TREATMENT OF WASTEWATER FROM THE OLIVE POMACE OIL EXTRACTION INDUSTRY BY FENTON

Alexandre Narcizo da Silva

Dissertation presented to the School of Agriculture of Bragança for the degree of Master in Environmental Technology in the scope of the double degree program with the Federal Technological University of Paraná

Supervised by:

Prof. Ramiro José Espinheira Martins

Profª. Juliana Bortoli Rodrigues Mees

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ABSTRACT

The olive pomace oil extraction industry (OPOEI) has shown significant growth, with an average of 4% annually since 2019, indicating its economic importance in the European Union (EU). Consequently, this industry generates large amounts of wastewater, approximately 1 m^3/ton of processed olive pomace, corresponding to about 5.4 million m^3/year worldwide. Industrial wastewater has a high content of suspended solids, pungent odor, high turbidity, low biodegradability, high organic content, mainly Chemical Oxygen Demand (COD), increased range of phenolic compounds, dark color, and antibacterial properties, making biological treatment difficult, because of its low biodegradability, toxicity to most microorganisms, and acidic pH (3-6). The composition of olive mill wastewater is complex. Usually, conventional treatments do not have a positive effect on the removal of pollutants. Therefore, new treatment techniques are required for the removal of these compounds. The Advanced Oxidation Process (AOP) by the Fenton process involves the use of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) at acidic pH to produce hydroxyl radicals that are capable of degrading organic compounds that are difficult to biodegrade. In this sense, to remove the high organic content (45 – 107 g L^{-1}), and high concentration of phenolic compounds (2.7 – 8.1 g L^{-1}) of this wastewater, an design of experiments was developed by Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD) method, correlating three factors: H_2O_2 concentration, $Iron^{2+}$ amount, and pH. For this, we performed 15 experiments, where 12 tests considered the intermediate, maximum, and minimum values for the concentration of reagents and pH; the other three tests corresponded to the central points and were equally analyzed to verify the reliability of the method, formerly developed by Box-Behnken. Thus, the best results obtained in this approach were 90% for COD and more than 99% for Total Phenolic Compounds (TPC), proving the efficiency of Fenton's methodology applied to this effluent.

Keywords: Advanced Oxidative Processes; Chemical Oxygen Demand; Fenton; Box-Behnken Design; Total Phenolic Compounds.

RESUMO

A indústria de extração do óleo de bagaço de azeitona (IEOBA) demonstra expressivo crescimento, com média de 4% ao ano desde 2019, indicando sua importância econômica para a União Europeia (UE). Consequentemente, o processo da IEOBA gera grandes quantidades de efluentes, em torno de 1 m^3 ton^{-1} de bagaço de azeitona processada, o que corresponde a cerca 5,4 milhões de m^3 por ano em todo o mundo. Este efluente industrial apresenta um alto teor de sólidos suspensos, forte odor, turbidez, pouca biodegradabilidade, elevado teor orgânico, principalmente de CQO (Carência Química de Oxigênio), alto teor em compostos fenólicos, coloração escura e caráter antibactericida, dificultando o tratamento biológico, por apresentar baixa biodegradabilidade sendo tóxicos para a maioria dos microrganismos e pH ácidos (3-6). Devido à complexidade na composição do efluente da IEOBA, tratamentos convencionais normalmente não surtem efeito positivo na remoção dos seus poluentes, necessitando assim, da aplicação de novas técnicas de tratamento para a remoção destes compostos. O Processo de Oxidação Avançado (POA) por Fenton consiste no uso de peróxido de hidrogênio (H_2O_2) e um íon ferroso (Fe^{2+}) em pH ácido, para produzir radicais hidroxila, capaz de degradar os compostos orgânicos de difícil biodegradabilidade. Neste sentido, com o objetivo de remover a elevada carga orgânica (45 – 107 g L^{-1}), e alta concentração de compostos fenólicos (2,7 – 8,1 g L^{-1}) desse efluente, desenvolveu-se um desenho de experimento pela Metodologia de Superfície de Resposta (MSR) com base no método de *Box-Behnken Design* (BBD), correlacionando os fatores de concentração de H_2O_2, $Ferro^{2+}$ e o pH, foi realizado. Para tal, 15 experimentos foram executados, onde 12 testes considerou-se os valores intermediários, máximos e mínimos para a quantidade de reagentes e pH, os outros 3 testes, correspondem aos pontos centrais e analisados igualmente, a fim de verificar a confiabilidade do método, anteriormente desenvolvido por *Box-Behnken.* Desta forma, os melhores índices obtidos nessa abordagem foram de 90% para CQO e maior que 99% para Compostos fenólicos totais (CFT), provando a eficiência da metodologia de Fenton aplicada, para este efluente.

Palavras-chaves: Processos Oxidatívos Avançados; Fenton; *Box-Behnken*; Compostos fenólicos totais; Radicais Hidroxila; Carência Química de Oxigênio.

SUMMARY

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LIST OF ACRONYMS.

OPOEI	Olive Pomace Oil Extraction Industry
OOEI	Olive Oil Extraction Industry
EU	European Union
COD	Chemical Oxygen Demand
AOP	Advanced Oxidation Process
H_2O_2	Hydrogen Peroxide
OO	Olive Oil
RSM	Response Surface Methodology
BBD	Box-Behnken Design
IWW	Industrial Wastewater
BOD_5	Biochimical Oxygen Demand
ºOH	Hydroxyl Radical
$FeSO_4.7H_2O$	Heptahydrated Iron Sulfate
Na_2CO_3	Sodium Carbonate
H_2SO_4	Sulfuric Acid
NaOH	Sodium Hydroxide
$K_2Cr_2O_7$	Potassium Dichromate
Ag_2SO_4	Silver Sulfate
RSAMM	Regulation of Public Water Supply Services and Urban Wastewater Sanitation in the Municipality of Mirandela
ELV	Emission Limit Value
KHP	Potassium Hydrogen Phthalate
DO	Dissolved Oxygen
TPC	Total Phenolic Compound
IPB	Polytechnic Institute of Bragança
CIMO	Mountain Research Center
TOC	Total Organic Carbon
OC	Organic Carbon
IC	Inorganic Carbon
TS	Total Solids
FS	Fixed Solids

VS	Volatile Solids
N	Total Nitrogen
LD	Limit of Detection
LQ	Limit of Qualification

1 INTRODUCTION

Worldwide, water security is a fundamental factor for human life; however, with climate change, society's ability to have sufficient quantities of water with quality at its disposal has been affected (Domingues et al., 2018). Humans depend on water for survival, which has always conditioned society's behavior, enabling the expansion of agriculture, hydroelectric energy production, and industrialization.

