Technical and economic feasibility of Fenton and Photo-Fenton's oxidation for industrial wastewater treatment

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DEDICATION

I dedicate my work to my beloved families **Mansouri** and **Toumi**. My parents **Rached Mansouri** and **Akila Toumi**, who instilled in me the values of perseverance and determination; my siblings **Safouene Mansouri** and **Ranim Mansouri**, whose unwavering support and encouragement have been a source of strength to me. I’m thanking them for always believing in me, boosting my confidence and supporting all my decisions through my whole journey hoping that my success will bring them as much happiness as they filled me with since day one.

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ABSTRACT

The Olive Pomace Oil Extraction Industry (OPOEI) has grown by 4% annually since 2019, highlighting its economic importance in the European Union (EU). This growth has led to the generation of significant amounts of wastewater, approximately 1 cubic meter per ton of processed olive pomace, totaling about 5.4 million cubic meters annually worldwide. The wastewater from this industry contains pollutants that pose environmental and public health risks. It is characterized by high levels of suspended solids, strong odors, high turbidity, low biodegradability, and the presence of Chemical Oxygen Demand (COD), phenolic compounds, dark color.

Olive mill wastewater is complex, necessitating innovative treatment techniques beyond conventional methods. Advanced Oxidation Processes (AOP), particularly the Fenton and Photo-Fenton processes, use hydrogen peroxide (H_2O_2) and ferrous ions ($Fe^{2+)}$ at acidic pH to generate hydroxyl radicals that degrade tough organic compounds, with the Photo-Fenton process additionally using UV light. This study aimed to identify the optimal pH and concentrations of Fe^{2+} and H2O2 for effective organic matter removal.

In the Fenton process, the impact of iron ion (0.5 to 14 g/L) and H_2O_2 dosage (1.5 to 20 g/L) was assessed at pH values of 2.5, 3.0, and 3.5. Optimal conditions were identified as 20 g/L H_2O_2 and 7 g/L Fe^{2+} at pH 3.5, achieving 45% COD and 82% TPC removal. For the Photo-Fenton process, the best conditions were 15 g/L H_2O_2 and 7 g/L Fe^{2+} at pH 3.5, resulting in 75% COD and 86% TPC removal.

Reaction time is critical for the efficiency of these processes. The Photo-Fenton process achieved approximately 80% COD removal and 97% TPC removal in 60 minutes, while the Fenton process achieved 55% COD removal and 93% TPC removal in 40 minutes. The economic viability of these processes involves evaluating chemical costs, energy requirements, and overall efficiency for treating one cubic meter of olive pomace oil wastewater.

Keywords: Economic feasibility; Fenton; Olive pomace oil extraction; photo-Fenton; technical feasibility.

RESUMO

A Indústria de Extração de Óleo de Bagaço de Azeitona (OPOEI) tem crescido 4% ao ano desde 2019, destacando sua importância econômica na União Europeia (UE). Esse crescimento levou à geração de quantidades significativas de águas residuais, aproximadamente 1 metro cúbico por tonelada de bagaço de azeitona processado, totalizando cerca de 5,4 milhões de metros cúbicos anualmente em todo o mundo. As águas residuais dessa indústria contêm poluentes que representam riscos ambientais e para a saúde pública. São caracterizadas por altos níveis de sólidos suspensos, odores fortes, alta turbidez, baixa biodegradabilidade e a presença de Demanda Química de Oxigênio (DQO), compostos fenólicos e cor escura.

As águas residuais dos lagares de azeite são complexas, necessitando de técnicas de tratamento inovadoras além dos métodos convencionais. Os Processos de Oxidação Avançada (AOP), particularmente os processos Fenton e Foto-Fenton, utilizam peróxido de hidrogênio (H_2O_2) e íons ferrosos (Fe^{2+}) em pH ácido para gerar radicais hidroxila que degradam compostos orgânicos difíceis, com o processo Foto-Fenton utilizando adicionalmente luz UV. Este estudo teve como objetivo identificar o pH ideal e as concentrações de Fe^{2+} e H_2O_2 para a remoção eficaz da matéria orgânica.

No processo Fenton, o impacto dos íons de ferro (0,5 a 14 g/L) e da dosagem de H_2O_2 (1,5 a 20 g/L) foi avaliado em valores de pH de 2,5, 3,0 e 3,5. As condições ideais foram identificadas como 20 g/L de H_2O_2 e 7 g/L de Fe^{2+} a pH 3,5, alcançando 45% de remoção de DQO e 82% de remoção de TPC. Para o processo Foto-Fenton, as melhores condições foram 15 g/L de H2O2 e 7 g/L de Fe^{2+} a pH 3,5, resultando em 75% de remoção de DQO e 86% de remoção de TPC.

O tempo de reação é crucial para a eficiência desses processos. O processo Foto-Fenton alcançou aproximadamente 80% de remoção de DQO e 97% de remoção de TPC em 60 minutos, enquanto o processo Fenton alcançou 55% de remoção de DQO e 93% de remoção de TPC em 40 minutos. A viabilidade econômica desses processos envolve a avaliação dos custos dos produtos químicos, requisitos de energia e eficiência geral para o tratamento de um metro cúbico de águas residuais do óleo de bagaço de azeitona.

Palavras-chave: Extração de óleo de bagaço de azeitona; Fenton; foto-Fenton; Viabilidade económica; Viabilidade técnica.

RÉSUMÉ

L'industrie de l'extraction de l'huile de grignons d'olive (OPOEI) a connu une croissance de 4 % par an depuis 2019, soulignant son importance économique dans l'Union européenne (UE). Cette croissance a conduit à la génération de quantités importantes d'eaux usées, environ 1 mètre cube par tonne de grignons d'olive traités, totalisant environ 5,4 millions de mètres cubes annuellement dans le monde. Les eaux usées de cette industrie contiennent des polluants qui posent des risques pour l'environnement et la santé publique. Elles se caractérisent par des niveaux élevés de solides en suspension, des odeurs fortes, une forte turbidité, une faible biodégradabilité et la présence de la demande chimique en oxygène (DCO), de composés phénoliques et d'une couleur sombre.

Les eaux usées des moulins à huile d'olive sont complexes, nécessitant des techniques de traitement innovantes au-delà des méthodes conventionnelles. Les procédés d'oxydation avancée (AOP), en particulier les procédés Fenton et Photo-Fenton, utilisent du peroxyde d'hydrogène (H2O2) et des ions ferreux (Fe^{2+}) à pH acide pour générer des radicaux hydroxyles qui dégradent les composés organiques difficiles, le procédé Photo-Fenton utilisant en plus la lumière UV. Cette étude visait à identifier le pH optimal et les concentrations de Fe^{2+} et H_2O_2 pour une élimination efficace de la matière organique.

Dans le processus Fenton, l'impact des ions ferreux (0,5 à 14 g/L) et du dosage de H_2O_2 (1,5 à 20 g/L) a été évalué à des valeurs de pH de 2,5, 3,0 et 3,5. Les conditions optimales ont été identifiées comme étant 20 g/L de H_2O_2 et 7 g/L de Fe^{2+} à un pH de 3,5, atteignant 45 % de réduction de DCO et 82 % de réduction de TPC. Pour le processus Photo-Fenton, les meilleures conditions étaient 15 g/L de H_2O_2 et 7 g/L de Fe^{2+} à un pH de 3,5, entraînant une réduction de 75 % de DCO et 86 % de TPC.

Le temps de réaction est crucial pour l'efficacité de ces processus. Le processus Photo-Fenton a atteint environ 80 % de réduction de DCO et 97 % de réduction de TPC en 60 minutes, tandis que le processus Fenton a atteint 55 % de réduction de DCO et 93 % de réduction de TPC en 40 minutes. La viabilité économique de ces processus implique d'évaluer les coûts des produits chimiques, les besoins énergétiques et l'efficacité globale pour le traitement d'un mètre cube d'eaux usées d'huile de grignons d'olive.

Mots-clés : Extraction d'huile de grignon d’olive ; Faisabilité économique ; Faisabilité technique;Fenton; Photo-Fenton ;

TABLE OF CONTENTS

INDEX OF ABBREVIATIONS

AOPs : Advanced Oxidation Processes

COD : Chemical Oxygen Demand

ELV : Emission Limit Value

IWW : Industrial Wastewater

OOEIW : Olive Oil Extraction Industry Wastewater

OOEI : Olive Oil Extraction Industry

OPOEI : Olive Pomace Oil Extraction Industry

OO : Olive Oil

TPC : Total Phenolic Compound
WW : Wastewater

INDEX Of FIGURES

INDEX OF TABLES

1. INTRODUCTION

1.1. INTRODUCTION

The olive pomace oil extraction industry (OPOEI) recorded an average annual growth of 4%, underscoring its economic importance in the EU. The countries with the most significant potential for olive oil (OO) production is the Mediterranean region, which suffers from severe drought. Due to this climate challenge, it is important to use techniques and technologies to protect this resource, ensure its productivity and minimise the impact on natural resources (Babic et al., 2019; Domingues et al., 2018).

The olive oil extraction process generates large amounts of wastewater (approximately 1 m^3 per ton of processed olives). This equates to approximately 5.4 million cubic meters per year worldwide. Spain, Italy, Greece, and Portugal are among the countries that produce the most OO, and therefore, the highest amount of wastewater (Domingues et al., 2021; Hodaifa and Reza 2019; Yazdanbakhsh et al., 2015). The OPOEI wastewater has various chemical compositions, is dark in color, contains much organic matter, and is difficult to biodegrade. This composition of wastewater from the OPOEI makes it impossible to incorporate it into conventional biological treatment systems, such as aerobic or anaerobic lagoons, indicating the need for pretreatment techniques. They also contain phenolic substances that have phytotoxic and antibacterial effects, making the disposal of wastewater from conventional water and wastewater treatment systems impossible (Khdair et al., 2019). Several pretreatment techniques can modify the properties of OPOEI wastewater at the system inlet to significantly reduce or eliminate initial contamination levels. Among these techniques, filtration, ultrafiltration, flocculation, coagulation, electrocoagulation and adsorption have attracted considerable attention (Esteves et al., 2019). However, such methods require advanced treatments to improve performance. This study investigates the use of Fenton and Fenton's advanced oxidation processes as an alternative means of treating wastewater from an extraction plant in Mirandela, Portugal, characterised by high levels of total phenolic compounds, chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total solids.

AOPs represent an innovative approach to WW treatment because of their economic and easy-to-apply nature. This involves the generation of hydroxyl radicals by the reaction between the Fe-based catalysts and hydrogen peroxide. High levels of BOD and COD that cannot be reduced by anaerobic digestion pose another threat to recipients (Inglezakis, 2012; Kapellakis, 2008; Mercé Sole, 2021).

This offers advantages such as cost-effectiveness, short reaction time, and no need for additional energy to activate hydrogen peroxide. The use of Fenton and photo-Fenton techniques has proven effective in decontaminating industrial wastewater containing organic pollutants. The economic feasibility of these processes is a crucial aspect evaluated in this study, considering the energy and equipment costs involved in treating 1 m^3 of effluent from olive pomace oil wastewater treatment.

