 % Bacterial inhibition of ~61 – 65 %	This work
Fenton	[Fe–Ce–O]=1500 mg/L $[H_2O_2]$=3910 mg/L pH=4	~25% COD removal ~100% phenolic compounds removal	Martins et al. 2010a
Fenton	[Fe–Ce–O]=500 mg/L $[H_2O_2]$=8296 mg/L pH=3	~5% TOC removal ~44% phenolic compounds removal	Martins et al. 2010b
S-AOP	[Fe–Ce–O]=1600 mg/L $[Fe^{3+}]$=480 mg/L $[S_2O_8^{2-}]$=600 mg/L pH=5	~27% COD removal ~5% TOC removal ~55% phenolic compounds removal	This work

From the analysis of Table III.5.10, it appears that to achieve a similar removal of TOC in the Fenton process with red mud, less catalyst and less oxidizing agent are used. Whereas, regarding Fe-Ce-O, it is noted that for the Fenton process to achieve the same removal efficiency for TOC and phenolic compounds, a smaller amount of catalyst and a greater amount of oxidant are required. If one bears in mind COD abatement, to reach the same efficiency, the Fenton process requires a higher amount of oxidant and catalyst compared to S-AOP.

III.5.3.7. Comparison between homogeneous and heterogeneous processes

All the catalysts used in the PS activation were compared to evaluate the best catalysis mode. This evaluation was done based on the optimal operating conditions for each catalyst and the results; both are shown in Table III.5.11.

Table III.5.11. Comparation between the different catalysts.

Catalyst	**Optimal Conditions**	**Results**
Iron (II) Sulfate	[Iron] = 300 mg/L [PS] = 600 mg/L pH = 5	~39% COD removal ~63% phenolic compounds removal ~37% TOC removal GI ~33% Bacterial Inhibition ~65–69%
Red Mud	[Red Mud] = 1600 mg/L [Iron] = 94.4 mg/L [PS] = 600 mg/L pH = 5	~23% COD removal ~55% phenolic compounds removal ~1% TOC removal 0.008 ± 0.003 mg iron leaching/mg catalyst GI ~1% Bacterial Inhibition ~61–65%
Fe–Ce–O	[Fe–Ce–O] = 1600 mg/L [Iron] = 480 mg/L [PS] = 600 mg/L pH = 5	~27% COD removal ~55% phenolic compounds removal ~5% TOC removal 0.027 ± 0.002 mg iron leaching/mg catalyst GI ~23% Bacterial inhibition ~89–95 %

The homogeneous catalysis exhibits the best performance regarding removal efficiency as well as toxicity. These results were expected as, in homogenous systems, the mass transfer resistance is smaller. Even so, the discrepancy between the removal efficiency in heterogeneous catalysis and in homogeneous catalysis is not that significant.

Regarding the heterogenous catalysts, Fe-Ce-O shows the best COD removals results and toxicity results. Thus, Fe-Ce-O is better than red mud for PS activation. The use of heterogeneous catalysts allows the catalysts' recovery and reuse. In addition, it avoids iron sludge formation and management, which are required in homogeneous systems.

An interesting result is the fact that the use of 100 mg/L of iron (II) in the homoegenous systems shows the same efficiency as 1600 mg/L of red mud (94.4 mg/L of iron (III)). Bearing in mind that the same amount of iron (II) and iron (III) provide the same degradation efficiency of organic matter, the theory, mentioned by Xiao et al. (2017), that Fe (III) is less efficient in the activation of PS seems to be contradicted. However, since the sludge is composed of other metals in addition to iron, these may also be acting in the persulfate activation process. Fan et al. (2019) and Hoa et al. (2020) found that PS can also be activated by manganese, aluminum, zinc, and copper, all of which are present in the RM.

Comparing the red mud optimum with the Fe-Ce-O optimum, since the removal efficiencies are similar, it is verified that the synergistic effect between the iron and the cerium may be as efficient as using various metals.

III.5.4. Conclusions

S-AOP is a selective and fast process, since, when applied to the treatment of synthetic wastewater, it was able to degrade 100% of the compound with more substitutes and 50% of the compound with the longest substitute, in 5–10 min. However, it was not able to degrade the remaining compounds.

Homogeneous S-AOP applied to synthetic wastewater allowed a removal of 39% of the COD, 63% of the phenolic compounds, and 37% of the TOC at the best operating conditions (pH = 5, (Fe^{2+}) = 300 mg/L, (PS) = 600 mg/L). In terms of toxicity, at the optimum operating conditions, the treated effluent has a similar toxicity to the original for both the bacteria *A. fischeri* and the plant *L. sativum*, which may be due to the formation of intermediate compounds, such as hydroquinone.

As for the heterogeneous S-AOP, among the catalysts tested (red mud and Fe-Ce-O), Fe-Ce-O showed the best results, since it allowed achievement of the lowest toxicity, the highest COD removal, and the lowest leaching, under the optimal operating load of 1600 mg/L. However, the toxicity of the treated wastewater was higher than that of the untreated wastewater.

Among the heterogeneous and the homogeneous S-AOPs, the homogenous had the best efficiency and led to the lowest toxicity. However, the efficiencies between the two processes were similar. In this context, the use of heterogeneous catalysts may be preferable, since it allows catalyst recovery and reuse while avoiding iron sludge formation and management.

The increased interest in the subject of persulfate-based treatment processes, especially in persulfate forms of activation, reveals that these technologies are promising. The evaluation of persulfate technology as a substitute for the Fenton process, which is already well established in the industry, requires a careful analysis of various factors, such as water matrix effects, byproduct formation, toxicological consequences, costs, and engineering challenges. In fact, persulfate could be an alternative to Fenton's process for the treatment of olive mill wastewater. However, the process must still be studied using other activators, such as thermal, electro activation, and other catalysts.

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III.6. Advanced oxidation processes at ambient conditions for olive oil extraction industry wastewater degradation

It is based on the publication: Domingues, E., Fernandes, E., Gomes, J., Castr-Silva, S., Martins, R. C., (2022) Advanced oxidation processes at ambient conditions for olive oil extraction industry wastewater degradation. Chemical Engineering Science. 263, 118076.

III.6.1. Introduction

The olive oil production is a well-founded sector of the European industry, especially in the Mediterranean Basin, with countries such as Spain, Greece, Italy and Portugal accounting for more than two-thirds of the worldwide production (IOOC, 2020).

There are different processes used to produce olive oil, being the most common the two and three-phase continuous methods (Messineo et al., 2020). Both methods are intrinsically associated with the formation of liquid effluents, olive mill wastewater (OMW), and solid residues, olive pomace (OP), containing toxic phenolic components and high organic loads. The discharge of these wastes without treatment is a great problem for Mediterranean countries (Pedrero et al., 2020). To increase the overall sustainability of the production, the OP can be further directed to an extraction process where further products are recovered. However, even if olive oil mills are going towards a green path where the wastes are being directed to other industries for valorization, a new environmental problem is raising with the production of a new olive oil extraction industry wastewater (OOEIW). The treatment of these streams is yet not fully investigated (Manzanares et al., 2020). In fact, to the best of our knowledge, there are not manyworks dealing with this new wastewater coming from the OP extraction units. In comparison, many technologies have been applied for the treatment of the common OMW. Biological processes are vastly explored, such as anaerobic digestion and composting, but the toxic properties of this type of effluents hinders their direct appliance (Aquilanti et al., 2014, Vuppala et al., 2019). Reverse osmosis, nano and ultrafiltration and other filtration methods have shown high efficiencies regarding organic content removal but have the shortcoming of membranes fouling and the need of operating with low flow rates (Ioannou-Ttofa et al., 2017, Sánchez-Arévalo et al., 2020), moreover, a concentrated stream with high pollutant load is produced. Coagulation and flocculation are also usually applied but mainly as a pre or post-treatment processes (Vuppala et al., 2019; Ai et al., 2020).

Advanced oxidation processes (AOPs) are also the focus of several studies due to their high efficiencies towards the treatment of different effluents (Fernandes et al., 2020). They are associated with the production of highly oxidative radicals ($^{\cdot}OH$), which can degrade a variety of pollutants (Iboukhoulef et al., 2019, Kilic et al., 2019). Ozonation and Fenton's process are very used treatment methods, occurring generally at room conditions and with simple operation (Salimi et al., 2017). Fenton peroxidation involves the formation of oxidative species through H_2O_2 decomposition by an iron source at low pH values (2–4) (Domingues et al., 2019). Ozone is a very effective electron receptor and can easily interact with electron rich molecules, such as phenols, and produce $^{\cdot}OH$, $^{\cdot}O_3^{-}$ and other radicals (Gomes et al., 2017). This process generally occurs in bubbling reactors with the gas being fed to the liquid bulk through a suitable gas/liquid contactor.