However, one of the biggest environmental problems today is the release of untreated or inadequately treated agricultural, domestic, and industrial wastewater into the water systems. This problem is alarming when wastewater sources come from industries with large or small production volumes (Bethi et al., 2016; Yazdanbakhsh et al., 2015).

The olive pomace oil extraction industry (OPOEI) has demonstrated significant growth, with an average of 4% per year, indicating its economic importance in the EU. Countries with the highest potential for olive oil (OO) production are in the Mediterranean Sea, suffering from severe droughts and water scarcity. This climatic difficulty makes it essential to use techniques and technologies to safeguard this resource, ensure productivity, and minimize its impact on natural resources (Babic et al., 2019; Domingues et al., 2018).

The OO extraction process results in large amounts of effluents, and approximately 1 m^3 of effluent is generated per ton of processed olive, corresponding to about 5.4 million cubic meters per year worldwide. Spain, Italy, Greece, and Portugal stand out among the countries that produce the most OO and, consequently, the most significant volumes of wastewater (Domingues et al., 2021; Hodaifa et al., 2019; Reza et al., 2019; Yazdanbakhsh et al., 2015).

The wastewater from the OPOEI has variable chemical compositions, such as dark coloration, high organic content, and difficult biodegradability. This composition of wastewater from the OPOEI makes it impossible to incorporate it into conventional biological treatment systems, such as aerobic and anaerobic lagoons, indicating the need for pretreatment techniques. It also contains phytotoxic and antibacterial phenolic substances, which make it impossible to dispose of effluents from conventional water and sewage treatment systems (Khdair et al., 2019).

Many pretreatment techniques can modify the characteristics of OPOEI effluents at the entrance to a system, substantially reducing the initial pollutant content or eliminating unwanted substances. Among these techniques, filtration, ultrafiltration, coagulation, flocculation, electrocoagulation and adsorption have been highlighted (Esteves et al., 2019).

However, such techniques need the help of a posterior advanced treatment, to improve their performance. In this sense, this work studies the use of Fenton's advanced oxidative process as an alternative for the treatment of this wastewater. This technique uses hydrogen peroxide, activated by a ferrous ion responsible for the release of hydroxyl radicals, which can oxidize organic matter and be used in effluents such as those presented by the OPOEI industry.

2 STATE OF ART

2.1 INDUSTRIAL WASTEWATER

The industrial revolution in the mid-17th century led to society being constantly exposed to intense global changes, which intensified the exponential growth of industrialization and accelerated trade. Industrialization has brought several benefits to the community, such as the modernization of work, new jobs, and economic development. However, this accelerated industrialization demands an exorbitant amount of natural resources, particularly water (Nassar et al., 2022).

Clean water is essential to sustain human subsistence, achieve sustainable development, and maintain ecosystem health. All major human activities, such as agriculture, livestock farming, manufacturing of goods, energy generation, and domestic activities, require adequate quantities and water quality (Jones et al., 2021).

Agriculture is responsible for 70% of the global freshwater consumption available on the planet. However, most surface and groundwater contamination originate from industrial activities (Iqbal et al., 2022). Thus, agro-industrial processing of products such as oils from olive pomace contributes significantly to water insecurity, especially when effluent production is not included in efficient wastewater treatment systems.

Industrial wastewater (IWW) generally has high pollutant content, which can cause environmental problems if not treated correctly. Among pollutants, heavy metals, solvents, dyes, pesticides, microbial toxins, cleaning products, and pharmaceuticals stand out (Oller et al., 2011).

Furthermore, food processing generates large quantities of IWW, which contains a high organic content. In the olive oil extraction industry, IWW typically has a COD higher than 50 g L^{-1} (Khdair et al., 2019; Rodrigues et al., 2022).

In this sense, aiming at the sustainable development of byproduct processing industries, where economic growth is linked to environmental protection, laws and regulations establish norms, criteria, and quality objectives to protect the aquatic environment and improve water quality according to its use.

In Portugal, at the federal level, Decree-Law no. 236/98, issued on August 1, 1998, governs water quality standards, such as their use, whether for human consumption, support of aquatic life, bathing, and irrigation, as well as the parameter values that frame these waters in each of their categories. This decree also establishes the Emission Limit

Values (ELV) of IWW in water bodies for various parameters, such as pH, color, COD, Biochemical Oxygen Demand (BOD_5), and metals (Ambiente, 1998). However, in Portugal, other regulations give each municipality the responsibility of establishing ELVs for parameters, as in the case of Mirandela City, where ELVs are based in the Regulation of Public Water Supply and Sanitation Services of Urban Wastewater in the Municipality of Mirandela (Mirandela, 2009).

Nevertheless, in Portugal, other regulations give each of its municipalities the responsibility to establish ELVs for parameters, as in the case of Mirandela, where ELVs were found in the Regulation of Public Water Supply and Sanitation Services of Urban Wastewater in the Municipality of Mirandela (A. S. Rodrigues et al., 2022).

2.1.1 Wastewater from the Olive Pomace Oil Extraction Industry

Wastewater from the OPOEI arose from the need to valorize the solid waste (olive pomace) generated by the olive oil extraction industry (OOEI), a very active economic sector in the European Union (EU) due to the high production of olive pomace and the commercial power associated with this product.

Furthermore, the EU is the largest producer of olive oil (OO), accounting for approximately 67% of the world's production, and the largest consumer and exporter (European Commission, 2021).

More than 97% of the world's olive tree plantations are in the Mediterranean region, totaling more than 800 million trees (Khdair et al., 2019). Among the producing countries, Spain stands out, followed by Italy, Greece, and Portugal (Hodaifa et al., 2013). These countries are characterized by a Mediterranean climate (Domingues et al., 2021; Esteves et al., 2022; Flores et al., 2018; Solomakou & Goula, 2021. The production of olive oil by these four countries was 2,032 thousand tons in 2022 (Figure 1).