Overall, this study contributes to understanding and potential solutions for the environmental impact of olive pomace oil extraction on water resources and ecosystems. (Stoller, 2010; Aziz, 2019).

1.2. OBJECTIVES

1.2.1. MAIN OBJECTIVE

This thesis aims to study the effluent treatment from an olive pomace oil extractor industry using Fenton and photo-Fenton processes in Frechas-Mirandela (Portugal).

1.2.2. SPECIFIC OBJECTIVES

- Physicochemical characterisation of wastewater produced by an industrial olive pomace oil extractor industry.
- To p;ropose different initial treatments for the effluent generated in an olive pomace oil extractor plant.
- Study Fenton and photo-Fenton processes for the effluent produced by the olive pomace oil extractor effluent industry.
- ToTreat the wastewater effluent using the Fenton and photo-Fenton (UV/Fe2+/H2O2) processes in order to achieve environmental and economic feasibility of the treatment .

2. STATE OF ART

2.1. OLIVE OIL INDUSTRY

According to Tsagaraki et al. (2006) and Reis (2016), olive oil extraction has three main methods. The pressing process (traditional system) involves two-phase centrifugation and three-phase centrifugation.

The pressing process is the oldest method for producing olive oil, whereby olive paste is pressured to release an oily containing both water and oil. The resulting mixture is separated using centrifugation to yield the virgin olive oil and raw water. A small amount of water is added during the extraction to reduce the effluent, resulting in concentrated wastewater. In the two-phase centrifuge process, a decanter is used, which rotates at different speeds, allowing the bagasse to be directed to the ends of the equipment and the liquid phase to its interior. This process produces a large amount of wet pomace (da Cunha, 2014; Reis, 2016). Petrakis (2006) reported that wet bagasse can be subjected to another three-phase centrifugation to decrease humidity and recover a small percentage of oil. In the three-phase centrifugation process, the olive paste is centrifuged at a high speed, promoting the separation of the solid and liquid phases. The liquid phase is again submitted to centrifugation to separate oil and dark water (Reis, 2016). According to Petrakis (2006), this process uses 1.25 to 1.75 times more water than traditional systems, increasing the wastewater produced in the extraction. According to Petrakis (2006) and Gebreyohannes et al. (2016), the extraction process produces effluent with a dark colour, acid, and foul odour, mainly called olive mill wastewater (OMWW).

2.2. OLIVE POMACE OIL PRODUCTION

Olive pomace is a solid by-product of olive oil production that consists of skin, pulp, and olive stones (Moral and Méndez, 2006). It contains a considerable amount of oil and can be a source of valuable compounds.

Olive pomace is mainly used to extract residual oil via solvent extraction.

According to Petrakis (2006) and Domingues et al. (2021), the end of the three-phase extraction process produces a new type of effluent, the olive oil extraction industry wastewater (OOEIW), as shown in Figure 1.

According to Domingues et al. (2021), a little or almost unstudied effluent presents physicochemical characteristics like those of OMWW. The traditional press, three-phase, and two-phase decanter centrifuge methods are commonly used to extract olive oil.

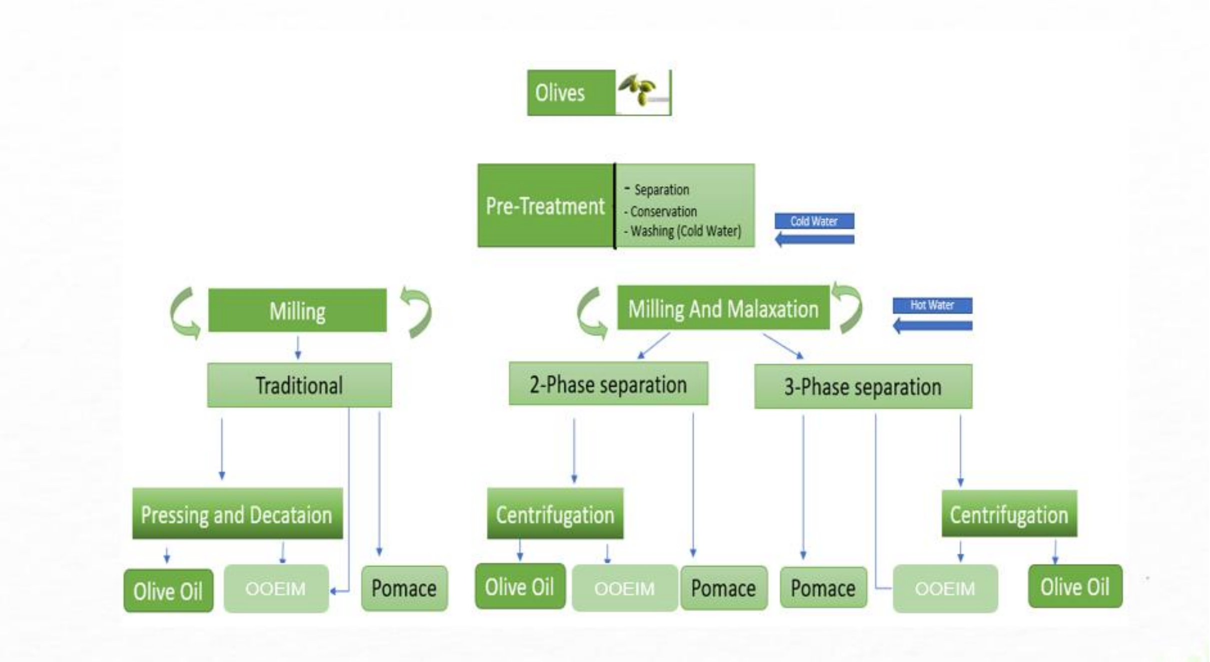

Figure 1: Olive oil production routes.

The olive pomace reprocessing system to generate olive pomace oil also generates liquid waster standard , which must be appropriately treated.

Inadequate management of this effluent by olive pomace oil producers is dangerous to the environment. It can quickly create high pollutant loads in receiving water bodies and threaten animals, vegetation, and soil (Esteves et al., 2019; Sar et al., 2020).

In the EU, effluents from these industries are commonly used for agricultural irrigation, provided they are adequately treated and meet the necessary standards. However, much legislation has yet to establish these standards and maximum parametersfor effluent use in the EU's fertigation, and each country is responsible for monitoring and control (Halalsheh et al., 2021).

In Portugal, Law No. 626/2000 limits this type of effluent to 80 m^3 ha^{-1} per year, indicating its use in the irrigation of trees and shrubs. However, each municipality in Portugal has general laws for the disposal of IWW, provided by Decree Law 236/98, which indicates the necessary standards for obtaining licenses from regulatory entities. For example, the municipality of Mirandela , located in the northern region of Portugal, has Regulation No.

169/2015, which sets the maximum parameters for the discharge of IWW COD < 1 g L^{-1}, BOD_5 < 0.5 g L^{-1}, and total suspended solids (TSS) < 1000 mg L^{-1} (Esteves et al., 2019; Halalsheh et al., 2021; Koutsos et al., 2018).

The effluents from the OPOEI are similar to those generated in the OOEI, having the characteristics of being a dark liquid with acidic pH, high organic content(Solomakou and Goula, 2021), and high COD (Sar et al., 2020). It also contains toxic components, such as tannins, phenols, and other acidic compounds (Flores et al., 2018), which are associated with adverse environmental effects such as antibiosis and phytotoxicity(Vagelas and Giurgiulescu, 2019).

The most relevant parameters studied for wastewater from the OOEI and OPOEI are listed in Table 1.

Table 1: Characterization of the wastewater from OOEI and OPOEI.

Parameter	Unit	Value	References
pH		4.3 – 6.8	**(Domingues et al., 2021 ; Flores et al., 2018 ; Lucas and Peres, 2009 ; Sar et al., 2020)**
COD	g L^{-1}	1.4 – 102.5	**(Domingues et al., 2021 ; Flores et al., 2018 ; Lucas and Peres, 2009 ; Sar et al., 2020)**
BOD_5	g L^{-1}	0.4 – 10.5	**(Domingues et al., 2021 ; Flores et al., 2018 ; Lucas and Peres, 2009)**
Total Suspended Solids	g L^{-1}	0.6 – 6.8	**(Domingues et al., 2021 ; Lucas and Peres, 2009)**
Total Volatile Solids	g L^{-1}	0.74 – 52.8	**(Domingues et al., 2021 ; Flores et al., 2018 ; Sar et al., 2020)**
Total solids	g L^{-1}	1.9 – 65.2	**(Domingues et al., 2021 ; Flores et al., 2018 ; Sar et al., 2020)**
TPC	g L^{-1}	0.56 – 4.3	**(Domingues et al., 2021 ; Lucas and Peres, 2009)**

The chemical composition of the wastewater from the OPOEI is highly variable, both qualitatively and quantitatively, depending on many factors, such as climate, crop type, and OO extraction method, thus generating different pomaces (Khdair et al., 2019). Other treatment techniques, such as AOP, must be used.

2.3. OLIVE OIL INDUSTRY WASTEWATER TREATMENT

When the principles of circular economy are incorporated into industrial processes, the objective is to repurpose waste materials into usable resources that can be reintegrated into the production cycle. This approach enhances the efficiency of the process, while minimising costs and reducing the environmental impact associated with the disposal of hazardous waste (Korhonen et al., 2018; Mazur, 2021; Donner et al., 2022).

As mentioned by Tsagaraki et al. (2006), the residue from the olive oil industry has a dual nature; it is a potent pollutant and a source of valuable resources.

The effluent produced has high cytotoxic potential and antimicrobial properties, mainly because of the high concentration of phenolic compounds, making the residue highly polluting (Galiatsatou et al., 2002; Layachi et al., 2022). Phenolic compounds and their derivatives are a family of common environmental contaminants, even at low concentrations, which present an obstacle to the use/reuse of water; their presence causes bad taste and odour in drinkable water and causes adverse effects on biological processes (Dąbrowski et al., 2005).

Various treatment and compound recovery methods have been tested to address the growing environmental concerns surrounding the management of this effluent type, including mechanical, physical, biological, thermal, physical-chemical, and soil application techniques. (Azbar et al., 2004; Ferraz, 2012). Thus, in more recent studies, flexible and efficient treatments have been evaluated to reduce the capital costs of their treatment with the recovery and recycling of economically attractive components (Tsagaraki et al., 2006).

2.4. TREATMENT OF INDUSTRIAL WASTEWATER (IWW)

Effluent treatment methods are crucial for maintaining water quality and preserving the environment, such as in a well-tended garden. According to Sathya et al. (2022), industries churn out a deluge of discharge containing dissolved debris and toxic substances that can harm aquatic life and ecosystems. Proper effluent treatment is essential for maintaining clean water sources for human consumption and shielding the environment as a sanctuary for future generations. Therefore, it is necessary to implement advanced and modern treatment methods to remove these pollutants before they are released into the environment to cautiously pluck out poisonous plants that could otherwise render the waterway barren. Biological treatments, such as activated sludge process and anaerobic digestion, have been proven effective in removing organic matter from effluents and carefully pruning decayed leaves that would otherwise contaminate the water flow. Additionally, physicochemical treatments play a vital role in removing heavy metals from wastewater to remove any remaining hazardous waste. These methods help protect natural resources and contribute to sustainable development by reducing industrial waste debris. Overall, the gold standard for effluent management requires techniques, with alacrity and care taken to sustain the waterscape for years.