As an alternative to the conventional AOPs, peroxymonosulfate (PMS) or peroxydisulfate (PS) can be used as chemical oxidants. These technologies are usually called sulfate radical based advanced oxidation processes (S-AOP). The highly reactive, short-life sulfate radicals ($SO_4^{\bullet -}$) are produced in situ by cleavage of the peroxide bond in the persulfate molecule through energy and electron transfer reactions (Genç et al., 2020). Unlike H_2O_2, persulfate can also oxidize some organics directly, without involving radical species (Shaoxiong et al., 2022). S-AOP are processes still little studied in the treatment of olive mill wastewater.

Bearing in mind the new paradigm in olive oils extraction and considering the growth in this sector, it is essential to establish suitable treatment techniques for the new effluents produced in the olive pomace extraction units the OOEIW.

Thus, this study aims to further investigate the treatment of the new olive oil extraction industry wastewater, applying Fenton, S-AOPs, ozonation and the combined process for the removal of phenolic compounds and organic matter, and the decrease of the effluent toxicity. To the best of our knowledge this is the first work investigating such technologies for the treatment of this novel wastewater.

III.6.2. Material and Methods

III.6.2.1. Effluent collection and characterization

The OOEIW was retrieved from an oil extraction plant in Europe. This unit receives olive mill wastes from several olive mills spread all over the country. Samples were stored in 25 L plastic containers. Prior oxidation treatment, the effluent was coagulated using 40 mg/L of a 0.1 % polydiallydimethylammonium chloride (PDADMAC) solution, following a typical coagulation procedure described elsewhere, to reduce the organic content and turbidity (Amaral-Silva et al., 2017). The general physic-chemical characteristics of the OOEIW (post-coagulation) are present in Table III.6.1.

Table III.6.1: Physic-chemical parameters of OOEIW post-coagulation.

Parameters	**Values (±SD)**
COD (g/L)	33.11 ± 0.33
TOC (g/L)	8.98 ± 1.27
TPh (g_{GA}/L)	4.11 ± 0.33
pH	4.83
Luminescence inhibition (%) after 15 min	99.78 ± 0.05

III.6.2.2. Oxidation procedures

The oxidation occurred in a magnetically stirred 2 L glass reactor. In each reaction, 1.5 L of the effluent was used. For the Fenton's process, initially a certain amount of $FeSO_4$ was added to the solution corresponding to 2 g/L of Fe^{2+} and the pH was altered to 3 using a H_2SO_4 solution (0.1 M). The reactions were started by the addition of 4 g/L of H_2O_2 and at the end the reaction was stopped increasing pH to 11 with some drops of NaOH solution These conditions were previously optimized in a work of our group (Domingues et al., 2021).

Ozonation was carried out in the same reactor in a semi-batch way. While the 1.5 L of effluent were added initial to the reactor, the gaseous ozone stream was produced from a pure oxygen stream using an ozone generator (802 N, BMT) and continuously bubbled through a gas diffuser located in the bottom of the reactor. The gas inlet flowrate was kept at 0.2 L/min and both inlet and outlet ozone concentrations were measured using BMT 963 and BMT 964 gas analyzers. Ozone process were generally conducted at pH 3 for comparative reasons. Samples were taken during reaction for further analysis.

The S-AOP experiments took place in a 500 mL spherical reactor made of glass. To this reactor, 250 mL of coagulated OOEIW was added and magnetically stirred at 500 rpm. Then, the catalyst (2 g/L of Fe^{2+} from $FeSO_4$) was added without pH correction. The reaction was then started through the addition of the oxidant agent (PS or PMS). The reaction was stopped, after 120 min, by pouring drops of NaOH and H_2SO_4 solution until pH7. Then, the solution was centrifuged in a Nahita centrifuge model 2655 for 5 min at 4000 rpm, and finally was filtered through a 0.45 µm cellulose acetate filter before further analysis.

III.6.2.3. Analytical techniques

Chemical oxygen demand was measured following the standard method 5220D (Greenberg et al., 1985). After 2 h of digestion in a HANNA Instruments thermoreactor at 150 °C followed by cooling, the absorbances were measured at 605 nm and compared to a calibration curve with COD values within 0–5000 mg/L prepared using potassium hydrogen phthalate solutions.
Total Organic Carbon was evaluated using a TOC analyzer (TOC-5000A, Shimadzu, Japan) equipped with an autosampler (ASI-5000A, Shimadzu, Japan).

The phenolic content (TPh) was determined spectrophotometrically (PG Instruments T60 spectrophotometer) using the colorimetric Folin-Ciocalteau method (Yılmaz et al., 2015).

The toxicities of the treated solutions after 120 min treatments were tested against *Aliivibrio fischeri* bacteria considering their luminesce inhibition. The samples were inoculated in a LUMISTherm at 15 °C during 15 min and compared to a blank containing a solution of 2 % NaCl. These toxicities were compared with the initial OOEIW result (Table III.6.1).

III.6.3. Results and discussion

III.6.3.1. Processes efficiency on COD removal

Different advanced oxidation processes were studied in this work in the treatment of OOEIW, either alone or in combination. The Fenton, Ozonation, Sulfate-AOPs process were studied individually, all reactions were carried out at pH 3.

In the case of the Fenton reaction, the optimal conditions were previously optimized (Domingues et al. 2021) $[H_2O_2]$ = 4 g/L and $[Fe^{2+}]$ = 2 g/L during 120 min. For comparative purposes, S-AOPs were carried out using the same iron catalyst concentration (2 g/L) while using as oxidant PMS or PS at an initial concentration of (4 g/L).

The combination of Fenton’s reaction and ozonation was also evaluated, with the Fenton reaction under the conditions indicated above but with a reaction time of 30 min followed by ozonation with a duration of 90 min, being this last process studied at pH 3 (F + O) and pH 9 (F + O pH 9). The amount of residual H_2O_2 after Fenton’s peroxidation, which later passed to the ozone process was about 1 g/L. Fenton’s process and ozonation as a simultaneous process was also evaluated (F and O), in this case the operation pH was 3.

Figure III.6.1. shows the evolution of COD removal along time for the various processes studied.

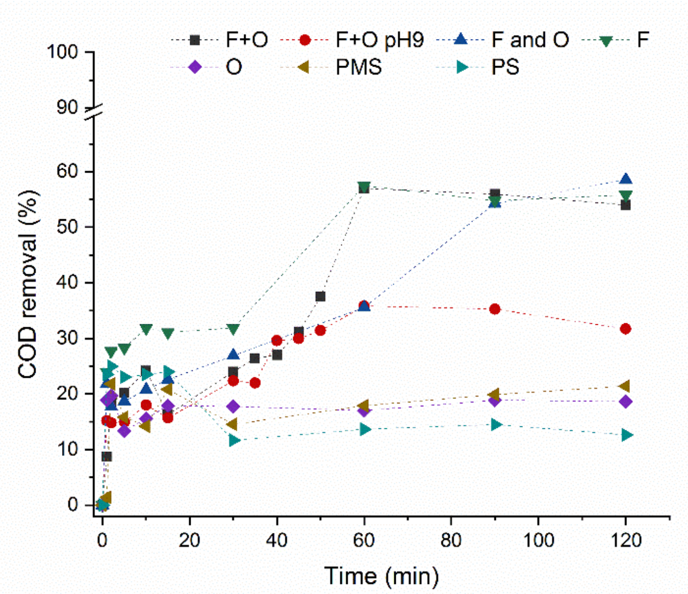

Figure III.6.1. Chemical oxygen demand (COD) removals during 120 min for different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH 9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

The process that allows the highest reduction in COD (~58.5 %) is the combination of the Fenton and Ozone reaction simultaneously (F and O), although the combination of Fenton followed by ozone at pH 3 (F + O) lead to a very close removal, about 54 %.

The highest COD removal by the combination of Fenton and ozone, both simultaneously and in sequence, can be explained by the presence of different oxidant species in the reaction medium. In the Fenton's process, the decomposition of H_2O_2 due to the oxidation of Fe^{2+} leads to the formation of $^{\cdot}OH$, being this the main actor in the degradation in these reactions. In what regards ozonation, pH is a key parameter, as it determines the extension of hydroxyl radical's formation. In acidic conditions the direct attack of ozone prevails, which is very effective towards electron-rich molecules, while in alkaline medium, ozone tends to decompose forming $^{\cdot}OH$, able to degrade a wide range of pollutants (Martins and Quinta-Ferreira, 2014). Thus, the simultaneous existence of molecular ozone and $^{\cdot}OH$, that can interact with different types of compounds in the effluent, promotes a higher mineralization level. This is very important due to the complexity of the real water matrix, involving different molecules with different affinities which will require different oxidant moieties to react. Moreover, the presence of the hydroxyl radical and ozone together can be a source of more hydrogen peroxide as can be seen in the Equations (III.24 - III.25) (Mehrjouei et al., 2015) as well as due to the reaction of molecular ozone with unsaturated organic bounds that will also produce H_2O_2.

$$O_3 + HO^{\cdot} \longrightarrow HO_4^{\cdot} \longrightarrow O_2 + HO_2^{\cdot} \qquad \text{III.24}$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \qquad \text{III.25}$$

On this way, as after Fenton´s process iron (Fe^{2+}) remains in the reaction medium, the production of extra hydrogen peroxide will be promoting the Fenton´s reaction during ozonation. Therefore, this will allow a higher degradation of organic matter.