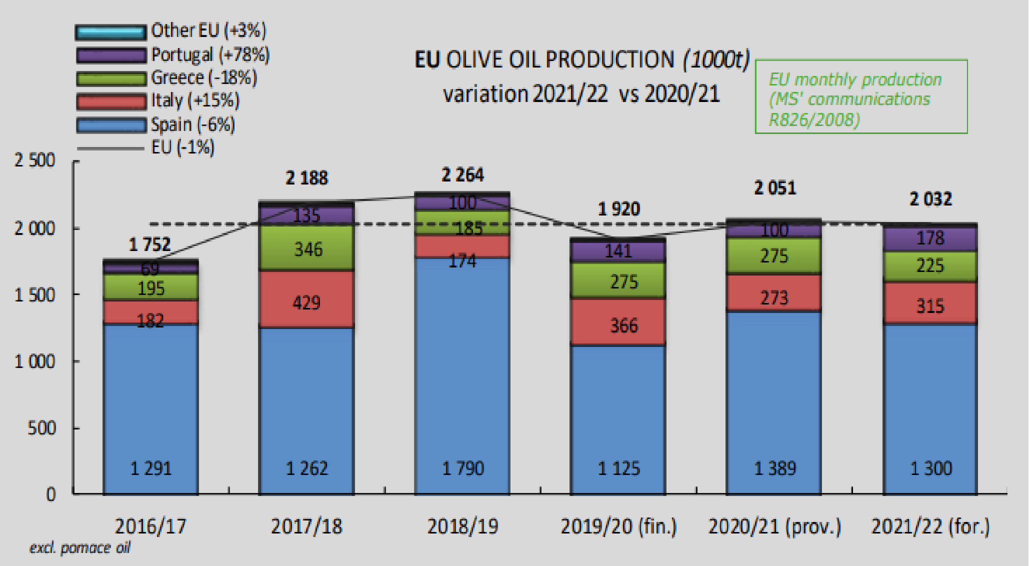

Figure 1: Annual production of olive oil in the EU (European Commission 2021).

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Portugal's OO production stood out with a 78% growth rate, going from 100 tons in 2021 to 178 tons in the following year, while there was a slight 6% decrease in Spain's OO production, which remains the world's largest (European Commission, 2021).

However, OO production is seasonal and directly linked to the harvest period, usually between November and February in Europe (Claudio Rocha, M.A. Soria, 2019; Sar et al., 2020).

Olive oil mills are classified into three types of oil extraction systems: extraction by pressing and two- or three-phase extraction. (Figure 2)

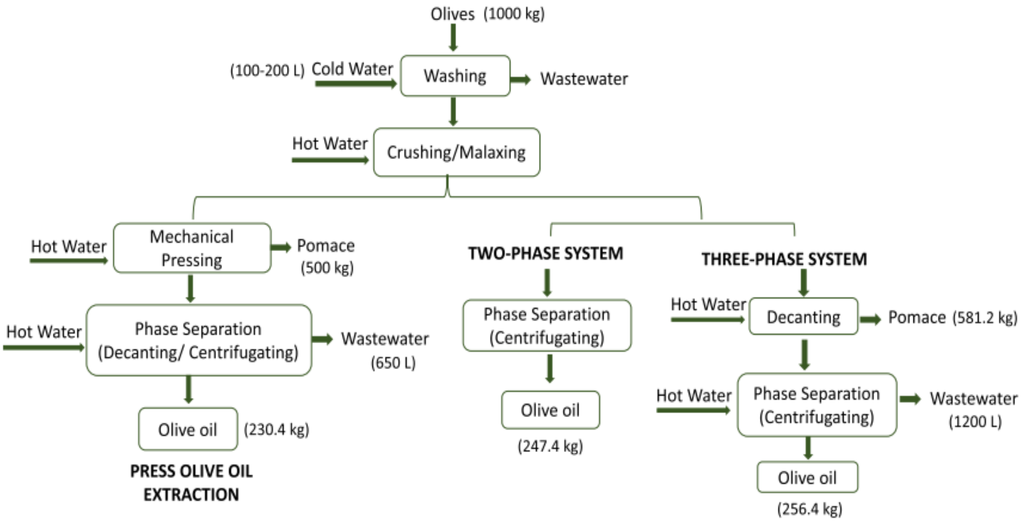

Figure 2: Olive Oil Extraction Process. (Solomakou & Goula, 2021)

For every 1000 kg of olives, approximately 240 kg of OO and 500 kg of extracted pomace, about 40% pulp, and 60% pit are produced. These percentages vary according to the extraction system (press, three- and two-phase centrifugation), olive variety, and territorial conditions (Solomakou & Goula, 2021).

The two-phase extraction system generates approximately 25% of the initial olive mass in AO, generating a byproduct that contains all the rest (pulp, leaf, and pit), which is directed to a new extraction by the OPOEI, called wet olive pomace (75%). For mills that operate with three-phase systems, in addition to producing 20% of OO, approximately 50% of a dark-colored and unpleasant-smelling liquid residue called "dirty water" and about 30% of a solid residue made up of a mixture of pits, skins, and cellulose, called olive pomace, are generated (Domingues et al., 2021).

Depending on the extraction system, the resulting pomace can still be reprocessed to remove approximately 8% to 15% of the residual oil. If only pressing is applied, the resulting oil is referred to as olive pomace oil. The extraction with organic solvents (usually hexane) is called refined olive pomace oil, according to Regulation CE 1234/2007 (Europeia, 2007).

The olive pomace reprocessing system to generate olive pomace oil also generates solid and liquid wastes, which must be appropriately treated.

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

In the EU, it is common to use effluents from these industries for agricultural irrigation, provided they are adequately treated and meet the necessary standards. However, no single legislation has established these standards and maximum parameters for effluent use in the EU's fertigation; 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 for 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 Braga, located in the northern region of Portugal, has Regulation No. 169/2015, which sets the maximum parameters for the discharge of IWW as COD < 1000 mg L^{-1}, biochemical oxygen BOD_5 < 500 mg 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 an acidic pH, high organic content (Solomakou & 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), associated with adverse environmental effects, such as antibiosis and phytotoxicity (Vagelas & Giurgiulescu, 2019).

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

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

Parameter	Unit	Value	References
pH	g $L^{-1.}$	4.3 – 6.8	(Domingues et al., 2021; Flores et al., 2018; Lucas & Peres, 2009; Sar et al., 2020)
COD	g L^{-1}	1.4 – 102.5	(Domingues et al., 2021; Flores et al., 2018; Lucas & Peres, 2009; Sar et al., 2020)
COB$_5$	g L^{-1}	0.4 – 10.5	(Domingues et al., 2021; Flores et al., 2018; Lucas & Peres, 2009)
Total Suspended Solids	g L^{-1}	0.6 – 6.8	(Domingues et al., 2021; Lucas & 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 & 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 pomace (Khdair et al., 2019). Other treatment techniques, such as AOP, must be used in such cases.

2.2 TREATMENT OF IWW

Global effluent production is approaching 359.4 billion m3 per year, where about 48% of the wastewater generated worldwide is discharged into the environment without treatment. One of the biggest problems in the industrialized world is solving environmental contamination by identifying efficient effluent treatment methods (Park et al., 2022).

Conventional effluent treatments are divided into (a) physical processes, such as sedimentation, filtration, or flotation; (b) physico-chemical processes, such as coagulation/flocculation, oxidation, and adsorption; and (c) biological processes, such as anaerobic and aerobic digestion (Chen et al., 2023; Esteves et al., 2022).