2.5. ADVANCED OXIDATION PROCESSES

Techniques for removing organic compounds from IWW include biological, thermal, and chemical treatments (Paraskeva and Poulos, 2006). Biological treatment is an environment-friendly process at a reasonable cost. However, they are unsuitable for use in wastewater containing non-biodegradable compounds and typically require long residence times for microorganisms to degrade contaminants (Gizgis et al., 2006; McNamara et al., 2008). However, there are still some issues that need to be addressed. Heat treatment brings many disadvantages, including releasing large amounts of other harmful compounds (Giuffrè et al.,2012). Physical and chemical treatments, such as flocculation, precipitation, activated carbon adsorption, and reverse osmosis, do not fully cover post-treatment requirements, especially phenol treatment (Rahmanian et al., 2014). AOPs are characterised by their standard chemical qualities. The high reactivity of hydroxyl radicals to achieve complete reduction further drives the oxidation process by mineralising less reactive pollutants (Elkacmi and Bennajah, 2019). Many studies have applied advanced oxidation techniques to treat OPOEI wastewater. Contaminants are oxidised using four different reagents: ozone, hydrogen peroxide, oxygen, air, or a combination to choose the best one .

In addition to technology, the concentration and type of pollutants and the volume of wastewater should also be considered (Domingues et al., 2018; Elkacmi and Bennajah, 2019). Bhupala et al. (2022) first treated OPOEI wastewater with 10 g L^{-1} COD and 164 mg L^{-1} TPC, combined with aluminium sulfate coagulation (0.8 g L^{-1} at pH 4.5), followed by biological and photo-Fenton (UVA) treatment; COD and TPC were removed by 93% and 97%, respectively. Kirmachi et al. (2018) compared the use of the Fenton advanced oxidation process and ozone/Fenton combination on wastewater initially using 38 g L^{-1} chemical oxygen demand (COD). The Fenton method achieved the highest removal rate when the H_2O_2:Fe^{2+} ratio was 10, resulting in a COD removal rate of 51.6%. An additional 49% removal improvement was observed when an ozone generator was used under the same conditions. Flores et al. (2018) used a combination of electrocoagulation, electro-Fenton, and electron-optical Fenton methods to treat turbid water using different electrode combinations. With a treatment time of 600 min, the total organic carbon (TOC) removal rate was 97.1%. The most promising studies have suggested using AOPs in the following ways: UV, UV/H_2O_2, photo-Fenton (UV/H_2O_2/Fe), ozonation, catalytic oxidation in humid air, electricity and Fenton processes .However, these studies also point out that the Fenton is the basic principles of AOP and emphasise their importance.

Advanced oxidation processes (AOPs), Figure 2, have recently emerged as an essential class of technology for the oxidation and destruction of a wide range of organic pollutants in water and wastewater (Legrini et al. 1993; Alvares et al. 2001; Oppenländer 2003).

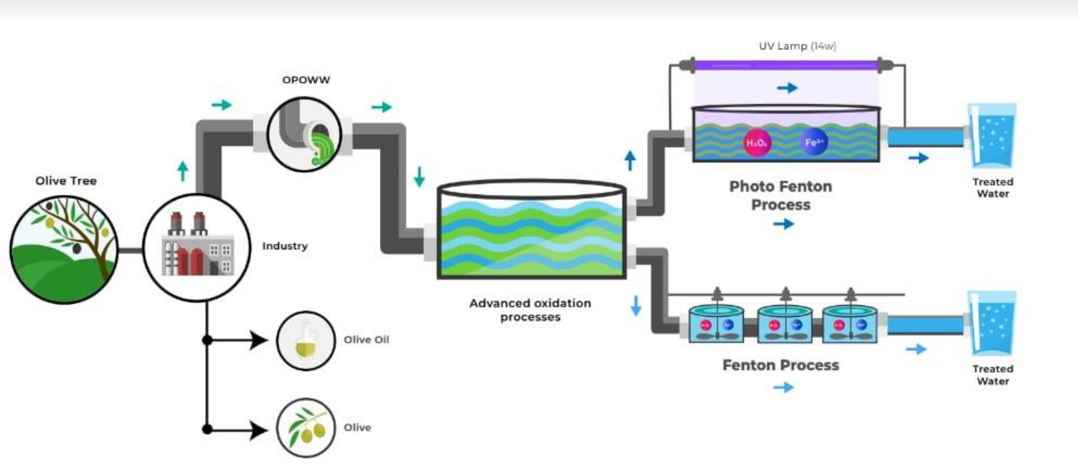

Figure 2: Advanced oxidation processes.

2.5.1. Fenton process

More than a century ago, H.J. Fenton described how adding a catalyst at an acidic pH enhances the oxidation power of H_2O_2 of specific organic molecules via H_2O_2 decomposition (Fenton 1894; Haber and Weiss 1934). It was later discovered that this process generates $HO\cdot$ via the following reaction (Walling 1975):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \qquad \text{(Equation 1)}$$

The Fenton process is highly efficient at pH values between 2 and 5, with the most effective range being pH 2.8-3.0 (Pignatello 1992). One advantage of the Advanced Oxidation Process (AOP) is that it is relatively inexpensive, abundant, and infinitely water-soluble. The potential of Fenton's reaction in industrial wastewater treatment has been extensively studied (Legrini et al. 1993; Prousek 1996).

2.5.2. Photo-Fenton processes

The photo-Fenton process combines Fenton's reaction with UV light (180–400 nm), generating additional HO· and enhancing the response. UV light also facilitates the photo-reduction of Fe^{3+} (ferric hydroxo complexes, i.e., $[Fe\ (OH)n]^{(3-n)\ +}$) to Fe^{2+} ions, leading to the production of more HO· according to the following reaction (Pignatello and Huang 1993; Wadley and Waite 2004):

$$\mathrm{Fe^{3+} + H_2O \overset{uv}{\rightarrow} Fe^{2+} + HO^{\cdot} + H^{+}} \qquad \text{(Equation 2)}$$

The produced Fe^{2+} reacts with H_2O_2 to generate more HO· through Fenton's reaction. This continuous cycle of ferrous iron, as long as hydrogen peroxide is available, reduces the amount of iron salts needed for Fenton's reaction, making the photo-Fenton treatment more attractive than the dark Fenton's oxidation process (Wadley and Waite 2004). Additionally, UV-C irradiation can contribute to HO· production via H_2O_2 photolysis. At higher (near UV, even visible) wavelength ranges, ferric carboxylate complexes, $Fe\ (RCO2)^{2+}$, may produce additional Fe^{2+} and organic radicals (R●) through the following reaction (Pignatello and Huang, 1993):

$$\mathrm{Fe(RCO_2)^{2+} \rightarrow Fe^{3+} + CO_2 + HO^{\cdot}} \quad (< \text{ca. } 500 \text{ nm}) \text{ (Equation3)}$$

The quantum yields of Equations (2) and (3) strongly depend on pH and wavelength (Safarzadeh-Amiri et al. 1996). As previously mentioned for the dark-Fenton process, the primary limitation of iron-based AOPs is the requirement to operate in the acidic pH (2–5) range, as iron salts would start to precipitate as ferric hydroxide at higher pH values (Wadley and Waite 2004). Moreover, the remaining iron in the solution must be eliminated after treatment. We can resume the advantages and disadvantages of both processes (Fig 3) s Fenton and photo Fenton in the table 2.

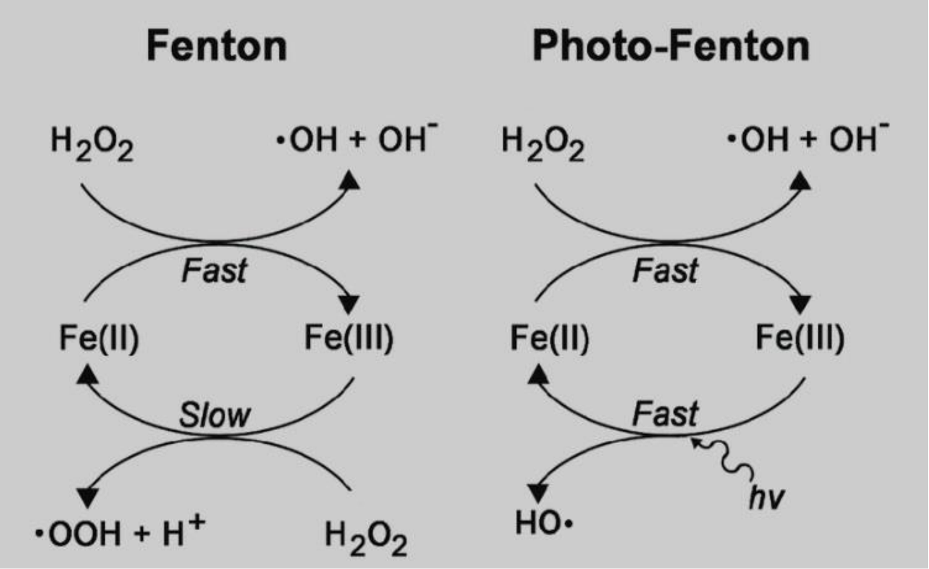

Figure 3: The Processes of Fenton and Photo-Fenton

Table 2: Advantages and disadvantages of Fenton and Photo Fenton processes

	ADVANTAGES	DISADVANTAGES
FENTON PROCESS	**Removal of polyphenolic compounds** can effectively remove a large amount of recalcitrant polyphenolic compounds from OMW, improving its biodegradability. . **Reduced toxicity**: The electro-Fenton process has been shown to decrease the toxicity of OMW from 100% to 66.9%, improving the performance of subsequent anaerobic digestion. . **Integrated treatment**: The Fenton process can be combined with other treatment methods, such as electro-coagulation or anaerobic digestion, to further improve the quality of the treated wastewater.	**Potential formation of toxic byproducts: can effectively** remove polyphenolic compounds, it may also form toxic byproducts, which could pose environmental concerns. **High energy and chemical requirements:** The Fenton process typically requires high energy inputs and the use of hazardous chemicals, such as hydrogen peroxide and iron salts, which could make it less sustainable and economically viable for large-scale applications. **Complexity:** is a complex reactive system, with various parameters (e.g., time, pH, hydrogen peroxide, and iron concentrations) affecting its efficiency This complexity may make it challenging to optimize and control the process on a large scale.
PHOTO FENTON PROCESS	**Efficient Degradation**: Photo-Fenton oxidation has been proposed as an efficient method for the treatment of olive mill wastewater (OMW) **Color Reduction**: It has been found to be effective in reducing the color of OMW. **Reduction of Pollutants**: The process can lead to significant reductions in chemical oxygen demand (COD), total phenolic content, and organic compounds content in OMW .**Sequential Treatment**: When used in combination with biological treatment, photo-Fenton oxidation has shown potential for further reducing COD, total phenolic content, and organic compounds content in OMW	**Toxicity**: Despite its effectiveness in reducing pollutants, OMW remained highly toxic after photo-Fenton oxidation in some cases **Limited Impact of Biological Treatment:** The benefits of biological treatment in reducing COD, total phenolic content, and toxicity were not substantial when applied after photo-Fenton oxidation.