This may also be an explanation for the lower performance of the Fenton + Ozone at pH 9. The decomposition of ozone into hydroxyl radicals occurs at this pH which will reduce the variety of oxidant moieties and consequent reactions that remove a larger amount of organic matter. In fact, at alkaline conditions the decomposition of hydrogen peroxide in water and oxygen can occur as well as the production of hydroxyl radicals via ozone decomposition. The excess of hydroxyl radicals can react with the remaining hydrogen peroxide producing hydroperoxyl radical ($HO_2^{\cdot}$) with lower oxidant power (Domingues et al., 2018). Besides, molecular ozone will not be available for the direct attack to the organic compounds. Although Fenton and ozone simultaneously had a slightly higher efficiency, in 60 min the sequence Fenton's followed by ozonation achieved 57 % of COD removal which is similar to the efficiency attained when both processes are ran simultaneously. Besides, the sequential approach represents a lower injected ozone dose and consequently lower operating costs.

The ozonation process (pH 3) alone had a low COD removal (~17 %), which is due to the more selective degradation of molecular ozone. In fact, this oxidant can readily oxidize molecules prone to suffer electrophilic attacks but leading to the generation of a high concentration of intermediates (mainly carboxylic acids) that cannot be further oxidized by molecular ozone due to their low electronic density (Cañizares et al., 2007; Martins and Quinta-Ferreira, 2014). Moreover, the oxidative potential of ozone is lower compared to hydroxyl radical. Regarding Fenton's, the higher performance in comparison with ozone can be explained by the already discussed tendency of the hydroxyl radicals to react with a higher variety of molecules.

As far as S-AOPs are concerned, PMS has a better result compared to PS and even ozone alone. However, the percentage of COD removed is much lower than the Fenton process and the integrated/combined processes of Fenton and Ozone. Although the reduction potential of $SO_4^{\bullet -}$ and $\cdot OH$ radical species are very similar, 2.5–3.1 and 2.8 V, respectively, very different efficiency results were obtained for the treatment of this real wastewater, with the hydroxyl radical being more effective in the degradation of organic matter. This result can be explained by the fact that the $SO_4^{\bullet -}$ radical is more selective than the $\cdot OH$ and therefore does not act with the same intensity on all organic matter (Manos et al., 2020). However, the operating conditions for the OOEIW treatment by S-AOPs were not optimized. In fact, the optimal conditions for the Fenton treatment were used to allow a direct comparison between the two techniques. Thus, before discarding the potential of S-AOPs, a processes optimization for the real effluent of

OOEIW treatment is required in the future. All assays were performed in duplicate and never yielded an error greater than 8 %.

III.6.3.2. Effluents mineralization

Since the S-AOPs had not satisfactory results for COD removal, the following study only involved Fenton's process and ozonation. Figure III.6.2 shows the degree of mineralization obtained (measured as TOC removal) after 120 min of ozonation, Fenton's process and their combinations.

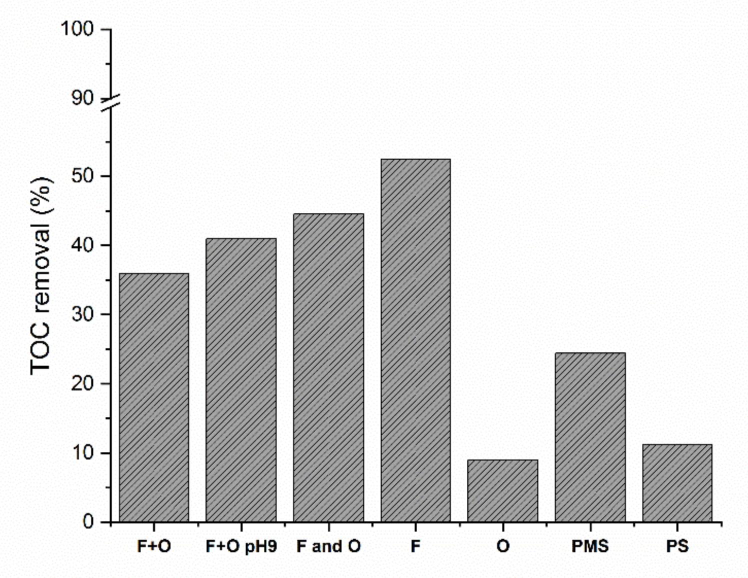

Figure III.6.2. Total organic carbon (TOC) removals during 120 min for different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH 9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Differently from the results of COD removal (Figure III.6.1), total organic carbon removal for single Fenton's process was the highest achieved among all tested reactions (~55 %). To better understand the mineralization efficiency obtained, the partial oxidation yield (μCOD_{partox}) was calculated following Equations (III.26 - III.27) (Hellenbrand et al., 1997).

$$\mathrm{COD_{partox}} = \left(\frac{\mathrm{COD_0}}{\mathrm{TOC_0}} - \frac{\mathrm{COD}}{\mathrm{TOC}}\right) \times \mathrm{TOC} \qquad \text{III.26}$$

$$\mu_{\mathrm{COD_{partox}}} = \frac{\mathrm{COD_{partox}}}{\mathrm{COD_0} - \mathrm{COD}} \qquad \text{III.27}$$

where COD_0 and TOC_0 represent the initial effluent COD and TOC, respectively. COD and TOC are the treated effluent COD and TOC after 120 min of reaction and COD_{partox} indicates the COD removed through partial oxidation (i.e not towards the formation of CO_2 and H_2O).

The μCOD_{partox} may have values between 1, which indicates that the chemical oxygen demand removal is due to partial oxidation route, and 0, representing total mineralization. The calculated parameters are present in Table III.6.2 for all the treatment strategies under evaluation.

Table III.6.2. Partial oxidation yield for OOEIW treatment by the different processes: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH 9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	$\mu_{COD_{partox}}$
F + O	0.33
F+O (pH=9)	0.00
F and O	0.22
F	0.00
O	0.54
PS	0.19
PMS	0.11

Fenton’s process had a partial oxidation yield near 0, meaning that all the removed COD is due to total mineralization, leading to the formation of CO_2 and H_2O. This result corroborates the TOC and COD removals, as the main route of COD removal is due to mineralization, which is accounted as TOC abatement. Contrarily, ozonation is prone to promote partial oxidation without much mineralization occurring (μCOD_{partox}=0.54). In fact, as referred before, ozone is able to cleave high electronic density organic molecules leading to partial oxidation by-products that are no longer reactive with molecular ozone. Thus, mineralization is not the preferential route. One can observe that the partial oxidation yield is always different of 0 when ozone is present (Table III.6.2) except for the case of Fenton + Ozone (pH = 9). In fact, for pH 9 ozone decomposition into hydroxyl radicals is promoted and these radicals preferably react in a mineralization pathway.

III.6.3.3. Phenolic content removal and toxicity abatement

Even with high phenolic content in the olive fruit, only a small percentage goes to the oil phase (~2%), meaning that most of these substances are present in the formed OMW (approximately 53%) and OP (approximately 45%) (Rodis et al., 2002; Cardoso et al, 2005). Phenols present a high instability when in storage, easily suffering polymerization and producing high molecular-weight polymers with higher difficulty to be degraded (Crognale et al, 2006) besides their potential environmental impact. It is therefore essential to find a way to remove these compounds from the treated effluent. This is special important due to the high toxicity associated to these compounds. Table III.6.3 shows the removals of TPh after each process studied.

Table III.6.3. Total phenolic concentration removal (%) after 120 min of different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH 9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	**TPh Removal (%) (±SD)**
F + O	54.1 ± 0.9
F +O (pH=9)	74.9 ± 0.7
F and O	41.3 ± 1.3
F	30.0 ± 1.1
O	56.3 ± 0.4
PMS	18.5 ± 0.7
PS	11.7 ± 0.9

Regarding the removal of TPh, the best solution is the combination of Fenton followed by Ozone at pH 9 (~76 %). Ozone alone achieved a 64 % TPh removal. Even with a lower COD removal, Fenton + Ozone at pH 9, had the highest removal of TPh (Table III.6.3). The increase in pH to 9 alone already has a positive effect on the degradation of phenolic acids but this is not reflected in the removal of COD since intermediates are formed that are not read as TPh but as COD. PMS and PS were the treatments that removed the least amount of phenolic compounds and once again the selectivity of these processes may be the justification for these results.

Although the phenolic content not being totally representative of the total organic matter present in the OOEIW, they are important pollutants in olive oil industry effluents due to their resulting problems regarding toxicity (Lanciotti et al, 2005).