Due to the complexity of treating wastewater from OPOEI, some studies have been conducted using unconventional treatments. Sponza (2021) used a sequential nanoZno-Magnetite membrane reactor combined with reverse osmosis to achieve 85% COD and 75% TPC removal from olive oil mill wastewater.

Advanced Oxidation Processes (AOP) are among the many other types of wastewater treatment that use various pathways to generate hydroxyl radicals through chemical, electrochemical, or photochemical reactions.

2.3 ADVANCED OXIDATION PROCESSES

Several technologies for removing organic compounds from IWW include biological, thermal, and chemical treatment (Paraskeva & Diamadopoulos, 2006). Biological treatments are usually environmentally friendly processes with reasonable costs. However, they are unsuitable for applying to wastewater containing non-biodegradable compounds, usually requiring long residence periods for microorganisms to degrade pollutants (Gizgis et al., 2006; McNamara et al., 2008).

However, issues remain to be addressed, such as thermal treatments present many inconveniences, including significant emissions of other hazardous compounds (Giuffrè et al., 2012).

Physical and chemical treatments, including flocculation, precipitation, activated carbon adsorption, and reverse osmosis, do not fully address post-treatment demands, particularly phenol treatments (Rahmanian et al., 2014).

AOPs are characterized by a standard chemical quality: the ability to exploit the high reactivity of hydroxyl radicals in driving oxidation processes that are suitable for achieving complete reduction and through the mineralization of even less reactive pollutants (Elkacmi & Bennajah, 2019).

Many studies have applied advanced oxidation technologies to the treatment of OPOEI effluents. Contaminants are oxidized using four different reagents: ozone, hydrogen peroxide, oxygen, and air or their combination. To choose the most suitable technology, the concentration and nature of pollutants and the effluent volume must be considered (Domingues et al., 2018; Elkacmi & Bennajah, 2019).

Vuppala et al. (2022) treated OPOEI effluent, initially with 10 g L^{-1} de COD e 164 mg L^{-1} de TPC, combining aluminum sulfate coagulation (0.8 g L^{-1} at pH 4.5) followed by biological and photo-Fenton (UVA) treatment, achieving 93% and 97% removal for COD and TPC, respectively.

Kirmaci et al. (2018) compared the use of the Fenton advanced oxidation process with the Ozone/Fenton combination for wastewater, initially with 38 g L^{-1} of chemical oxygen demand (COD). The Fenton process achieved the highest removal when the H_2O_2:Fe^{2+} ratio was 10, resulting in a COD removal of 51.6%. Subsequently, with the use of an ozone generator under the same conditions, an improvement in removing an additional 49% was observed.

Flores et al. (2018) used a combination of electrocoagulation, followed by the electro-Fenton and electro-photo-Fenton methods, using various electrode combinations to treat turbid water. At a treatment time of 600 minutes, the total organic carbon (TOC) removal rate was 97.1%.

The most promising studies indicate using AOPs with the following methodologies: UV, UV/H_2O_2, photo-Fenton (UV/H_2O_2/Fe), ozonation, humid air catalytic oxidation, electro-Fenton, Fenton, and Fenton-like processes. However, these studies also point to Fenton reactions as the basic principle of POAs, underscoring their importance (Cai et al., 2021; Esteves et al., 2022; Yazdanbakhsh et al., 2015).

2.3.1 Fenton Process

The Fenton process was named after its developer, H.J.H. Fenton, who 1894 developed it for the oxidation of tartaric acid (Cai et al., 2021; Gao et al., 2022).

This process produces hydroxyl radicals (HO^o), which degrade organic matter in various industrial effluents such as OPOEI (Domingues et al., 2018; Esteves et al., 2019).

This technology utilizes the catalytic decomposition of hydrogen peroxide (H_2O_2) activated by iron ions (Fe^{2+}, Fe^{3+}) to produce HO^o, as shown in Equation (1). In the subsequent reaction cycle, the ferric ions generated by oxidation in the first reaction react with hydroperoxyl radicals which produce hydrogen peroxide and regenerate the catalyst, as described in Equation (2). Hydroperoxyl reacts with ferric ions, which can restore the catalyst, as indicated in Equation (3) (Esteves et al., 2022).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\circ} + OH^{-} \quad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HOO^{\circ} + H^{+} \quad (2)$$

$$Fe^{3+} + HOO^{\circ} \rightarrow O_2 + H^{+} + Fe^{2+} \quad (3)$$

This process has several advantages in the treatment of wastewater, such as (a) easy and straightforward operation, possible in existing treatment plants; (b) no need for input energy to carry out the process; (c) use of commercial reagents that are easy to handle; (d) its operation is carried out at ambient temperature and pressure (Domingues et al., 2021).

However, the following disadvantages were also observed: (a) high costs and risks associated with the storage and transportation of H_2O_2; (b) the need for large quantities of chemicals for the acidification of effluents at pH 2–4 before decontamination or for neutralizing treated solutions before disposal; (c) accumulation of sludge, with a significant iron content that must be removed at the end of the treatment (Gao et al., 2022; Pan & Qian, 2022).

As previously demonstrated, the effluent from the OPOEI has heterogeneous characteristics that are difficult to degrade. The Fenton process is an alternative pretreatment method for reducing the initial organic load. Another essential characteristic of the Fenton process is its ability to improve the BOD_5/COD ratio. This chemical process can be followed by a biological system, such as activated sludge (Domingues et al., 2021).

2.3.2 Phenolic Compounds in Advanced Oxidation Processes

Phenolic compounds are a class of chemical compounds with hydroxyl groups directly attached to the aromatic hydrocarbon groups. The simplest phenolic compound is phenol, the specific name for hydroxybenzene. These antioxidant compounds are also found in agro-food waste from different sectors, such as wastewater from olive oil extraction industries, table olive processing, effluents from pickle manufacturing, wine industry, and citrus processing (Cifuentes-Cabezas et al., 2022).

Several studies have focused on investigating, designing, developing, and optimizing processes to lower the concentration and purify phenolic compounds from effluents, such as electrocoagulation, liquid/liquid extraction, cooling crystallization, ultrasound treatment, and adsorption. However, the success of these techniques has been uncomplete for reasons ranging from economic considerations to low removal yields. Studies have also focused on the recovery of these compounds due to their characteristics, such as protection against oxidative damage and cellular aging (Azzam & Hazaimeh, 2021; Cifuentes-Cabezas et al., 2022; Dauber et al., 2022; Hernández-Francisco et al., 2017).