2.6. ECONOMIC FEASIBILITY

The economic feasibility of wastewater treatment using Fenton and photo-Fenton processes demonstrates the efficiency of biooxidation, membrane filtration, and solar Fenton oxidation after coagulation/pre-coagulation treatment in olive factory wastewater treatment. (Ioannou-Ttofa, 2017) . This study showed that the solar Fenton oxidation process achieved more than 94% COD removal and completely removed the phenol content. An economic evaluation of the photo-Fenton process was also conducted in a study evaluating various solar reactors for photocatalytic water treatment (Jorda et al., 2011). In this study, the photo-Fenton process was economically feasible for wastewater treatment. These studies suggest that the Fenton and photo-Fenton processes may be economically viable for wastewater treatment. However, the specific economic feasibility depends on the particular applications and conditions and has been the subject of several studies. The efficiency of treating olive pomace oil wastewater using Fenton and light-Fenton processes has significant economic implications. These processes were found to be effective in removing organic matter from the Olive Mill Wastewater (OMW), with the photo-Fenton system achieving a higher chemical oxygen demand (COD) removal rate of 80%, as proven by Garcia and Hodaifa (2017).

However, it is essential to note that the effectiveness of these treatments varies, and some are less efficient, such as air oxidation and UV/photooxidation (Agabo-Garcia et al. 2021).

Moreover, studies analysing the efficiency of fungal and photo-Fenton oxidation treatments show that the latter has great potential to significantly reduce COD, total phenolic content, and organic compound content, which has a significant economic impact. It turns out that it can potentially reduce toxicity, as studied by Justino et al., 2009.

3. METHODOLOGY

The study was conducted at the Laboratory of Chemical Processes, Escola de Tecnologia e Gestão, Instituto Politécnico de Bragança, from September 2022 to June 2024. The effluent was collected on January 3rd, 2023, from an extracting unit of olive pomace oil located in Frechas, Mirandela, Portugal.

This study conducted two distinct experiments: Fenton and Foto-Fenton oxidation processes. The removal of total phenolic compounds (TPC) and the reduction of organic load (COD), the primary pollutants, were evaluated.

3.1. MATERIALS

3.1.1. Equipments

A variety of laboratory glassware and equipment necessary for the experiments are employed in this study.

- Glass Rod;
- Magnetic stirrer (Hanna HI 180);
- pH meter (Hanna EDGE);
- Test Tube;
- Screw Cap Test Tub;
- COD Reactor (Hanna HI 839800);
- Spectrophotometer (Jasco V-530).
- Jar test;
- UV photoreactor (UV Lamp, 14 W);

3.1.2. Reactants

- Hydrogen Peroxide (H_2O_2) 30 vol;
- Heptahydrated Iron Sulfate ($FeSO_4.7H_2O$);
- Folin-Ciocalteu (reagent) ;
- Sodium Carbonate (Na_2CO_3);
- Sulfuric Acid (H_2SO_4) ;

- Sodium Hydroxide (NaOH);
- Potassium Dichromate ($K_2Cr_2O_7$);
- Silver Sulfate (Ag_2SO_4).

3.2. WASTEWATER PHYSIOCHEMICAL CHARACTERIZATION

The wastewater characterisation includes pH, Biochemical Oxygen Demand, Chemical Oxygen Demand, Phosphorus, Organic Nitrogen and Ammonia, Oil and Grease, Total Organic Carbon, Aromaticity, Phenolic compounds, Alkalinity, Total Solids, Total Dissolved Solids, fixed and Volatile Solids. The parameters were determined following the Standard Methods for Examination of Water and Wastewater, as described below.

According to the American Public Health Association and Water Environment Federation's Standard Methods for the Examination of Water and Wastewater (1998), APHA 20th Edition the natural effluent and post-treatments were characterised by analysing the following parameters: pH, Total Phenolic Compounds (TPC), and Chemical Oxygen Demand (COD).The preparation of the analyses were performed in Figure 4 using appropriate procedures.

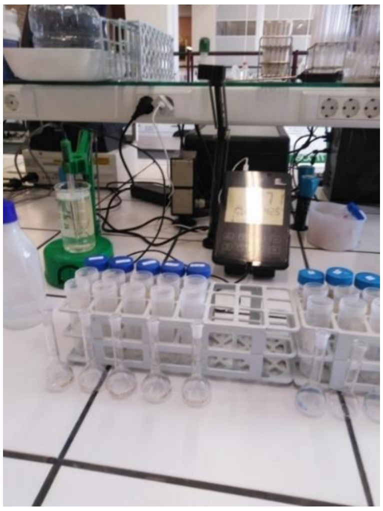

Figure 4: Preparation of the COD and TPC Samples

3.2.1. pH measurement

After the wastewater was delivered to the laboratory, an homogeneous sample was used to measure the hydrogen potential using a HANNA pH meter under magnetic agitation at a temperature of 20ºC.

3.2.2. Determination of chemical oxygen demand (COD)

The COD is a crucial parameter in diverse water quality analyses, enabling the quantification of the oxygen required to oxidise constituents within a sample, including organic matter. The closed reflux method outlined in the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2017) under number 5220 was selected for this study. Employing a JASCO V-530 spectrophotometer configured at a wavelength of 600 nm, this method facilitates the determination of COD within the range of 100–900 mg O_2/L. Despite this range accommodating high COD levels, the sample from industrial wastewater (IWW) used in this study necessitated a dilution of at least 100 times to align with the method's reading parameters. A calibration curve for COD determination was established following literature guidelines (APHA et al., 2017), utilising known quantities of potassium hydrogen phthalate (KHP). Notably, 1 mg of KHP was equivalent to 1.176 g L^{-1} of O_2, as depicted in Figure 5. We add to about 250 mL distilled water 212.5 mg KHP, previously dried at 110°C for two h, and dilute to 250 mL; this solution has 1000 mg O_2 L^{-1}, and prepare the dilutions proposed. The absorbance was measured at 600 nm.

Figure 5: Standard solution.

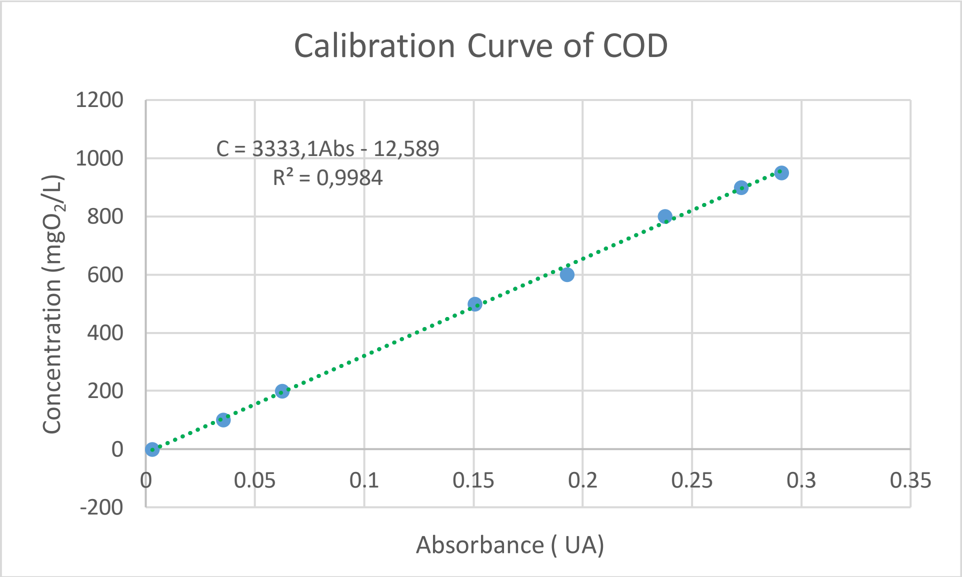

Figure 6: Calibration curve for COD determination

The R^2 value of 0.9984 shows that, for the range 100 to 900 mg of O_2 L^{-1}, Equation (4) is valid for determining COD.

$$C = 3333.1Abs + 12.589 \qquad (4)$$

3.2.3. Total phenolic compounds

The Folin-Ciocalteu method was employed to determine the total phenolic compounds (TPC). In this process, 0.5 mL of Folin-Ciocalteu reagent, 0.2 mL of homogenised sample, and 8.2 mL of distilled water were combined in a 30 mL test tube. This mixture was vortexed for homogenisation and allowed to rest for 10 minutes. Subsequently, 1 mL of 10% Sodium Carbonate (Na_2CO_3) was added, shaken, and undisturbed for 60 min. Following incubation, the absorbance was measured using a JASCO V-530 spectrophotometer configured for UV-VIS absorbance reading at 765 nm (Gueboudji et al., 2022; Mastoras et al., 2022; Russo et al., 2022).

To establish a calibration curve, known quantities of gallic acid ranging from 0 to 100 mg L^{-1} were utilised (Figure 6 and Equation 5). This approach provides a reliable reference for quantifying Total Phenolic Content in subsequent samples.

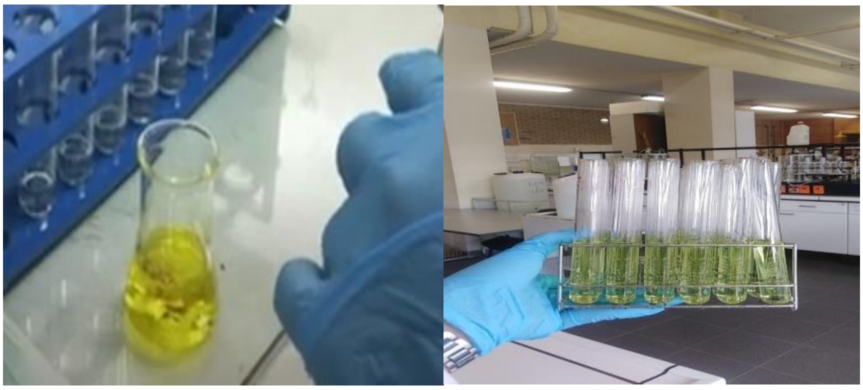

Figure 7: The experimental steps of the TPC removal test

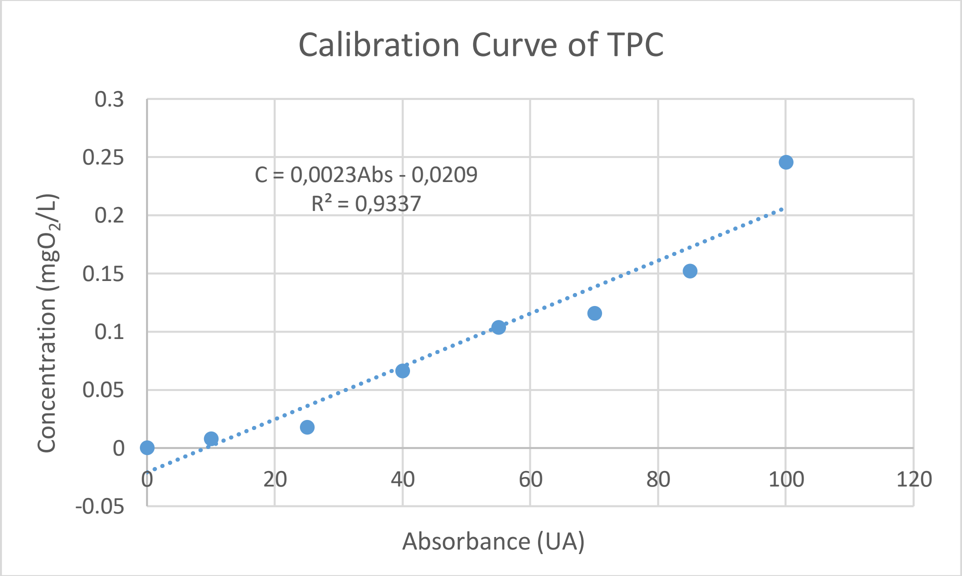

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Figure 8: Calibration curve for TPC

$$C = 0.0023Abs + 0.0209 \qquad (5)$$

$R^2 = 0.9337$ indicates excellent precision and reliability of the obtained values. Another essential aspect to note is the sensitivity of the absorbance reading, represented by the angular coefficient of the line, with a value of 0.7864 (mg L^{-1} nm^{-1}), indicating thatthe equipment can detect values above this absorbance.