As said, due to the toxicity of the phenolic compounds, it was also assessed the ecotoxicity of the treated solution towards *Allivibrio fischeri* bacteria (Table III.6.4) and compared to the raw effluent.

Table III.6.4. Luminescence inhibition for the treated OOEIW by the different processes:: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	**Luminescence inhibition (%) after 15 min (±SD)**
Coagulated Efluent	100 ± 0.05
F +O	95.68 ± 1.16
F +Oz (pH=9)	73.44 ± 3.45
F and O	91.42 ± 0.81
F	94.31 ± 0.14
O	99.80 ± 0.03
PS	99.30 ± 0.21
PMS	99.48 ± 0.07

The luminesce inhibition results corroborates the previously stated for the reaction at pH 9, that even still being considered toxic as it has a value higher than 30 %, it leads to a considerably lower inhibition compared with the remaining solutions (Miralles-Cuevas et al., 2017). Still, it is verified that none of the treatment approaches is able to satisfactorily reduce this cumbersome effluents' toxicity. But one should bear in mind that *A. fischeri* is a very sensitive species. Still further depuration shall be required before the effluents is ready to be discharged into the natural water courses. However, the high reduction on the organic charge specially promoted by the Fenton's process may allow the treated water to be directed to a municipal wastewater treatment plant to be further depurated through biological processes.

III.6.4. Conclusions

The solid waste produced in two phase decantation olive oil mills is nowadays sent to refined oil extraction units where further oil is extracted through drying and solid/liquid extraction processes. The effluent produced in these extraction units is an even more concentrated stream than the conventional olive mill wastewater. To the best of our knowledge it this new effluent was never treated by advanced oxidation processes.

In this work, several advanced oxidation processes were analysed in order to identify which is the most efficient in terms of COD, TPh and ecotoxicity:

The process that allows the greatest reduction in COD (∼58.5 %) is the combination of the Fenton and Ozone reaction simultaneously;
For TOC removal the best result is achieved with Fenton´s process alone;
Fenton plus Ozone at pH 9, had the highest removal of TPh;
After reaction of Fenton and Ozone at pH 9, even still being considered toxic as it has a value higher than 30 %, the treated OOEIW has a considerably lower inhibition compared with the remaining solutions.
The selection of the best treatment approach must bear in mind the final destination of the effluent and the operating costs associated to each process. Thus, further work is being performed in order to understand the treated wastewater biodegradability and phytotoxicity.

III.6.5. References

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III.7. Swine wastewater treatment by Fenton´s process and integrated methodologies involving coagulation and biofiltration

It is based on the publication: Domingues, E., Fernandes, E., Gomes, J., Martins, R.C. (2021) Swine wastewater treatment by Fenton´s process and integrated methodologies involving coagulation and biofiltration. Journal of Cleaner Production. 293, 126105.

III.7.1. Introduction

Pork meat consumption has been increasing in the last years (FAO, 2020). Even if studies related with the climatic changes reveal that swine meat production is less hazardous for environment regarding to greenhouse gases emissions (GHG) when compared with cow meat (Gupta and Singh, 2015), the increasing pork meat demand is promoting a high scale pigs' production. This intensive production will have a strong environmental impact related with water consumption and swine wastewater generated (Liu et al., 2016).

Water scarcity is a global problem and wastewater remediation could be an alternative to minimize this shortcoming. Animal products generally have a large water footprint; in the case of pigs the water footprint is 6000 m^3 of water for each ton of pork produced. The water volume to feed the animals refers to 98% of the water footprint. The remaining 2% is for animals drinking water (1.1%), service water (0.8%) and feed mixing water (0.03%).

Swine wastewater is composed mainly by faeces, urine and wash water (Burton and Turner, 2003). Due to the intensive pork production, antibiotics and hormones are frequently detected on this type of wastewaters. In fact, pigs' intestinal tract just absorbs about 10–30% of these recalcitrant compounds (Cheng et al., 2018) and 70–90% of antibiotics will be excreted intact or in metabolites by faeces and urine (Massé et al., 2014). Another persistent problem in swine wastewater is related to the amount of nutrients such as nitrogen and phosphorous (Zhang et al., 2019). Part of these nutrients and antibiotics are not processed by pigs and can reach the farmlands due to the conventional application of the swine wastewater (Joshi and Wang, 2018). In fact, these wastewaters in some developed countries are used as farmland soils fertilizer which will be a source of pollutants (Huang et al., 2017) as well as nutrients that can promote eutrophication (Jämsä et al., 2017).

The conventional swine wastewater treatments encompass a solid liquid phase separation, anaerobic digestion and/or aerobic lagoons (Santonja et al., 2017). These conventional processes are usually efficient for the nutrient's removal (Cheng et al., 2018). However, these technologies cannot be faced against antibiotics and other persistent compounds due to their recalcitrant character. Effectively, these contaminants are increasing in aquatic sources due to their continuous discharge (Ebele et al., 2017). Therefore, to face against the raise on the pork production it is important to find a suitable solution for this kind of wastewater aiming water remediation for at least agriculture irrigation. Since a high fraction of swine manure is composed by particles and colloids, coagulation/flocculation processes can be used efficiently in the reduction of turbidity, ammonia, nitrite and nitrate. In fact, previous studies show high removal percentages using this methodology (Gabriel et al., 2019).

A novel alternative based on the biofiltration capacity through the invasive bivalve *Corbicula fluminea* was studied. In fact, this bivalve has great capacity to resist in adverse environmental conditions and has high biofiltration activity (Gomes et al., 2014). Also, Domingues et al. (2020) proved that *C. fluminea* can remove organic matter from the olive mill wastewater which is another problematic agro-industrial wastewater. On this way, this ambitious technology can be used as a pre-treatment of swine wastewater.

Due to the presence of refractory compounds the advanced oxidation processes (AOPs) can be suitable alternative treatments for this kind of wastewater (Domingues et al., 2018). AOP’s encompass several technologies for wastewater treatment such as electrochemical oxidation, ozonation, photocatalysis, Fenton’s process, among others (Gomes et al., 2017). Fenton’s process seems to be the less expensive since it just requires an iron source and an oxidant, typically hydrogen peroxide. Besides it can be efficient at ambient pressure and temperature (Riaño et al., 2014). On this way Fenton’s process can be a good option due to the formation of hydroxyl radical through the interaction between iron source and hydrogen peroxide (Walling, 1975). Hydroxyl radicals are highly reactive species capable to promote the degradation of a wide spectrum of refractory compounds. In fact, this process has shown potential in the treatment of complicated effluents, such as olive mill wastewater (Domingues et al., 2018) and wineries effluents (Ferreira et al., 2018). One of the disadvantages of the Fenton process is the presence of dissolved iron at the end of the process. The legal limit of dissolved iron for discharge into water resources is 2 ppm, according to current Portuguese law. Typically, the treated water is alkalinized to promote iron precipitation as iron hydroxide. However, this promotes iron sludge formation (Cao et al., 2009) which entails further management. Thus, it is important to apply some adjuvant treatment to accomplish this goal.
One of the concerns of this wastewater is the presence of antibiotics, since it contributes in the severe way for microorganism’s toxicity impact (Välitalo et al., 2017). On the other hand, for human health it can be problematic since the continuous discharge of antibiotics in the water

sources can increase the presence of antibiotic resistant genes and/or bacteria (Brandt et al., 2015). Typically, this kind of contaminants is identified by high performance liquid chromatography. However, the developed methods cannot cover all the contaminants at the same time. Alternatively, the presence of these compounds can be indirectly detected by the luminescence inhibition of *Aliivibrio fischeri* (Wang et al., 2016).

The novelty of the present research relies on the development of an integrated treatment strategy for swine wastewater. The aim is to overcome the drawback associated to the conventional depuration processes typically applied to this kind of effluents. In fact, these wastewaters are usually treated by biological processes entailing high retention times which imposes large tanks so that the required efficiency may be reached. This can be an important shortcoming for swine producers without high available space. In this context, advanced oxidation processes may be suitable alternatives since the degradation kinetics are faster.

Among them, Fenton's process is a simple technology not demanding sophisticated equipment nor dangerous reactants. To the best of our knowledge, the optimization of Fenton's process to raw swine wastewater was not much explored in literature. The use of coagulation as a pre-step before Fenton's process is essential due to the high load of solids in these effluents which may affect Fenton's peroxidation efficiency. Moreover, another important novelty of this paper is the application of biofiltration using *Corbicula fluminea* as host as a final depuration technology. These Asiatic clams are a freshwater pest with high environmental and economic impacts (Rosa et al., 2011). Due to their high resilience to toxicants and biofiltration capacity, an environmental application can be given to this species. Namely, it is worthy to evaluate their capacity to remove iron from a Fenton's treated effluent. In fact, the amount of iron required is a drawback of Fenton's process. The iron load is typically higher than the legally allowed for the wastewater disposal. Here the *C. fluminea* can have an important role overcoming Fenton's process main shortcoming.