Initial concentrations of phenolic compounds in OPOEI can be high, ranging from 1.65 g L^{-1} (Magdich et al., 2022), 4.6 g L^{-1} (Mastoras et al., 2022) to 7.1 g L^{-1} (Mancuso et al., 2022), while the limit value of phenol discharge allowed in wastewater according to Portuguese law (Decree-Law 236/98) is less than 0.5 mg L^{-1} C_6H_5OH (Ambiente, 1998). Moreover, the range of phenolic compounds found in these waters is characterized by a great variety and complexity and may contain several different phenolic compounds, among which the most abundant in olive pomace are hydroxytyrosol, tyrosol; p-coumaric and vanillic acid (Skaltsounis et al., 2015).

To comply with discharge regulations, developing a pretreatment of industrial effluents that can reduce their toxicity and improve their biodegradability is essential. Therefore, advanced oxidation processes should be considered as viable alternatives. They mainly apply to mineralize contaminants or converting organic compounds into less harmful or lower-chain compounds (Justino et al., 2009; Kallel, Belaid, Boussahel, et al., 2009). Some studies on the degradation of phenolic compounds using advanced oxidation processes have been published (Kallel et al., 2009).

3 OBJECTIVE

3.1 GENERAL OBJECTIVE

This study aimed to evaluate the use of the Fenton process for wastewater treatment in the olive pomace oil extraction industry.

3.2 SPECIFIC OBJECTIVES

- Evaluation of the optimal operational conditions for treatment (pH, time, and required reagent quantities).
- Characterization of wastewater and its pollutant potential based on legal parameters.
- Effect of chemical oxidation on wastewater biodegradability.
- Investigate the effectiveness of the Fenton advanced oxidation treatment, taking into account the reduction of COD and phenolic compounds.

4 MATERIALS AND METHODS

4.1 MATERIALS

4.1.1 Equipment

- Beaker;
- Erlenmeyer flask;
- Glass Rod;
- Jar test (Apparatus);
- Magnetic stirrer (Hanna HI 180);
- Magnetic Stir Bar;
- pH meter (Hanna EDGE);
- Volumetric flask;
- Test Tube;
- Screw Cap Test Tub;
- COD Reactor (Hanna HI 839800);
- Spectrophotometer (Jasco V-530).

4.1.2 Reactants

- Hydrogen Peroxide (H_2O_2) 30 vol;
- Heptahydrated Iron Sulfate ($FeSO_4.7H_2O$);
- Folin-Ciocalteu;
- Sodium Carbonate (Na_2CO_3);
- Sulfuric Acid (H_2SO_4);
- Sodium Hydroxide (NaOH);
- Potassium Dichromate ($K_2Cr_2O_7$);
- Distillate Water;
- Silver Sulfate (Ag_2SO_4).

4.2 PRELIMINARY PREPARATION OF THE RAW SAMPLE

The raw effluent used in this study was obtained from a settling pond provided by an OPOEI located in the municipality of Mirandela, in the northern region of Portugal.

Initially, the effluent was collected from the uppermost part of the ponds to avoid suspended solids. Subsequently, the effluent was sieved through a 0.5 mm sieve to remove the maximum amount of insoluble particles from the effluent. Finally, the samples were stored according to methodology 1060 - *Collection and Preservation of Samples* (APHA et al., 2017).

4.3 WASTEWATER CHARACTERIZATION

Based on Decree-Law 236/98, the municipality of Mirandela established the Regulation of Public Water Supply Services and Sanitation of Urban Wastewater in the Municipality of Mirandela (RSAMM), which specifies ELVs for various characteristic parameters of IWW, such as legally permissible loads (Mirandela, 2009) (Table 2).

Table 2: ELVs for IWW

Parameter		**Law 236/98**	**RSAMM**
pH	Sorensen Scale	6 – 9	5.5 – 9.5
Total Nitrogen	mg L^{-1} N	15	90
Total Phosphorus	mg L^{-1} P	10	20
COD	mg L^{-1} O_2	150	1000
BOD_5	mg L^{-1} O_2	40	500
Total Suspended Solids	mg L^{-1}	60	1000
Volatile Solids	mg L^{-1}	-	
Fixed Solids	mg L^{-1}	-	
TPC	mg L^{-1} C_6H_5OH	0.5	10

These wastewater ELVs allowed by the municipality of Mirandela are higher than those described in Decree-Law 236/98, as such values are used when this effluent is discharged into public sewage collectors, which are subsequently sent to the system municipal treatment.

The characterization of the effluent provided for the study was carried out every three months, from October 2021 to June 2022, as outlined in (Table 3).

Table 3: Characterization of Raw Effluent

Parameter	**Units**	**Oct/2021**	**Dec/2021**	**Mar/2022**	**Jun/2022**
pH	Sorensen scale	-	-	4.68	4.84
Total Nitrogen	mg L^{-1} N	-	-	185.6	221
Total Phosphorus	mg L^{-1} P	-	-	492.6	763.1
COD	g L^{-1} O_2	45.96	48.32	70.59	86.41
BOD_5	mg L^{-1} O_2	1298	2046.25	5818	11925
Total Suspended Solids	g L^{-1}	45.96	31.8	45.99	61.74
Volatile Solids	g L^{-1}	27.94	21.74	28.83	36.93
Fixed Solids	g L^{-1}	18.02	10.06	17.16	24.8
TPC	mg L^{-1} C_6H_5OH	-	2759.4	3944.9	8127.3

The parameters of the IWW from OPOEI used in this study were determined at the Chemical Processes Laboratory of the Polytechnic Institute of Bragança (IPB). The evolution of pollutant concentrations, according to Table 3, showed a significant increase over time. These characteristics are attributed to the seasonal production of olive pomace oil (Domingues et al., 2021).

4.3.1 Determination of Chemical Oxygen Demand (COD)

COD is a parameter widely used in various water quality analyses, where it is possible to establish the amount of oxygen necessary to oxidize the sample's constituents, such as sample organic matter.

The closed reflux method described in number 5220 of Standard Methods for the Examination of Water and Wastewater (APHA et al., 2017) was chosen, where, using a JASCO V-530 spectrophotometer configured for a wavelength of 600 nm, this method can be used for the determination of COD between 100 and 900 mg O_2 L^{-1}. Although this reading range corresponds to a high COD rate, it was necessary to dilute the IWW sample used in this study at least 100 times to reach the reading range of the method.

The calibration curve for determining COD was developed based on the literature (APHA et al., 2017), with known quantities of potassium hydrogen phthalate (KHP), as it is known that 1 mg of KHP corresponds to 1.176 g L^{-1} de O_2 (Figure 3).