3.3. ADVANCED OXIDATION PROCESSES

The Fenton process involves hydrogen peroxide and ferrous ions to generate hydroxyl radicals that can oxidise organic pollutants in wastewater. The photo-Fenton process is similar to the Fenton process. Still, it uses ultraviolet light to activate hydrogen peroxide and ferrous ions, generating more hydroxyl radicals, efficiently removing COD and TPC from the treated water.

3.3.1. Fenton process

a. Fenton Reagents

The primary reagents used were hydrogen peroxide (373.1 g L^{-1}), and heptahydrate sulfate ($FeSO_4.7H_2O$), with an initial concentration of 50 g L^{-1}. The pH required for the Fenton reaction (between 2.5 and 3.5) at the start of the response and its neutralisation (pH between 10 and 12) to end the process was controlled using H_2SO_4 1M and NaOH 6M. Solutions containing 10-fold dilutions of these reagents were prepared to obtain a sufficient pipette volume, making the analysis more reliable.

b. Fenton Procedure

The experiments were conducted as follows:

1. Collect an aliquot of the filtered raw effluent for each sample (approximately 100 mL)
2. The samples were homogenised for at least 1 min using a magnetic stirrer.
3. The desired amount of hydrogen peroxide was gradually added during the first 3 minutes.
4. The pH of the samples was adjusted to the desired range using H_2SO_4 (1M) and NaOH (6M) between 2.5. and 3.5.
5. The desired amount of iron sulfate was added immediately before starting the jar test.
6. The samples were used for the jar test mentioned in Figure 9.
7. The reaction was performed with slow stirring at 80 rpm for another 20 min (Figure 9) (Yazdanbakhsh et al., 2015).
8. The pH of the sample was again adjusted between 9 and 11 to stop the reaction by adding Sodium Hydroxide (NaOH).
9. The sample was stabilised for at least 24 h (Figure 10).

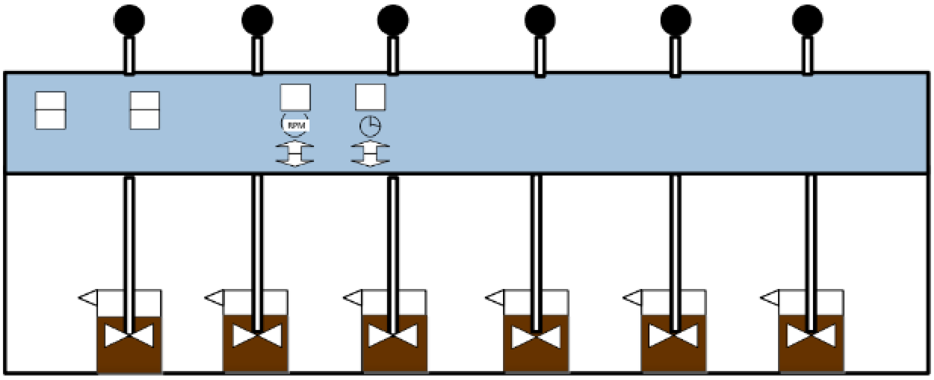


Figure 9: Jar test used equipment for the Fenton process.

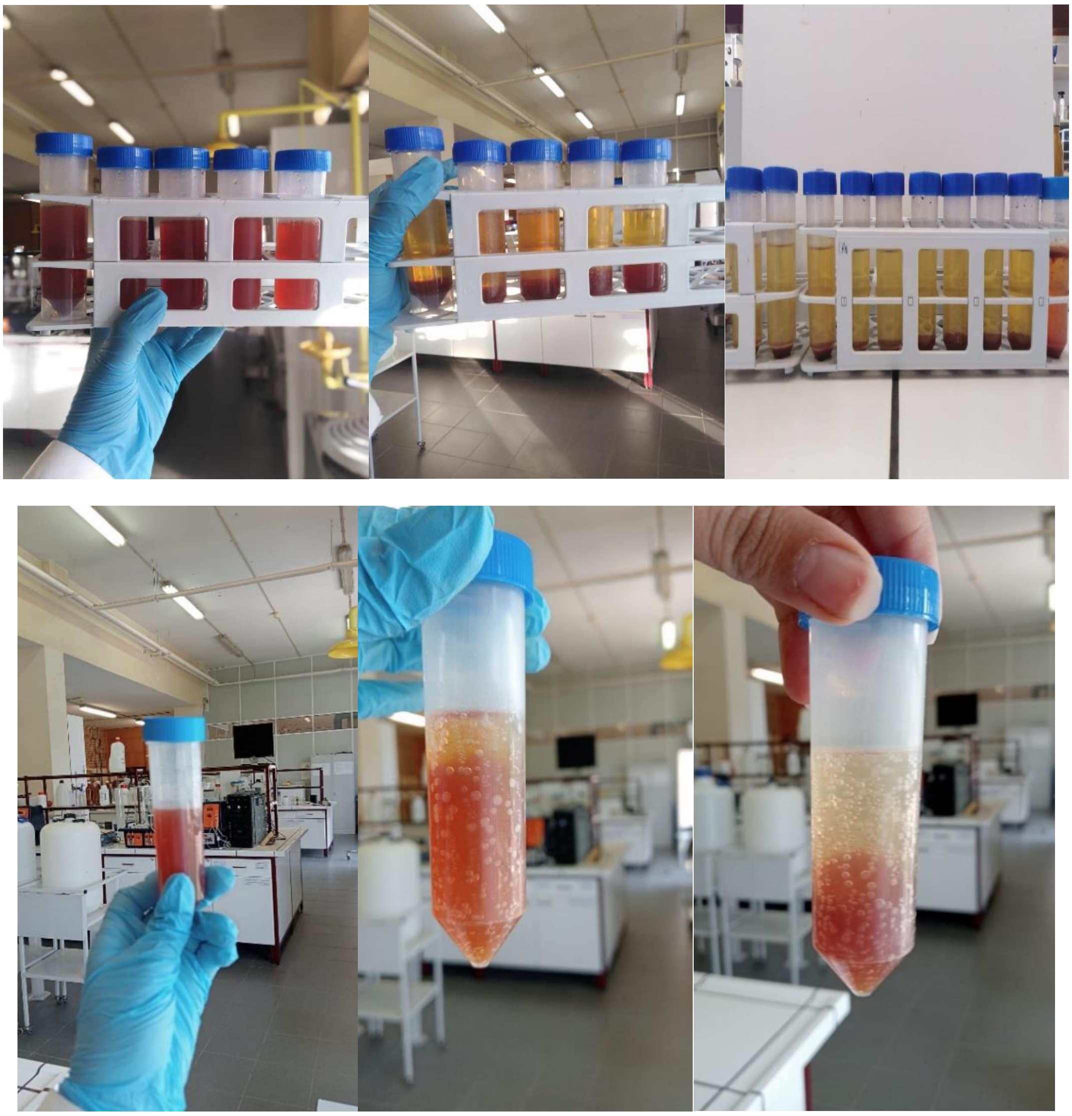


Figure 10: Fenton’s Samples after 24 hours.

3.3.2. Photo Fenton Process

a. Photo Fenton Reagents

The primary reagents used were hydrogen peroxide (342.6 g L^{-1}) and heptahydrate iron sulfate ($FeSO_4.7H_2O$), with an initial concentration of 50 g L^{-1}. The pH required for the Fenton reaction (between 2.5 and 3.5) at the start of the response and its neutralisation (pH between 10 and 12) to end the process was controlled by the use of sulfuric acid (H_2SO_4) 1M and sodium hydroxide (NaOH) 6M. Solutions with 10-fold dilutions of these reagents were prepared to obtain a sufficient pipette volume, making the analysis more reliable.

b. Photo Fenton Procedure

The photo-Fenton process is an advanced oxidation process that uses the hydroxyl radical to disinfect and decontaminate water. These experiments employing the process were conducted in the following manner.

1. An aliquot of the filtered raw effluent was collected for each sample (approximately 100 mL).
2. Homogenise the sample for at least 1 minute using a magnetic stirrer.
3. Add 700 mL of distilled water
4. Added gradually the desired amount of hydrogen peroxide.
5. Added the desired amount of iron sulfate in the first few minutes.
6. The pH of the samples was adjusted to the desired range between 2.5 and 3.5 using H_2SO_4 (1M) and NaOH (6M);
7. The sample was taken for the UV photo reactor (UV Lamp 14 W), as shown in Figure 11;
8. The reaction occurred in the first 5 min with fast stirring at 150 rpm, until the solution was stirred slowly at 80 rpm for another 20 min (Yazdanbakhsh et al., 2015).
9. Subsequently, the pH of the sample was adjusted again between 9 and 11 to stop the reaction.
10. The sample was allowed to stabilise for at least 24 h.
11. The sample volume for the removal analysis was obtained from the supernatant of the sample, with due care not to mix the two phases of the sample.