In this context, the aim of this study is the efficient treatment of swine wastewater production in a short period of time as an alternative to traditional processes. For that, some methodologies were approached: Fenton process was optimized and combined with other methodologies such as biofiltration and/or coagulation. This optimization considered both COD removal and the impact on toxicity regarding *A. fischeri* luminescence. Bearing in mind that the amount of dissolved iron in Fenton's treated effluent is a major drawback, coagulation and biofiltration processes were assessed as post-treatment steps. Biofiltration involving *C. fluminea* as host is a novel technology aiming to give an environmental application to a pest.

III.7.2. Material and Methods

III.7.2.1. Swine wastewater collection and characterization

The studied effluent is a real swine wastewater, collected directly from the farm in its concentrated state since no cleaning water was added. This swine farm is located in the Center Region of Portugal.

In the laboratory, a dilution of 1:12.5 was performed to simulate the real effluent considering the cleaning water that is usually added before processing the wastewater. For the characterization of the diluted effluent, the following parameters, presented in Table III.7.1, were considered: dissolved chemical oxygen demand (COD) (Greenberg et al., 1985), total solids (TS), total Kjeldahl nitrogen (TKN) (Pinho et al., 2017) and pH.

Table III.7.1. Characterization of initial swine wastewater used in the experiments.

Parameter	**Initial Concentration**
tCOD (g/L)	10.34 ± 0.78
sCOD (g/L)	4.40 ± 0.60
TS (g/L)	1.45
TKN (g/L)	0.26 ± 0.02
pH	7.25 ± 0.3

III.7.2.2. Fenton´s process

Fenton experiments were performed in glass spherical reactors with a capacity of 500 and 1000 mL. A stirring speed (magnetically) of 500 rpm was ensured. This stirring speed was selected to guarantee the homogeneity of sample. During the Fenton’s test, the volume of swine wastewater and the iron load (in the form of $FeSO_4$) were introduced in the reactor. pH was then adjusted to 3 with the addition of H_2SO_4. The reaction started when hydrogen peroxide (33% w/V, Panreac) was introduced 5 min after pH correction. Samples were taken periodically, and hydrogen peroxide was quenched by increasing pH until 12 and, as consequence, stop the reaction. In these experiments to optimize the swine wastewater degradation, the effect of iron load was tested in the range from 0.1 to 1 g/L. Moreover, the hydrogen peroxide concentration was also changed from 0.25 to 1 g/L. Besides, experiments at natural pH of wastewater were performed to minimize the impact of acid addition. All the experiments were made in duplicate.

III.7.2.3. Coagulation

In the coagulation tests, a certain volume of a 0.1% Polydiallyldimethylammonium chloride (PDADMAC) stock solution was added to 200 mL of wastewater during a first stage of fast stirring (140 ± 5 rpm) for 3 min, followed by 15 min of slow stirring (35 ± 5 rpm). After 30 min of sedimentation, supernatant's samples were taken for further chemical analysis. A jar-test equipment was used for these experiments.

The 40 mg/L of coagulant load used at the effluents' natural pH was previous optimized (unpublish work). Since pH has a significant impact in terms of COD removal efficiency, its' effect in coagulation process was also analyzed in this work. The selected pH range for these experiments was 2, 4, 7, 9 and 12. This effect was compared with and without coagulant. The experiments without coagulant were processed in the same way regarding to stirring stages.

III.7.2.4. Biofiltration

The clams were collected from a canal in Mira, Portugal (N40°25′06.90''/W8°44′13.18″), where a well-established population (density above 2000 clams/m^2) exists. This canal is composed by standing water where a great accumulation of organic matter and enteric pathogens occurs. Due to this, it was necessary an initial biodepuration of enteric pathogens and organic matter to avoid disturbing the clam's performance on the swine wastewater treatment. The clams used in the swine wastewater treatment were kept in dechlorinated water for about one week, where the water was changed every two days.

Swine wastewater treatment by *C. fluminea* was made in 500 mL glass biofilters. These tests were carried out at 20 ± 2 °C during 4 h and continuous aeration. The tests were performed with a ratio of 1:150 of clams per liter of swine wastewater. Individuals with shell length in the range 20–30 mm were selected to perform these experiments. To control the effect of the clams on the swine wastewater treatment and the bear in mind the aerobic degradation of the effluent through microorganisms, a glass biofilter with the wastewater in duplicate was maintained at the same conditions but without clams. Moreover, to validate the test, a blank with dechlorinated water was placed with the clams. Samples were taken for chemical oxygen demand (COD) determination. The clam's mortality was verified by checking if there was evidence of siphoning activity or, if clams were closed, by measuring resistance when gently forcing valve opening (Gomes et al., 2014).

III.7.2.5. Analytical methods

The concentration of organic matter in swine wastewater was measured by chemical oxygen demand (COD) quantification. Only soluble COD was measured since the swine wastewater contains a high amount of solid waste that quickly precipitates. Therefore, the samples COD was measured after 5 min of precipitation. COD was determined according to the standard method 5220D (Greenberg et al., 1985). To prepare a calibration curve with COD values within the range 100–4500 mgO_2/L, potassium hydrogen phthalate, obtained from Panreac, was used. Absorbance values, after 2 h of digestion at 150 °C (ECO25 – Velp Scientifica), were measured at 605 nm in a WTW photolab S6.

Total solids (TS) were obtained by drying samples at 105 °C until constant weight. For TKN analysis 10 mL of swine wastewater were mixed with a Kjeldahl catalyst tablet (Velp) and 10 mL of H_2SO_4 (96%). Digestion was carried out at 420 °C during 2 h. After cooling, 10 mL of distilled water and 50 mL of NaOH solution (40 g/L) were added before distillation (Pinho et al., 2017). These procedures were followed according to the Standard Method 1684 (EPA, 2001).

For pH determination a Crison micropH 2002 apparatus was used.

III.7.2.6. Toxicity assessment

To evaluate the toxicity of the samples towards a sensitive species, *A. fischeri*, the sample pH was corrected to values within the range of 6.5–7.5 by adding drops of a solution of either sodium hydroxide or sulfuric acid.

Bacteria were placed in a 2% NaCl solution and the luminescence inhibition of treated solutions was performed in comparison with a blank. The inhibition of luminescence was measured after 15 and 30 min of incubation (15 °C), of treated and untreated samples, using a LUMIStox 300 apparatus (Dr. Lange).

III.7.3. Results and discussion

III.7.3.1. Fenton´s process

Fenton’s process performance is affected by different parameters such as pH, hydrogen peroxide and iron load. In this section these parameters were optimized concerning toxicity and COD reduction.

This treatment optimization should bear in mind iron and hydrogen peroxide load. However, pH is also a key factor. In fact, pH has a strong effect on the Fenton’s reaction since it will command Fe^{2+} and Fe^{3+} ions solubility. At lower pH, the solubility of these ions increases which favors hydroxyl radical’s production. On the other hand, at high pH, precipitation will occur due to the formation of $Fe(OH)_3$ lowering the concentration of Fe^{3+} in the solution (Manenti et al., 2015).

Previous studies proven that the maximum performance of the Fenton's reaction is reached for a pH between 2.8 and 3.0. Above these values the efficiency decreases due to the precipitation of iron and the degradation of H_2O_2 into O_2 and H_2O (Barbusinski, 2009). Fig. III.7.1 shows the results for COD removal of swine wastewater when treated by Fenton's process at different pH values ($[Fe^{2+}]$ = 1000 mg/L, $[H_2O_2]$ = 750 mg/L and 60 min of reaction). pH 3 was selected based on the performance revealed on the literature for Fenton's process and pH 7 which is the natural pH of the effluent.

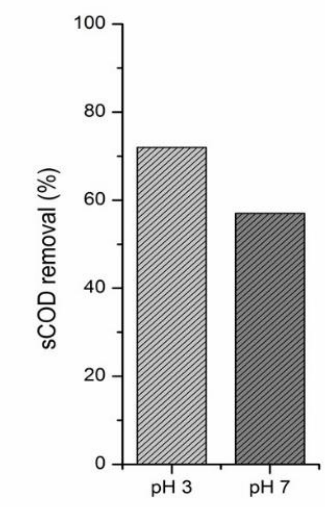

Fig. III.7. 1. COD removal by Fenton's process at pH 3 and pH 7 ($[Fe^{2+}]$ = 1000 mg/L and $[H_2O_2]$ = 750 mg/L) (standard error was smaller than 5%).

As can be seen in Figure III.7.1, when the reaction takes place at an acidic pH there is a noticeable improvement about the degradation of organic matter, reaching a COD removal of approximately 72%. When the reaction takes place at pH 7, the degradation of organic matter is noticeably lower, about 57% of COD removal. It is revealed that the presence of high amount of dissolved iron has a strong effect on the improvement of Fenton's reaction. Based on these results, the following experiments were performed at pH 3. This entails a pH correction which has implications into the operating costs of the process.