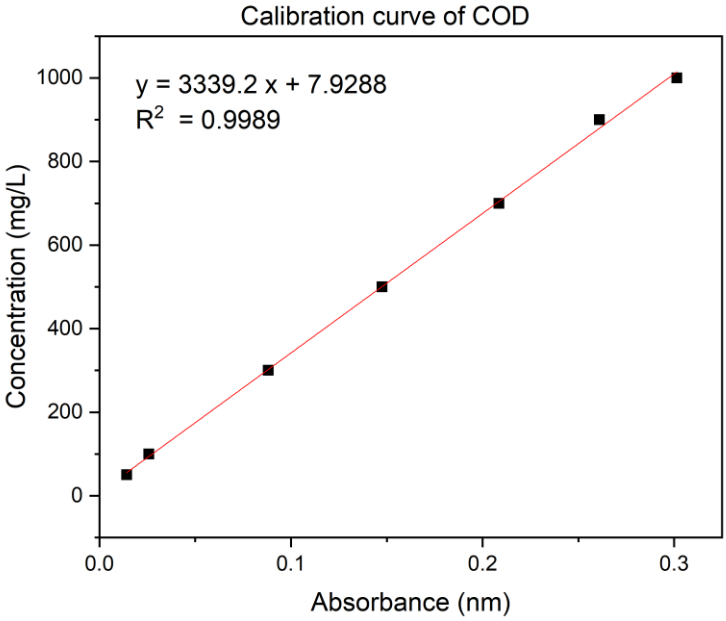

Figure 3: Calibration curve of COD

The R^2 value of 0.9989 shows that, for the range 0 to 1000 mg of O_2 L^{-1}, Equation (4) is valid to determine COD.

$$y = 3339.2x + 7.9288 \tag{4}$$

4.3.2 Biochemical Oxygen Demand (BOD_5) Determination

The BOD_5 test determines the oxygen consumed in the degradation of carbonaceous organic matter and the oxidation of inorganic ions such as sulfides, sulfites, and ferrous ions. Its value is calculated from the difference between the initial dissolved oxygen (DO) (initial DO) and after the incubation period (final DO).

This work used methodology 5210 of the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2017), which consists of analyzing the biodegradability of the organic fraction of a sample in 5 days, in the dark, at 20 ± 1ºC.

Due to the initial scarcity of microorganisms in the effluent from OPOEI, samples of domestic wastewater from the Wastewater Treatment Plant of Bragança were employed as an external inoculum for the breakdown of the organic matter contained in the sample.

4.3.3 Phenolic Compounds

The Folin-Ciocalteu method is using to determine TPC. For this, added 0.5 mL of Folin-Ciocalteu reagent, 0.2 mL of homogenized sample, and 8.2 mL of distilled to a 30 mL test tube. This mixture was vortexed for homogenization and left to rest for 10 minutes. Subsequently, 1 mL of 10% (v/v) Sodium Carbonate (Na_2CO_3) was added, shaken, and went to sleep for 60 min. After resting, the absorbance was read 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).

A calibration curve was prepared using known amounts of 0 - 100 mg gallic acid per liter (Figure 4 and Equation 5).

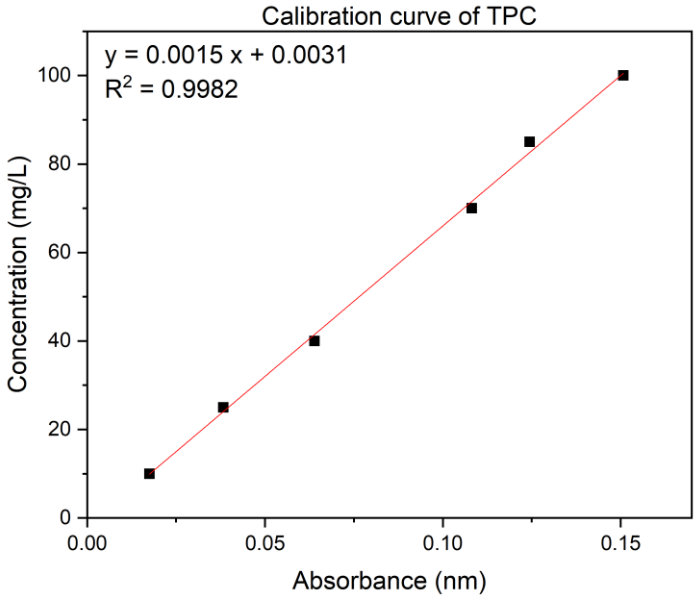

Figure 4: Calibration curve of TPC

$$y = 0.0015x + 0.0031 \tag{5}$$

R^2 = 0.9982 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 0.0015 (mg L^{-1} nm^{-1}), indicating that the equipment can detect values above this absorbance.

The Limit of Detection (LD) was determined using an equation to validate the tests (6).

$$LD = \frac{3 * s}{a} \tag{6}$$

Where,

s = Standard deviation of the blank repeated seven times

a = Angular coefficient obtained in the calibration curve (0.0015).

For the detection of TPC, the LD was equal to 2.45 mg L^{-1} of Gallic Acid, corresponding to an absorbance reading of 0.0067nm. Establishing the Limit of Quantification (LQ) values, Equation (7), was also possible.

$$LQ = \frac{10 * s}{a} \tag{7}$$

The LQ value obtained was 8.17 mg L^{-1}, corresponding to an absorbance of 0.0153nm. From an analytical point of view, these values ensure that the equipment can detect readings above LD with 95% confidence and that assignments above LQ can be determined accurately and reproducibly by the established method, thus obtaining an optimal absorbance reading range of 0.0153 to 0.1508 nm. (Penha, 2017)

4.3.4 Total Organic Carbon

Organic compounds containing carbon can be dissolved or present in water as non-dissolved, suspended, or liquid matter. Carbon is generally present in inorganic carbon (IC) and organic carbon (OC). TOC measures the amount of organic compounds in a water sample. The TOC index measures and subtracts the IC from the total carbon to produce the TOC value.

Another research group from the Mountain Research Centre (CIMO) at the IPB performed these analyses using SHIMADZU TOC-L equipment configured to read samples with TOC concentrations ranging between 20 and 100 mg L^{-1} of carbon.

4.4 PRELIMINARY TESTS

Preliminary tests established crucial reaction parameters, such as time, heating, pH, and relationships between the primary reagents, H_2O_2 and Fe^{2+}.

4.4.1 Fenton Reagents

The primary reagents used were hydrogen peroxide (373.1 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, as well as its neutralization (pH between 10 and 12) to end the process, were 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.

4.4.2 Fenton Procedure

The experiments were conducted as follows.

- Collect an aliquot of the filtered raw effluent for each sample (approximately 100 ml);
- Homogenize the sample for at least 1 minute using a magnetic stirrer;
- Added the desired amount of iron sulfate;
- The pH of the samples was adjusted to the desired range using H_2SO_4 (1M) and NaOH (6M) between 2 and 4;
- The sample was taken for the jar test;
- Added gradually the desired amount of hydrogen peroxide in the first few minutes;
- The reaction occurred in the first 5 min with fast stirring at 150 rpm, and with slow stirring at 80 rpm for another 20 min (Yazdanbakhsh et al., 2015);
- After this time, the pH of the sample was adjusted again, between 9 and 11, in order to stop the reaction;
- The sample waits for a stabilization time of at least 24 h;
- The sample volume for removal analysis was obtained from the supernatant of the sample, with due care not to mix the two phases of the sample, as shown in (Figure 5).