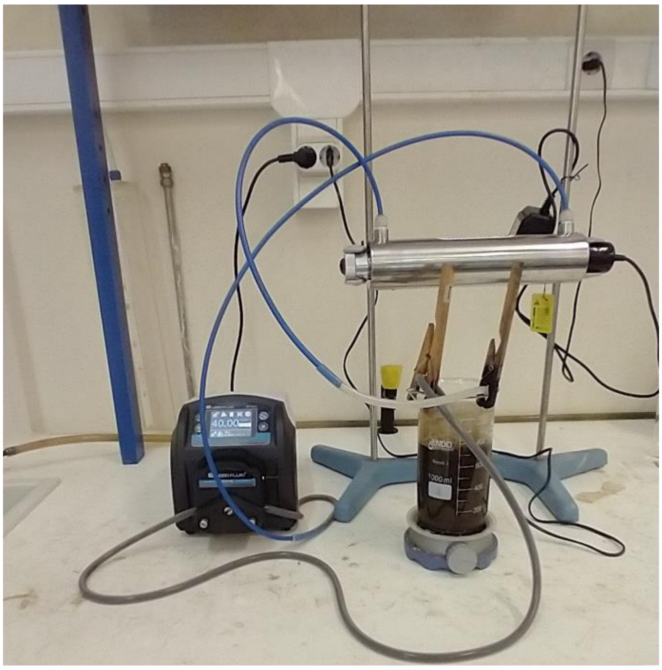


Figure 11: The Photo-Fenton test using UV Photo reactor (UV Lamp 14W)

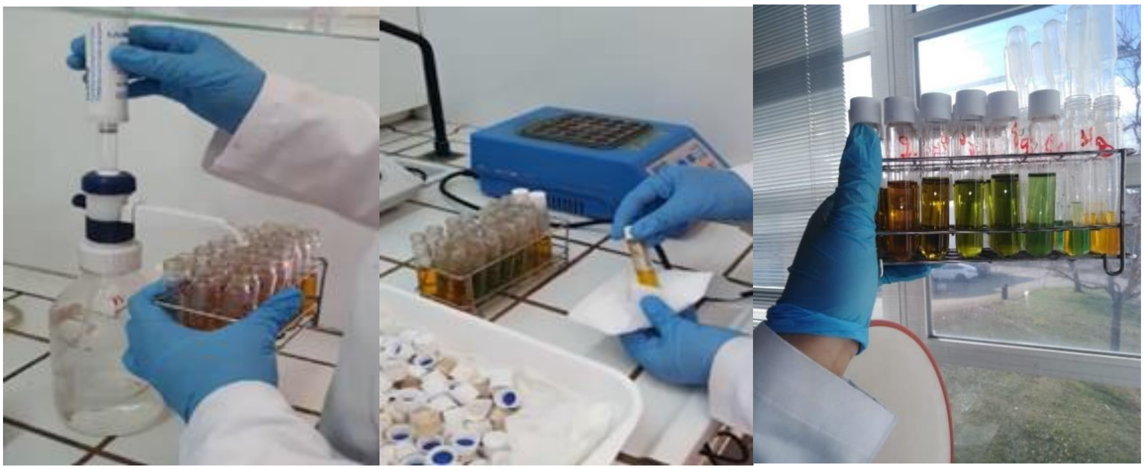


Figure 12: The experimental steps of the COD Removal test

4. RESULTS AND DISCUSSION

The removal percentages for the COD and TPC parameters were calculated by comparing the parameter's initial value (Parameter o) with the parameter's value at any time during the experiment (parameter i). The percentage removal was calculated as follows:

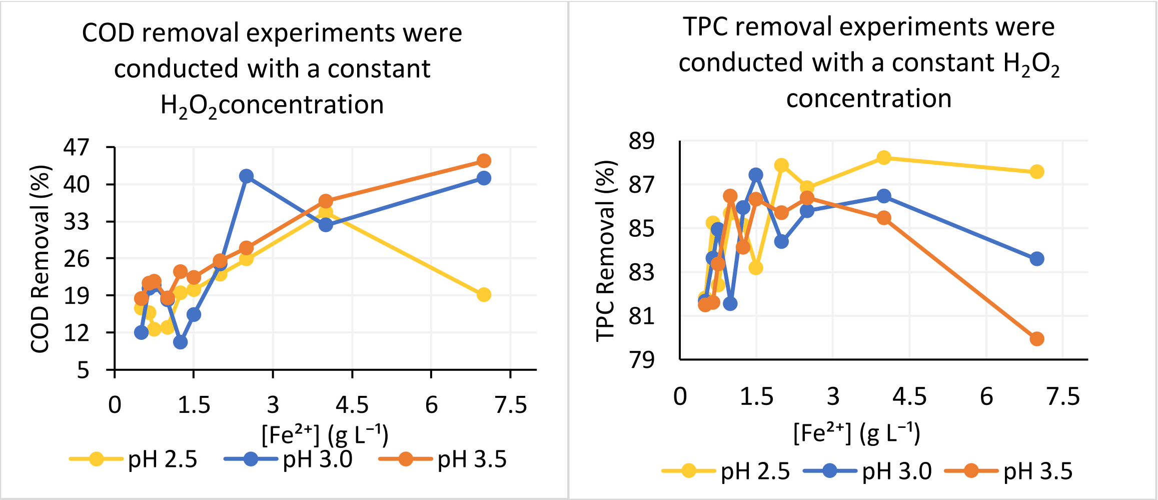
$$\text{Removal } (\%) = \frac{Parameter\ 0 - Parameter\ i}{Parameter\ 0} \times 100 \qquad \text{(Equation 4)}$$

This equation represents the percentage reduction in the value of the parameter from its initial value to the value at any time during the experiment.

4.1. COD AND TPC REMOVALS OF FENTON PROCESS

The H_2O_2, Fe^{2+}, and pH parameters were individually studied, with the others held constant to observe their respective variations. For this, 100 mL of OWW was used for each beaker, thereaction time was 20 min, the jar test rotation was set at 80 rpm, and the sample sedimentation time was one day. For these initial tests, 7 litres of the OWW sample were selected, homogenised, and characterised (COD and TPC).

Experiments on 30 separate samples were carried out at different pH values (2.5, 3, and 3.5).These values were selected for H2O2: Fe^{2+} (Figure 13). They were performed when the volumes of H_2O_2 were fixed and by varying the amount of iron ions in the inverse proportion $Fe^{2+}:H_2O_2$.



COD removal experiments were conducted with a constant H_2O_2concentration

TPC removal experiments were conducted with a constant H_2O_2 concentration

Figure 13: The iron load effect on Fenton for OOEIW after coagulation with $[H_2O_2]$ 20g L^{-1}

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Another experimentals was to fix the amount of Fe^{2+} and to vary theamount of H2O2 in the inverse proportion of Fe^{2+}:H2O2 (Figure 14).

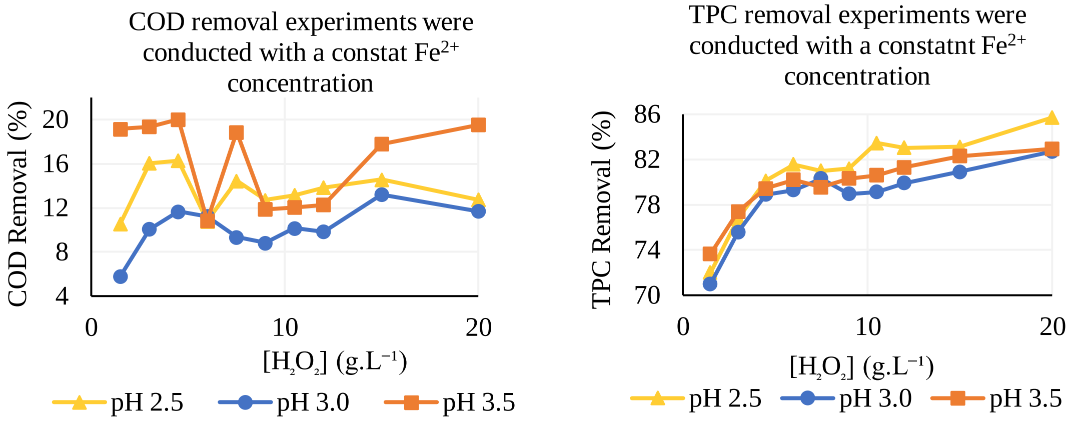

Figure 14: Hydrogen peroxide load effect on Fenton for OOEIW after coagulation with [Fe^{2+}] 0.5 g L^{-1}

The contaminant removal profiles shown in Figures 13 and 14 are similar. Figure 13 shows that the rate of COD removal increased with increasing iron ion concentration, and the highest COD removal of 41% and 45% was achieved at pH 3 and 3.5, respectively at Fe^{2+} 7 g L^{-1}.

At pH 2.5 (4 g $L^{-1)}$ of Fe^{2+}, 35% COD removal was achieved. TPC removal was more efficient, with an average removal of 85% and a maximum removal of 88%.

Domingues et al. (2021) also studied the effect of iron concentration with a constant H_2O_2 concentration of 4 g L^{-1} at pH 3, applying the Fenton reaction to OOEIW after coagulation. The authors observed a similar behavior to that observed in this study, with a maximum COD removal of approximately 40% obtained with Fe^{2+} 2.5 g L^{-1}. Regarding COD removal, increasing the H_2O_2 concentration when Fe^{2+} 0.5 g L^{-1} does not necessarily result in an increase in this parameter`s removal (Figure 14). In this test, increasing the [H_2O_2] from 1.5 to 20 g L^{-1} resulted in 11–16% at pH 2.5, 6–13% at pH 3.0, 11–20 g L^{-1} at pH 3.5, and 6–13% at pH 3.5.

The maximum removal was achieved with 4.5 g L^{-1} H_2O_2 at pH 3.5 (with 20% COD removal and 79% TPC removal). For TPC removal, increasing [H_2O_2] increased the contaminant removal. The average removal rate was 80% and the maximum removal rate of 86% was achieved at pH 2.5 using H_2O_2 20 g L^{-1} and 16% COD removal, and the TPC removal rates ranged from 72 to 86%, with the highest removal rate. Domingues et al. (2021) showed that the peroxide dosage effect at pH 3 showed a behavior similar to that observed at pH 3 in this study, but the authors achieved higher removal rates. The best value obtained was the maximum [H_2O_2] studied, at 28 g.L^{-1} with 53% COD removal and Fe^{2+} 2 g L^{-1}. Additionally, there was no significant change in the oxidation process by the Fenton process when the pH was decreased, which minimized the use of initial control reagents (H_2SO_4 and NaOH).

4.2. COD AND PHC REMOVALS BY PHOTO FENTON PROCESS

The same Fenton parameters were also studied for the photo-Fenton process according to their variations. For this purpose, 100 mL of OWW was used for each sample by adding 700 mL of distilled water. The UV photoreactor test rotation was set at 80 rpm for 20 min, and the sedimentation time was one day. For these initial tests, 7 liters of the OWW sample were selected,homogenised, and characterised, resulting in a COD and PHC of 56 g L^{-1}.

We carried out experiments on 30 separate samples at different pH values (2.5, 3.0, and 3.5).These values were selected for H2O2: Fe^{2+}. In the Figure 15. They were performed when the volumes of Fe^{2+} in the sample were fixed at 0.5 g L^{-1} and those of H2O2 varying from 1.5 to 20 g L^{-1}. This figure illustrates the impact of varying H_2O_2 concentrations at a constant concentration of Fe^{2+} (1 g L^{-1}) at three different pH values on removing COD and TPC.