Fenton's process efficacy for wastewater treatment is very dependent on the amount of iron (Fe^{2+}) and the hydrogen peroxide (H_2O_2). The ratio of Fe^{2+} and H_2O_2 should be carefully analyzed since the excess of iron and hydrogen peroxide can scavenge the hydroxyl radicals, inhibiting the degradation of contaminants (Domingues et al., 2018). Typically, the optimal amount of iron and hydrogen peroxide is analyzed as function of the organic matter or specific compounds removal. However, this may not necessarily mean an improvement on the toxicological effect of the treated wastewater. On this way, the toxicity regarding to *A. fischeri* was analyzed as function of iron and hydrogen peroxide load so that the process optimization may consider this parameter. Firstly, the optimal hydrogen peroxide concentration was assessed using the 1000 mg/L of Fe^{2+}. Figure III.7.2 represents the COD removal (a) and luminescence inhibition (b) as function of H_2O_2 concentration.

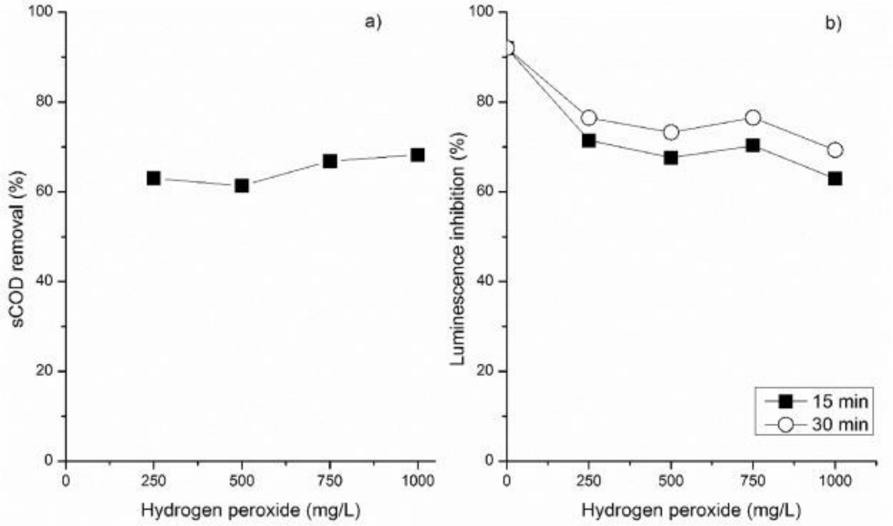

Figure III.7.2. COD removal (a) and Luminescence inhibition (b) as function of hydrogen peroxide concentration ($[Fe^{2+}]$ = 1000 mg/L) (standard error was smaller than 5%).

The hydrogen peroxide concentration does not affect significantly the COD removal within the range tested. In fact, a slightly increase from 61 to 68% of COD removal (Fig. III.7.2a) was observed with the increase of hydrogen peroxide concentration from 250 to 1000 mg/L, this fact was also verified by Riaño et al. (2014) when applying Fenton process to an effluent from biologically pre-treated swine manure. The effect of increasing the hydrogen peroxide charge was slight, setting the authors as an optimal load of 800 mg/L.

The luminescence inhibition for both exposure times (15 and 30 min) is not significantly different among the hydrogen peroxide concentration tested. Hydrogen peroxide concentration increasing leads to luminescence inhibition decrease in the same order of magnitude or very similar to the COD reduction.

According to previous studies (Domingues et al., 2019), it is known that the presence of hydrogen peroxide is toxic to bacteria due to its bactericide character. In the present study, it was ensured that there would be no residual hydrogen peroxide and therefore this effect does not occur. The reaction was stopped by raising the pH to 12 which promoted the total decomposition of residual hydrogen peroxide. The inhibition of luminescence is exclusively due to the organic load of the effluent which can include antibiotics. In a real system the reaction would not be stopped, which would continue to promote the degradation of organic matter and over time the decomposition of hydrogen peroxide and probably to a further decrease in the luminescence inhibition.

After analyzing hydrogen peroxide amount impact on the Fenton’s process, iron (Fe^{2+}) load effect was evaluated. For this purpose the amount of hydrogen peroxide was fixed at 750 mg/L, and iron load was changed from 100 to 1000 mg/L (Figure III.7.3).

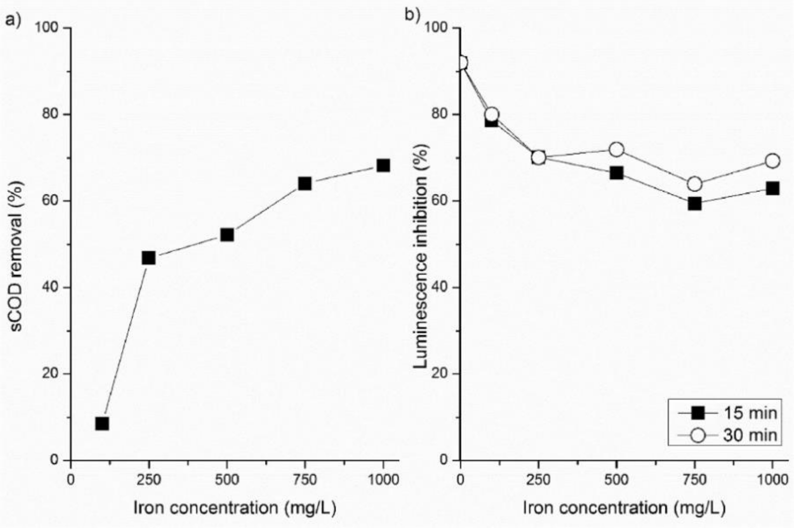

Figure III.7.3. COD removal (a) and *A. fischeri* Luminescence inhibition as function of iron concentration (hydrogen peroxide = 750 mg/L) (standard error was smaller than 5%).

Different from hydrogen peroxide concentration effect, the iron concentration can seriously influence COD removal (Figure III.7.3a). This can be related with high availability of Fe^{2+} which promotes the generation of more reactive oxidative species such as hydroxyl radical. On the contrary, Riaño et al. (2014) did not find an effect of iron load as noticeable as the one observed in the present study, probably since it was used an effluent previously subjected to biological treatment, which removed a high percentage of biodegradable organic load. The increase of iron load did not show a negative effect on luminescence inhibition although the higher concentrations of dissolved iron may be problematic for *A. fischeri*. Kurvet et al. (2017) showed that the presence of iron increases the luminescence inhibition. (EC_{50} = 0.44 mg Fe^{3+}/L). The concentration of iron in the cells should be kept at low level since high concentrations of this metal are toxic, mostly due to the generation of reactive oxygen species (Storz and Imlay 1999).

The Fenton’s reaction occurs at pH 3, but the sample analyzed must have a pH ∼7 which causes the precipitation of iron and the supernatant keep a minimum amount of this element. Only the residual dissolved iron is present in the supernatant which never exceed the 1.2 mg/L. Therefore, in this case, the decrease in the luminescence inhibition is essentially due to the COD reduction, which increases with the increase in the amount of iron. This increase is noticeable up to the 750 mg/L load. After this load, the COD removal improvement is not so marked, and this is considered the ideal iron load. However, the effect of residual dissolved iron over bacteria is clear with the increase of iron load from 750 to 1000 mg/L. In fact, the luminescence inhibition after 30 min of exposure increases from 65 to 71% (Figure III.7.3b). If a good catalyst recovery strategy is managed toxic effect may substantially decrease.

On this way, the selected conditions for further experiments were 750 mg/L of iron and hydrogen peroxide, since comprise the suitable commitment between COD removal and luminescence inhibition through *A. fischeri*.

III.7.3.2. Coagulation process

As previously referred, one of the preliminary steps in swine wastewater treatment is the solid liquid separation. On this way, the coagulation process can be relevant for this purpose. However, this technology can be influenced by the wastewater pH due to the electronic charges of coagulant and wastewater. The swine wastewater is negatively charged, therefore the PDADMAC appears as a suitable option since it has a cationic charge. Figure III.7.4 shows the COD removal as function of pH when using or not 40 mg/L of the coagulant. The effluent pH was raised using $Ca(OH)_2$.

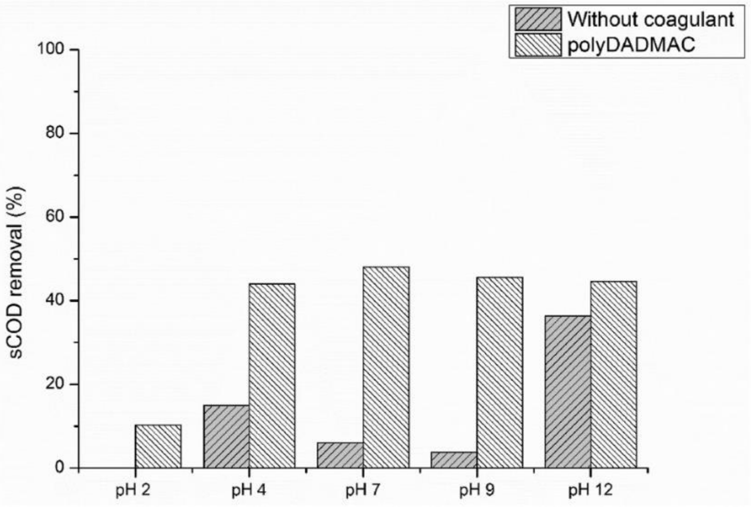

Figure III.7. 4. COD removal using or not coagulant at different pH (standard error was smaller than 5%).