Figure 5: Sample after 24 hours.

Despite the initially established methodology addressing most inquiries regarding the Fenton process, the next step was determining the maximum values for pollutant removal, particularly for high levels of organic matter and phenolic compounds. In this sense, new tests were conducted using the experiments approach and response surface methodology (RSM) design to determine such values.

4.5 RESPONSE SURFACE METHODOLOGY (RSM)

RSM was developed with the aim of optimizing laboratory analyzes and minimizing the cost of reagents used in Fenton tests, where the main methods used as RSM are Box-Behnken design (BBD) and Central Composite Design (CCD).

In this work, Box-Behnken design (BBD) was chosen as the method to investigate and associate three independent parameters: hydrogen peroxide, iron 2+ and pH. This method, are establish the relationship between these independent variables using second-order polynomial equations (8):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k=1} \beta_{ii} X_i^2 + \sum_{i<j} \sum_{j}^{k} \beta_{ij} X_i X_j \qquad (8)$$

Where X corresponds to the independent variables that affect the response Y, the values of "β" are equivalent to the regression coefficients for the intercept (β0), linear terms (βi), quadratic terms (βii), and interactions (βij), and "k" corresponds to the number of variables in the system (Pontes et al., 2022).

Subsequently, these variables were coded as X1 (hydrogen peroxide), X2 (Fe^{2+}), and X3 (pH), as well as their maximum (1), minimum (-1) concentration, and central value (0).

4.5.1 COD: H_2O_2 Ratio

Lucas and Peres (2009) carried out tests using the Fenton technique for the treatment of olive mill wastewater, at an average temperature of 30 °C and ambient pressure. In this study, they evaluated the COD removal, indicating the necessary stochiometric amount of hydrogen peroxide to oxidize the organic matter, expressed in grams of oxidizable oxygen (g O_2), Equations (9), (10),(11) (12).

$$\mathbf{1\,g\,COD} = 1\,\mathrm{g\,O_2} \tag{9}$$

$$1\,\mathrm{g\,O_2} = 0.03125\,\mathrm{mol\,O_2} \tag{10}$$

$$0.03125\,\mathrm{mol\,O_2} = 0.0625\,\mathrm{mol\,H_2O_2} \tag{11}$$

$$0.0625\,\mathrm{mol\,H_2O_2} = \mathbf{2.125\,g\,H_2O_2} \tag{12}$$

The sample used in the BBD assay had a COD of 108.5 g L^{-1}. According to a previously established relationship, the value required to degrade this amount of organic load is equivalent to 217 g L^{-1} of H_2O_2, the maximum value for the BBD assay. The minimum value used was 10% of the total value, 21.7 g L^{-1} hydrogen peroxide (37%). These concentrations were translated into volumes for the experimental design, where 2.9 to 29 mL of H_2O_2 was used for a 50 mL sample of IWW.

4.5.2 H_2O_2:Fe^{2+} Ratio

As seen in Equation (3), the presence of ferric ions in the solution is directly related to the generation of hydroxyl radicals; however, the quantity of iron required depends on the type of pollutant.

In preliminary tests, the addition of iron directly influences the removal of COD; however, there is concern about the excessive use of this reactant since, at high concentrations, the Fe^{2+} ion recombines with hydroxyl radicals (ºHO), forming new Fe^{3+} complexes such as $Fe(OH)_3$, which function as scavengers for the reaction (Lucas & Peres, 2009).

Therefore, the purpose of this study was to use different H_2O_2:Fe^{2+} ratios, with the central point being the ratio of 5.4:1 and the others ranging from 0.6:1 to 25:1 of Fe^{2+} (50 g L^{-1}), corresponding to volumes ranging from 14.3 to 58.6 mL of reactant.

An experimental design was developed to correlate the three parameters, H_2O_2 (X1), Fe^{2+} (X2), and pH (X3), in 12 tests, considering the intermediate, maximum, and minimum values for the number of reagents and the pH. Additionally, three other tests were performed, using only the central points and equally analyzed, to verify the reliability of the method previously developed by Box-Behnken (Table 4).

Table 4: Experimental Design BBD

Test	Encoded Variables			Real Variables		
	X1	X2	X3	H_2O_2 (mL)	Fe^{2+} (mL)	pH
1	-1	-1	0	2.9	14.3	3
2	1	-1	0	29.1	14.3	3
3	-1	1	0	2.9	58.6	3
4	1	1	0	29.1	58.6	3
5	-1	0	-1	2.9	36.4	2
6	1	0	-1	29.1	36.4	2
7	-1	0	1	2.9	36.4	4
8	1	0	1	29.1	36.4	4
9	0	-1	-1	16.0	14.3	2
10	0	1	-1	16.0	58.6	2
11	0	-1	1	16.0	14.3	4
12	0	1	1	16.0	58.6	4
13	0	0	0	16.0	36.4	3
14	0	0	0	16.0	36.4	3
15	0	0	0	16.0	36.4	3

The values listed in Table 4 correspond to the amount necessary to treat samples with a volume of 50 mL, using hydrogen peroxide (37%) and iron sulfate (50 g L^{-1}).

5 RESULTS AND DISCUSSION

5.1 PRELIMINARY TESTS AND PARAMETER ANALYSIS

5.1.1 H_2O_2, Fe^{2+} and pH

The parameters H_2O_2, $Fe^{2+,}$ and pH were studied according to their variation of one of them, with the others fixed. For this, 100 mL of OWW was used for each sample; the reaction time was 20 min, the jar test rotation was set at 80 rpm, and the sedimentation time was one day. For these initial tests, 7 liters of OWW sample were selected, homogenized, and characterized, resulting in a COD of 56 g L^{-1}.

Six separate experiments were carried out at different pH values (2.5, 3.0, and 3.5). These values were chosen for H_2O_2: Fe^{2+} ratios of 5:1 to 65:1 (mol mol^{-1}) (Figure 6). The first three experiments were performed when the volumes of Fe^{2+} in the sample were fixed at 5 g L^{-1} and those of H_2O_2 varying from 1.5 to 20 g L-1.