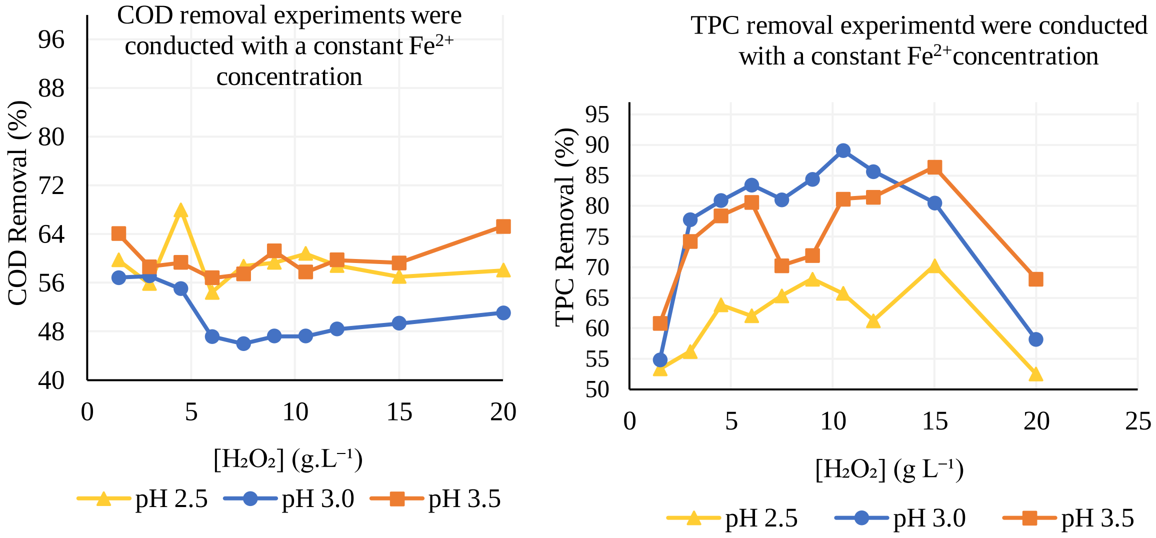

Figure 15: The Hydrogen peroxide load effect on Photo Fenton for OOEIW after coagulation with [Fe^{2+}] 0.5 g L^{-1}

Another experimental hypothesis was to fix the amount of 6 g L^{-1} H2O2 and vary the amount of iron ions in the inverse proportion of Fe^{2+}:H2O2 (Figure 16).

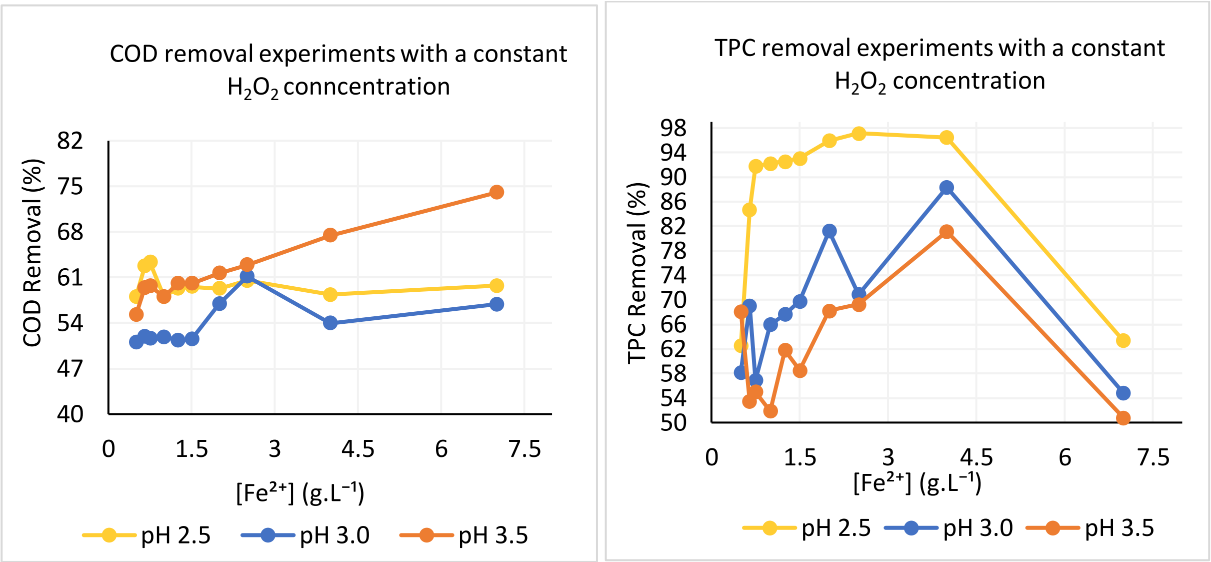

Figure 16: The iron load effect on Fenton for OOEIW after coagulation with [H_2O_2] 20 g L^{-1}

The contaminant removal profiles shown in Figures 15 and 16 are similar. Figure 15 illustrates that the rate of COD removal increased with increasing H_2O_2 concentration, achieving the highest COD removal rate of 75% at pH 3.5, with a Fe^{2+} concentration of 7 g L^{-1}. At Fe^{2+} 4.5 g L^{-1}, a COD removal of 68% was attained. In contrast, TP removal was more efficient, averaging 92% removal and reaching a maximum of 97 % at Fe^{2+} 3 g L$^{-1,}$ and at pH 2.5 under this condition, COD removal stood at 65% and 98% of TPC.

A study aimed at treating wastewater from the olive oil extraction industry using the photo-Fenton process achieved removals of 93% for total phenolic compounds TPC and 26% for COD in the diluted sample and 90% for TPC and 39% for COD in the raw sample (Grabowski et al., 2023).

Another study reported removal percentages with averages of 95.7% for COD and 93.6% for TPC using artificial ultraviolet light lamps in a photo-Fenton system (García and Hodaifa, 2017).

The photo-Fenton process is more efficient for degrading phenolic compounds than COD in olive mill wastewater (Agabo-García et al., 2021).

Therefore, the photo-Fenton process shows promise for removing phenolic compounds from olive pomace oil wastewater; however, its effectiveness for COD removal may vary. Was correlated with an increase in COD removal (Figure 16). In this instance, elevating [H_2O_2] from 1.5 to 20 g L^{-1} resulted in 59% to 67% COD removal at pH 2.5, 50% to 61% at pH 3.0, and 54% to 75% at pH 3.5. Maximum removal of 75% COD was attained with 7 g L^{-1} H_2O_2 at pH 3.5, coupled with 97% TPC removal.

4.3. PARAMETRES INFLUENCING THE EFFICACY OF BOTH PROCESSES

The efficacy of Fenton and photo-Fenton processes for treating olive pomace oil wastewater is influenced by various parameters. These processes are used to degrade organic compounds in wastewater.

4.3.1. Reaction Time

Reaction time plays a crucial role in the efficiency of the Fenton and photo-Fenton processes.

The efficiency of the process depends on various factors such as the iron catalyst concentration, oxidant concentration, and UV irradiation time. Longer reaction times generally lead to higher degradation and mineralisation efficiencies. The reaction time plays a crucial role, as it determines the effectiveness of the Fenton and photo-Fenton reactions, relying on the interaction between hydrogen peroxide and iron to generate hydroxyl radicals and, consequently, efficiently degrade organic matter. It is essential to highlight that improper reaction time selection may lead to more toxic or degradation-resistant by-products (Ziembowicz and Kida, 2022). The reaction time was determined by fixing the pH value (3.5), sample volume (100 mL), H2O2 volume (6 mL), and Fe^{2+} concentration (1 mL), and the removal of organic matter showed the best result at a reaction time of 40 min, reaching 35%. Before and after this time, COD removal was not higher than 30%,(Figure 17) and the variation in TPC was from 88% to 93%.

Various durations have been employed for the treatment of pollutants of concern, such as 30 min (Pan and Qian, 2022), 60 min (Domingues et al., 2021), the Fenton reaction (4 g L^{-1} of hydrogen peroxide, 2 g L^{-1} of iron (II) at pH 3 could achieve approximately 45 % COD removal, 120 min (Martins et al., 2010), and even extending to 8 h (Rodrigues et al., 2022).

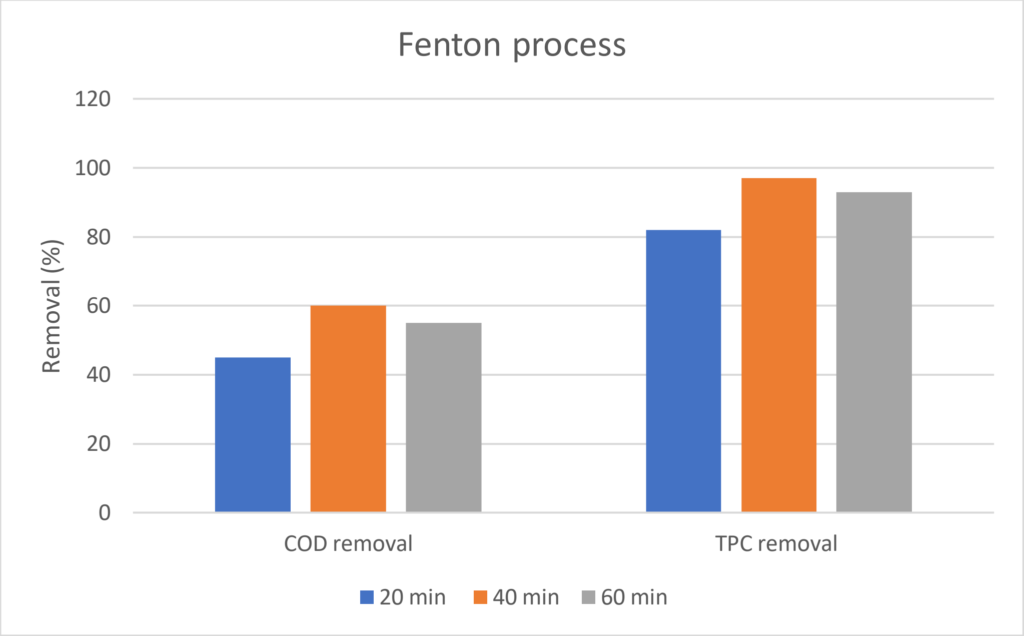

Figure 18: Determination of reaction time for the Fenton process

For the photo-Fenton process, the time was 60 min for pH 3.5 $[Fe^{2+}] = 3$ g L^{-1}, $[H_2O_2] = 5$ g L^{-1} COD from 61% to 68%, and for TPC from 70% to 82%(Figure 19).