Contrarily to pH 2, the effect of pH is almost negligible regarding COD removal in the presence of coagulant. The small effect verified at pH 2 can be related with the charge changes at this condition which inhibit the coagulation process. The effect of pH without coagulant was noticeable for basic pH (pH 12) that allowed to remove about 38% of initial COD.

In view of the results presented in Figure III.7. 4., it was decided to coagulate the effluent, with 40 mg/L at pH 7 (natural pH of the effluent), before Fenton's process. The coagulant load was optimized and the choice of pH 7 since for the other pH values COD removal was not significantly better to justify the use of reagents for pH adjustments.

III.7.3.3. Integrated methodologies

After Fenton's process and coagulation optimization, this section deals with the treatment methodologies integration. Firstly, the initial effluent was coagulated using PDADMAC. Besides, biofiltration using *C. fluminea* was applied before Fenton's process. In this section, the effect of several pre-treatments before Fenton's process was assessed. The coagulation process was previously optimized, Gomes et al. (2020a) ranged the coagulant concentrations from 10 to 80 mg/L. Concerning the coagulant load and in the present study the best pH (7) was obtained. The raise of pH with $Ca(OH)_2$ to 12 was also evaluated due to the impact of this procedure in COD removal (Figure III.7.4). Besides, biofiltration with *C. fluminea* proven to be efficient on the COD removal (Gomes et al., 2020a) leading to up to 60% of removal. Besides, this procedure may be considered a low-cost solution with impact on the mitigation of invasive capacity of this species.

After the first steps mentioned, the supernatant was subjected to a Fenton's process under the conditions optimized: pH 3 and 750 mg/L of H_2O_2 and Fe^{2+}. Figure III.7.5 shows the efficiency of each methodology separately and in combination with the Fenton process.

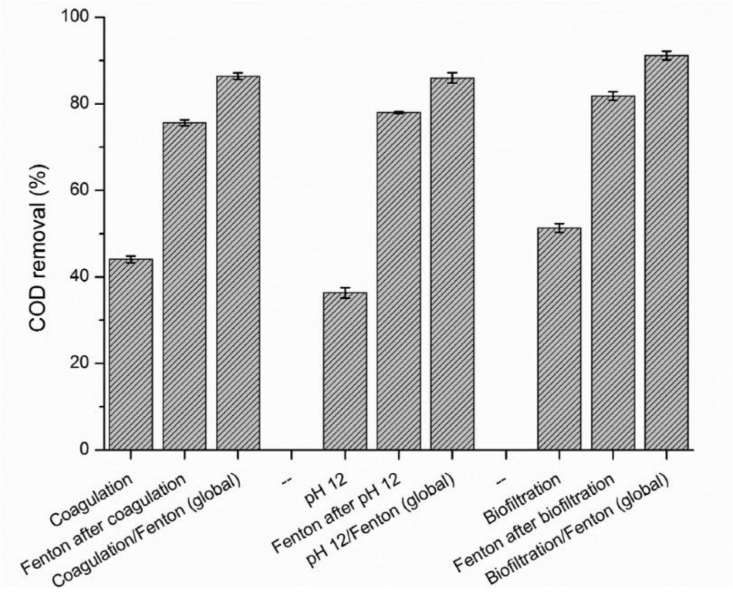

Figure III.7.5. COD removal using different methodologies.

As can be seen in the Figure III.7.5, it seems that the application of Fenton's process after biofiltration shows to be the most efficient integrated methodology removing about 91% of COD, while the application of Fenton after coagulation removes 86% of COD. The statistical analysis for integrated methodologies one-way ANOVA, followed by the post-hoc Tuckey test, using an alpha level of 0.05 was performed. In fact, the difference regarding COD removal between coagulation and biofiltration is small (about 5%), and for global treatment is not significant ($p > 0.05$). However, this improvement could be explained by the greater removal of organic and inorganic compounds by the biofiltration activity of clams. In fact, the removal of the inorganic compounds by the clams can enhance the performance of Fenton's process. The presence of sulfates, carbonates, hydrogen carbonates and nitrates can trap the hydroxyl radical (Rimodi et al., 2017). This trapping will reduce the performance of Fenton's process, since the main oxidative species produced by this process is the hydroxyl radical (Domingues et al., 2018). The biofiltration and coagulation process were studied by Gomes et al. (2020a), and it was found that biofiltration effectively has greater potential regarding the removal of COD as well as leading to a less toxic effluent regarding to *L. sativum* germination, due to their filtration power and coagulation capacity.

Moreover, the increase of the effluents' pH until 12 combined with Fenton's process proved to be slightly better than the combination of coagulation with Fenton. This can be related with the conversion of ammonia into ammonium at the pH 12. Huang et al. (2008) proved that the hydroxyl radical action over NH_3 is more efficient than to NH_4^+. This could explain the increase on the performance of Fenton's process on the COD removal after the pretreatment with the pH 12.

Considering the previous results for Fenton's process where with 750 mg/L of iron and hydrogen peroxide it was possible to obtain about 65% of the COD removal, the integrated methodologies improves this efficiency in about 25%. Therefore, the integrated methodologies seem to be a suitable option for swine wastewater treatment. Of special interest is the use of the invasive species *C. fluminea* as biofiltration host. This approach can give an environmental application to a pest besides reducing the treatment costs.

The integrated methodologies significantly enhance Fenton's process regarding to COD removal. However, it is important to verify the impact over bacteria luminescence inhibition, which indirectly means a removal of antibiotics. This toxicity assessment was verified for the Fenton's process after coagulation and biofiltration (Table III.7.2).

Table III.7.2. Luminescence inhibition (L.I.) over *A. fischeri* for Fenton's process after coagulation and biofiltration (standard error value in brackets).

	L.I. (%) 15 min	L.I. (%) 30 min
Swine wastewater	92 (± 1.0)	92 (± 1.4)
Fenton after Coagulation	27.5 (± 2.2)	36.2 (± 4.1)
Fenton after Biofiltration	36.2 (± 6.0)	30.7 (± 3.2)

As can be seen in Table III.7.2, the luminescence inhibition decreases significantly comparing with the optimized Fenton's process alone (Fig. III.7.3b). According to Miralles-Cuevas et al. (2017) the samples with the luminescence inhibition lower than 30% can be considered nontoxic. For all the samples provided from the integrated methodologies the values reached were not very far from that threshold, contrarily to the samples treated by Fenton's process alone which led to a light inhibition of about 65%.

The wastewater coming from Fenton's after coagulation presents lower toxicity after 15 min of exposure compared to the one obtained after biofiltration and Fenton's. However, when the exposure time increases to 30 min the inhibition decreases for the case where biofiltration was used as adjuvant process. This can be related with the removal of species by biofiltration (such as antibiotic) which have higher impact in terms of chronic effect, in this case 30 min of exposure. In fact, Gomes et al. (2020) proved that *C. fluminea* can remove antibiotic from the water through the biofiltration activity. Regarding to the luminescence inhibition over bacteria the differences observed for coagulation and biofiltration integrated with Fenton's were insignificant ($p > 0.05$). Despite of the small difference, biofiltration is a process that does not need the addition of chemical compounds in water and the clams can be reused during different cycles as was proved. Moreover, the application of this bivalve can result as a pest management approach since this species is an invasive bivalve.

III.7.3.4. Iron removal

Iron removal is an important factor in Fenton's process. On the one hand for environmental reasons, since there is a legal limit for iron discharge in water (2 mg/L of dissolved iron according to the Portuguese law), as well as for economic reasons. Usually, after Fenton's process, the effluent pH is increased to promote iron hydroxide precipitation. In this work, the integration of a coagulation and biofiltration processes were studied after several processes integrated with the Fenton process, referred above, with the objective of removing the iron from the treated effluent. The results are shown in Table III.7.3.

Table III.7.3. Concentration of dissolved iron in the treated effluent (standard error value in brackets).