In the study of Grabowski et al (2023), the optimal conditions for the photo-Fenton process were determined as $[Fe^{2+}]$ =3 g L^{-1},$[H_2O_2] = 23$ g L^{-1}, and a photo reaction time of 60 minutes, achieving removals of 93% (TPC) and 26% (COD) in the diluted sample (1:10) and 90% (TPC) and 39% (COD) in the raw sample

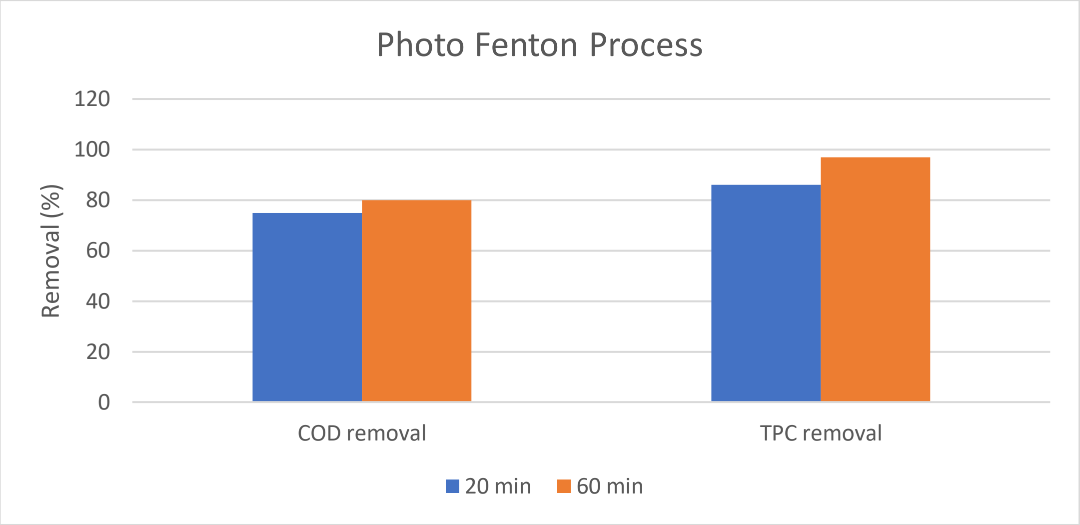

Figure 20: Determination of reaction time for the Photo Fenton process

4.3.2. Temperature

The temperature affects the efficacy of these processes. Higher temperatures can accelerate the reaction rates, leading to improved degradation of the organic compounds.

4.3.3. pH

The solution pH significantly influences the efficiency of the Fenton and photo-Fenton processes. For example, the optimal pH for the photo-Fenton process is nearly neutral for water disinfection.

4.3.4. Effects of H_2O_2 Concentration

The concentration of hydrogen peroxide (H_2O_2) is a critical parameter. This directly influences the generation of hydroxyl radicals, responsible for the oxidation of organic pollutants. Optimal H_2O_2 concentrations are essential to maximise the efficiency of these processes.

4.3.5. Effect of Fe^{2+} Concentration

The concentration of Fe^{2+} also significantly affects the efficacy of the Fenton and photo-Fenton processes. Fe^{2+} is essential for the generation of hydroxyl radicals, the primary oxidising agents in these processes. The optimal Fe^{2+} concentration is crucial for achieving high degradation and mineralisation efficiencies.

4.3.6. Light Source and Irradiation Power

In the case of photo-Fenton processes, the light source and irradiation power are essential parameters. The type of light source and its intensity can affect the efficiency of the process

The economic feasibility of using a 14 W UV lamp reactor for the photo-Fenton oxidation process for treating olive pomace oil wastewater was studied. The treatment of olive oil mill wastewater using a photo-Fenton system with artificial ultraviolet light lamps was assessed for economic viability. A study on treating olive mill wastewater by light and UV/H_2O_2 systems has also been conducted. Additionally, the operational costs of the ferrioxalate-assisted solar photo-Fenton process for wastewater treatment are demonstrating its economic feasibility.

The treatment of olive oil industry waste using the photo-Fenton system with artificial ultraviolet light lamps has been researched, indicating economic approaches for wastewater treatment.

Furthermore, a review of the state-of-the-art in olive oil wastewater management has highlighted the importance of sustainable processes for treating wastewater and recovering valuable constituents, emphasising the need for economically feasible recovery and treatment methods.

4.3.7. Costs

The financial implications of Fenton and photo-Fenton processes are paramount, encompassing expenditures related to reagents, equipment, and the energy necessary for treatment. These costs substantially influence the feasibility of large-scale applications. For example, the total cost of these processes can vary from 9.56-16.88 €/m^3 to 13.46-20.13 €/m3, contingent on the specific oxidation process and Fe^{2+}/H_2O_2 employed (Çalık and Çifçi, 2022).

Furthermore, operational costs, including maintenance, chemicals, and energy consumption, have emerged as pivotal factors that shape the overall cost of employing these treatment methods. Therefore, a comprehensive understanding and strategic optimisation of the costs associated with Fenton and photo-Fenton processes are indispensable for their practical implementation in treating olive pomace oil wastewater.

5. ECONOMIC FEASIBILITY OF THE BOTH PROCESSES

The assessment of the economic viability of Fenton and photo-Fenton oxidation processes for treating one cubic meter of effluent in olive pomace oil wastewater treatment involves a thorough evaluation of factors such as chemical costs, energy requirements, and process efficiency. Numerous studies, including those by Braun and Hinterholz, (2022), have investigated the economic aspects of these processes, offering valuable insights into their feasibility and cost-effectiveness for wastewater treatment.

Based on the work of Grabowskie et al. (2023), the photo-Fenton technique has been effective in treating olive mill effluent, achieving impressive removal rates of total phenolic compounds (TPC) of 90-93% and chemical oxygen demand (COD) of 39-50%. Nonetheless, the economic viability of this procedure is contingent on the specific conditions and requirements of the industry in question. Therefore, careful consideration of these industry-specific factors is imperative when determining the overall economic feasibility of the Fenton and photo-Fenton oxidation processes for olive pomace oil wastewater treatment.

5.1. ECONOMIC EVALUATIONS

Several studies have conducted economic appraisals of the photo-Fenton process and its integration with diverse treatment methods. For instance, a study focused on treating dairy industry wastewater by combining the photo-Fenton process with electrocoagulation, demonstrating the environmental and economic feasibility of the optimized process.

Another economic evaluation was conducted using a combined solar photo-Fenton/MBR process designed for the treatment of industrial ecotoxic wastewater (Esquius, L and Grandjean, D. 2013). Additionally, studies have probed the technical feasibility of implementing a large-scale combination of solar photo-Fenton and aerobic biological treatments for authentic wastewater remediation.

Moreover, when considering the chemical requirements, the photo-Fenton process necessitates the use of elements such as iron (III) iminodisuccinate (Fe-IDS) as a catalyst, hydrogen peroxide (H_2O_2) as an oxidant, and artificial ultraviolet (UV) light for the reaction (Faggiano and De Carluccio, 2023). The associated costs of these chemicals and the energy required for UV irradiation are pivotal factors that influence the economic viability of the entire process. To address energy needs, the process incurs energy consumption for the UV irradiation step, substantially contributing to the overall energy usage and treatment expenses. Furthermore, regarding catalyst reusability, adopting a reusable catalyst is recognised as a cost-alleviating strategy in the treatment process, exemplified by the Heterogeneous photo-Fenton Reaction for Olive Mill Wastewater Treatment—Case of Reusable Catalyst.

5.2 COMPARISON WITH OTHER TECHNOLOGIES

The technical and economic aspects have to assess the economic viability of Fenton and photo-Fenton oxidation processes for treating olive pomace oil wastewater. Martín et al. (2011) compared the financial feasibility of these processes with that of alternative technologies, considering factors such as energy consumption, equipment costs, and overall treatment efficiency. While specific values for reactors and equipment may vary based on the scale and location of the treatment facility, these economic evaluations offer valuable insights into the cost-effectiveness of the Fenton and photo-Fenton processes.

Silva (2023) examined the photo-Fenton process compared to other advanced oxidation processes, demonstrating impressive removal rates of 90% for COD and more than 99% for TPC. As suggested by Silva, a comprehensive analysis of the costs and benefits of these processes is crucial to determine the most economically viable option for olive pomace oil wastewater treatment.

Several studies have highlighted the photo-Fenton process's effectiveness in treating olive mill wastewater. M.V. dos Santos et al. (2023) observed significant removals of organic matter and phenolic compounds, while Agabo-García et al. (2021) explored a heterogeneous photo-Fenton reaction with artificial ultraviolet light, showing promising results in terms of catalyst reuse and organic matter degradation. Faggiano et al. (2023) also investigated using a photo-Fenton-like process as a polishing step for phenol removal from biologically co-treated olive mill wastewater.

The economic feasibility of these oxidation processes is inferred from their demonstrated effectiveness in treating the complex composition of olive mill wastewater, which is characterised by a high range of phenolic compounds, dark color, and antibacterial properties, making biological treatment challenging. The Fenton process, which utilises hydrogen peroxide and ferrous ions at acidic pH, has efficiently removed COD and total phenolic compounds from wastewater (Faggiano et al., 2023).

In conclusion, the collective research indicates the promise of both Fenton and photo-Fenton oxidation processes for treating olive pomace oil wastewater. In particular, the photo-Fenton process effectively removes organic matter and phenolic compounds. The economic feasibility of these processes is supported by their potential to treat the intricate composition of olive mill wastewater and achieve significant pollutant removal. Additional analysis and consultation with wastewater treatment experts are necessary for a more detailed understanding of specific cost comparisons and reactor/equipment values.

6. CONCLUSIONS

In a comparative study of Fenton and photo-Fenton oxidation processes for olive pomace oil wastewater, the latter proved more efficient in removal, COD, and TPC indices.

The Fenton process demonstrated high efficiency, but the photo-Fenton process, which utilises UV light at 14 W, achieved more efficient results for decontamination. The highest COD and TPC removal efficiencies were approximately 45% and 82% for the Fenton process and 75% and 86% for the photo-Fenton process, respectively. Because the wastewater studied had different characteristics, the use of Fenton's reagent was determined based on the contaminant concentration in the samples, primarily the COD and PHC. Among the difficulties in applying this technology is the seasonality of olive pomace oil production, which generates wastewater with specific pollutant loads discharged over time, making analysis difficult and requiring continuous methodology adjustment. The addition of reactants is essential for pH and time control, as the release of extra time for 40 min for Fenton shows hirst removal about 55 % of COD and 93% PHC not the same for Photo Fenton treatment for 60 min, proving more efficient values of removal 80% and 97%.

Despite the promise of Fenton and photo-Fenton oxidation for olive pomace oil, technical and economic challenges persist. Further research is essential to optimise the process parameters, develop low-cost photocatalysts, and find cost-effective methods for iron recovery from sludge before widespread adoption.

7. FUTURE WORKS AND SUGGESTIONS

Using AOPs in Integration

- ✓ Investigate synergies by fusing various Advanced Oxidation Processes (AOPs), such as ozonation with Fenton and photo-Fenton processes.
- ✓ Make thorough comparisons to determine the best course of action.

Catalyst and Reagent Diversification

- ✓ Substitute catalysts and reagents comparable to Fenton reactions are required to improve flexibility.
- ✓ Evaluation of viability and performance of conventional Fenton reagents.

Integrated biological reactors

- ✓ Investigation of the integration of treated wastewater into biological reactor systems.
- ✓ The long-term impacts on the system's sustainability and microbial communities were analysed.

Testing ecotoxicology

- ✓ Extensive ecotoxicological testing was performed to evaluate environmental safety.
- ✓ Assessment of ecological effects and toxicity using standardised bioassays.

Descriptive Analysis of By-Products

- ✓ Carry out an in-depth analysis of the substances generated in Fenton reactions.
- ✓ Determine and measure byproducts to understand the transformation processes and associated hazards.

System of Laboratory-Scale Treatment

- ✓ Create a laboratory-scale system that combines electrochemical, photo-Fenton, and Fenton analyses.
- ✓ Track and assess the system performance to understand possible practical uses.

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