Treatment	**[Fe] (mg/L)**
Coagulation + Fenton	0.25 (±0.05)
Coagulation + Fenton + Coagulation	below the detection limit
Biofiltration + Fenton	1.20 (±0.1)
Biofiltration + Fenton + Coagulation	0.01 (±0.0)
Biofiltration + Fenton + Biofiltration (after 4h)	0.02 (±0.0)

Analyzing the results in Table III.7.3, one can see that the amount of residual dissolved iron is higher in the case of biofiltration followed by Fenton's process compared to the integrated coagulation and Fenton processes. This can be explained by the fact that after the coagulation process there is still residual coagulant in the supernatant that may promote some iron precipitation after Fenton's process. This coagulant will also have interference in the Fenton process and may precipitate some iron, thus lowering the efficiency from the process, compared to the integrated biofiltration and Fenton process, as seen in Fig. III.7.5. However, biofiltration also shows to be efficient in removing iron after 4 h of exposure and with the advantage that the clams used to remove iron were the same as those used in the first phase of biofiltration before the Fenton process. This highlights the relevance of this invasive species environmental applications in wastewater treatment technologies.

III.7.4. Conclusions

Fenton's process proved to be a good alternative to conventional processes for the treatment of swine wastewater. The optimum conditions studied for the Fenton's process, considering the removal of COD (72%) and the luminescence inhibition (65%), were 750 mg/L for both the hydrogen peroxide and the iron load.

The potential of the Fenton process can be further increased if integrated with other methodologies. Fenton's process after biofiltration using *C. fluminea* removes about 91% of COD and the application of Fenton after coagulation removes 86% of COD. In the raw wastewater the luminescence inhibition to *A. fischeri* was 92%, while after the integrated methodologies it could be reduced to nearly 30%.

The application of integrated methodologies improves the swine wastewater treatment regarding to organic matter removal and toxicity reduction. The dissolved iron present in the treated effluent after the Fenton process can also be removed by either coagulation or biofiltration. The application of invasive bivalves in the integrated methodologies can be seen as a cleaner solution for the swine wastewater treatment. In fact, these clams enhance the Fenton's process and remove dissolved iron from water without the need of introducing further chemicals. Besides, this integration gives an environmental application to a pest species that has high environmental and economic impact contributing this way to a cleaner environment.

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IV. Final Conclusions

and

Future Work

IV. Final conclusions and Future work

IV.1. Final conclusions

Water reclamation should be considered as a strong possibility to deal with the problematic of water scarcity. There has been a great effort on the part of the scientific community, however, the trail is long and the steps are slow.

Agro-industrial wastewater management becomes a major task while environmental regulations are becoming stricter worldwide. Agro-industrial wastewaters are known by high content of organic pollutants that cause an adverse effect on the water bodies. Industries are looking for efficient, easy-to-use and affordable treatment processes.

In this study a treatment of a real effluent from an olive oil extraction industry, using the Fenton's process integrated with coagulation allowed to increase the biodegradability, to a ratio higher than 40 %, for further biological treatment application to definitively treat the effluent. The main drawback of Fenton′s process is the formation of ferric sludge, IE appears as a complement to the Fenton process, allowing, on the one hand, to remove the iron excess present in the sludge. On the other hand, this complementary treatment was able as well to further reduce the COD of a real OOEIW after Fenton's peroxidation. Another alternative to deal with iron sludge was addressed, the heterogeneous Fenton process was tested with low-cost solid catalysts. These are wastes rich in iron and other materials naturally present in nature, which were applied to treat a mixture of five phenolic compounds usually present in OMW (3,4 - Dihydroxybenzoic, 4 - Hydroxybenzoic, 3,4 - Dimethoxybenzoic, 3,4,5 - Trimethoxybenzoic and Trans-cinnamic acids). It was concluded that the removal of phenolic content reaches 100% for RM, while in the case of VRA and VRC this value is 72.0% and 74.6%, respectively.

S-AOPs were compared with advanced oxidation processes (namely Fenton's peroxidation) as a wastewater depuration alternative. Synthetic olive mill wastewaters were submitted to homogeneous and heterogeneous S-AOPs using iron sulfate and solid catalysts (RM and Fe-Ce-O) as the source of iron (II). The homogenous process was optimized by testing different pH values, as well as iron and persulfate loads. At the best conditions it was possible to achieve 39%, 63% and 37% COD, phenolic compounds and TOC removal, respectively. The catalytic potential of a waste (RM) and a laboratory material (Fe-Ce-O) was tested using heterogenous S-AOPs. The best performance was achieved by Fe-Ce-O, 27%, 55% and 5% COD, phenolic compounds and TOC removal were obtained, respectively.

The performance of different AOPs in the same multiphasic reactor was evaluated to minimize real oil extraction effluent environmental impact. In terms of COD removal, the combination of Fenton and Ozone reaction simultaneously, allowed the highest reduction (58.5%) although the combination of Fenton followed by ozone at pH3 lead to a similar removal, about 54%. In what regards mineralization, Fenton peroxidation alone was the most efficient process leading to 53% of TOC removal. Fentoń's process presents an interesting role in the effluent treatment. However, if one bears in mind phenolic content removal and toxicity abatement, the best results were obtained by Fenton peroxidation (pH 3) followed by ozonation (pH 9). The treatment processes selection should consider the target results as well as a suitable economic analysis.

In order to improve the depuration of swine wastewater, coagulation and biofiltration were integrated with Fenton's peroxidation. With the optimum loads of 750 mg/L of hydrogen peroxide and iron, this process was able to remove 72 % of COD and of lowering *A. fischeri* luminescence inhibition to 65 %. On the other hand, integration between Fenton's process and biofiltration removed 91 % of COD. Whereas, after coagulation COD degradation reaches 86 %. Regarding to luminescence inhibition, the treatment processes integration can decrease it to about 30 %. Coagulation and biofiltration after Fenton's process proved to be able to remove dissolved iron in the treated effluent and thus overcoming Fenton's process major disadvantage.

IV.2. Future work

It is urgent to recognize the importance of water safeguard the future availability of this resource. If it is true that we have the right to use this resource, it is also our duty to treat and manage it in a sustainable way. This work presents some steps to move towards the treatment of wastewater and, although the many studies in this respect, the work is not finished, it is necessary to go further.

Several studies indicate AOPs as favorable technologies for removing pollutants from agro-industrial effluents. However, these studies were essentially developed at the laboratory level. The applicability of these processes at the industrial scale is still limited. To increase the viability of AOPs at the industrial scale, several issues must be extensively studied in order to be improved. Research work has been and continues to be developed and other aspects must be widely researched, such as process costs, toxicity of effluents and by-products, (photo) catalysts technology and reactor design. The process costs must be analyzed as function of the destination of treated swine wastewater. If agriculture irrigation is the target, the requirements are less rigid, the treatment efficiency must not be so high. On the other hand, if the application is human domestic consumption the treatment must be more efficient. The reactor design is also relevant, but it will be closely linked with the AOP selected.

AOPs are very efficient in the treatment of some effluents leading to complete degradation of organic matter and forming CO_2 and water. However, sometimes mineralization is not complete, and reaction intermediates are formed. These by-products can be as or more toxic than the initial effluent. These new products may give rise to an entirely new kind of chemical toxicity or even to mutagenic or estrogenic activity. The identification of degradation products and process intermediates must be a central topic to understand the whole reaction phenomena and improve pollutants mineralization. Also, new processes taking advantage of persulfate or peroxymonosulfate action for oxidation of organic contaminants are being evaluated. The use of this highly oxidative radical can be a suitable solution for the swine wastewater treatment.

The integration of new and traditional technologies to achieve cheap and effective solutions must also be thoroughly assessed. In this context, arise as efficient approaches advanced oxidation processes, as previously referred, or even nanofiltration, ultrafiltration and/or reverse osmosis, or biofiltration through invasive bivalves.

Nevertheless, one should bear always in mind the impact of the treated effluents. Thus, the analysis of ecotoxicity over aquatic species or even agriculture crops must be considered as a tool to complement the evaluation of swine wastewater treatment. In fact, if water reuse is targeted, it is essential that the reclaimed water has no relevant impact on the aquatic life and human health. In Figure IV.1 the possibilities for the treatment of agro-industrial wastewaters and their possible reuse are presented.

The choice of the process must always consider the final objective of the treated water from the swine wastewater.

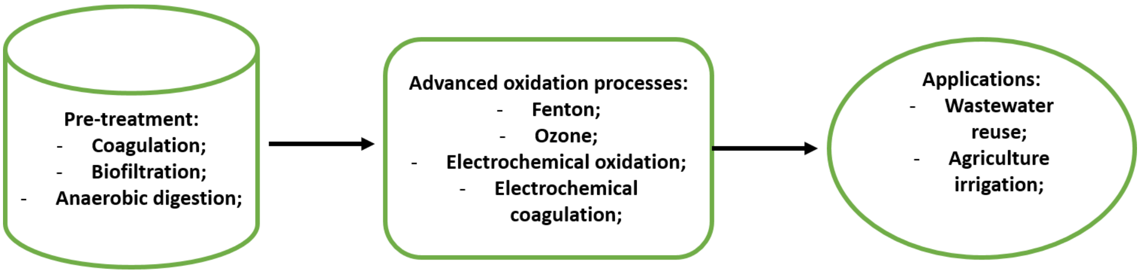

Figure IV.1. Scheme of purposed treatments.