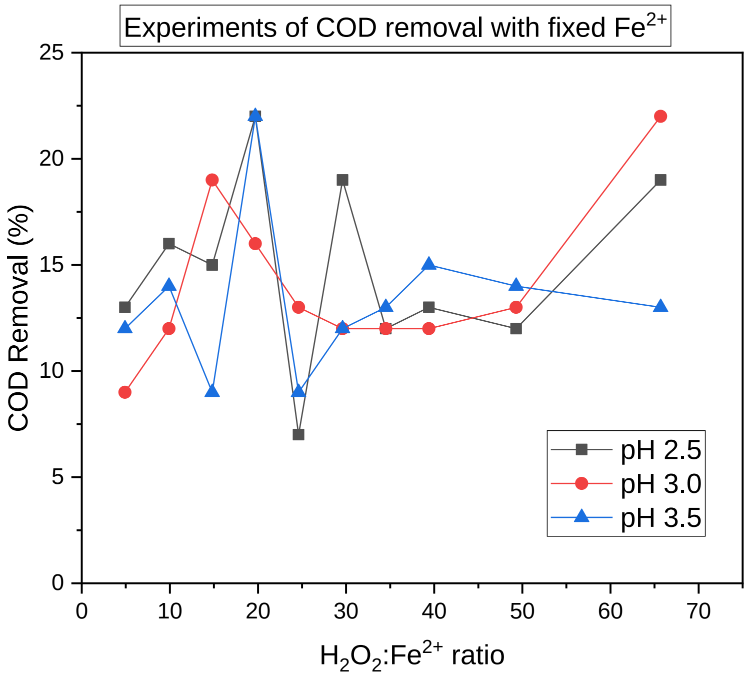

Figure 6: COD removal experiments with fixed Fe^{2+} concentration.

The COD removal showed a similar behavior in all pH values, and for pH 2.5 and 3.5 the maximum removal was 22.5% and 22% respectively, in a peroxide:iron ratio of 20 times, while for pH 3, the removal maximum was also 22%, but this removal was achieved in a ratio of 65 times.

This increase in the H_2O_2:Fe^{2+} ratio is consistent with the addition of more peroxide to the system, but the removal rates did not show an increasing evolution throughout the test.

Another experimental hypothesis was to fix the amount of H_2O_2 and vary the amount of iron in inverse proportion, i.e., Fe^{2+}:H_2O_2 (Figure 7).

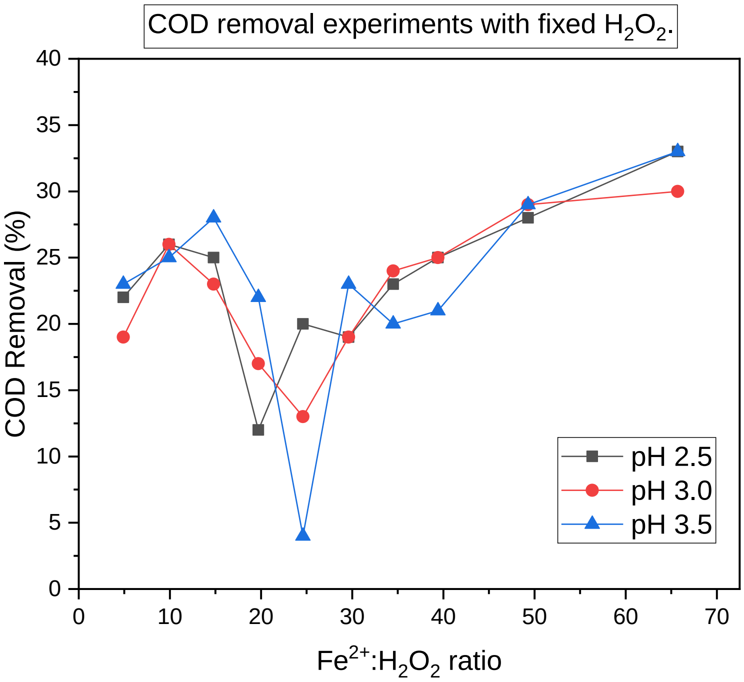

Figure 7: COD removal experiments with constant H_2O_2.

In this test, the Fe^{2+}:H_2O_2 ratio varied from 5:1 to 65:1 (mol mol^{-1}). However, to maintain these proportions, the amount of peroxide in the samples was 20 g $L^{-1,}$ and the iron concentration ranged from 0.5 to 7 g L^{-1}.

The highest removal efficiency was 34% at a pH of 3.5 and a ratio of 65:1 (mol mol^{-1}). The COD removal efficiency was similar at pH values of 2.5 (33.6%) and 3.0 (31%).

For the subsequent tests, a starting pH of 3.5 was chosen because the removal values showed similar behavior at all pH values. Additionally, there was no significant change in the oxidation process by the Fenton process when decreasing the pH minimized the use of the initial control reagents (H_2SO_4 and NaOH).

5.1.2 pH for the end of the Fenton Reaction and Sample Dilution.

The following tests aimed to determine: first, what happens to the samples when exposed to a longer reaction time; second, what happens when the samples are neutralized differently; and third, whether using the same dose of reagent, but diluting the samples in distilled water, would affect the results (Figure 8).

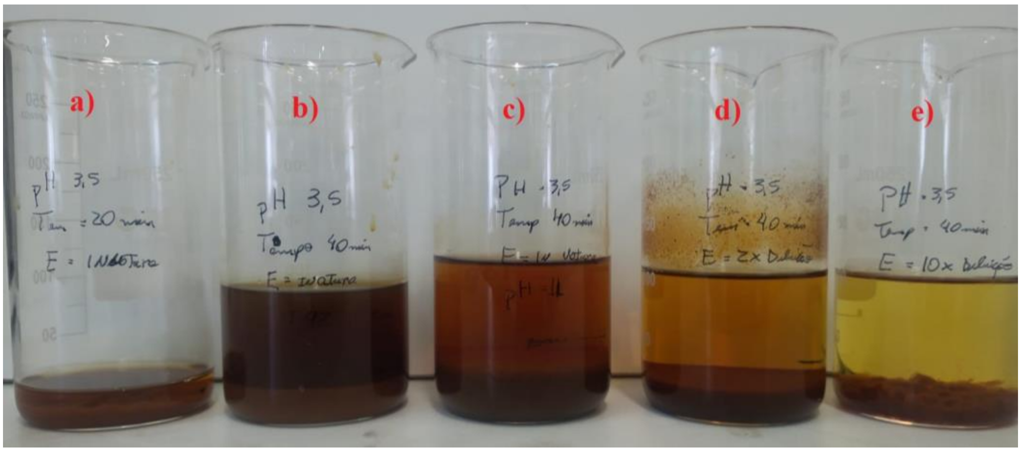

Figure 8: a) time reaction 20 min; b) time reaction 40 min, final pH 4,2; c) time reaction 40 min, final pH 11; d) 2–fold dilution e) 10–fold dilution.

The sample used initially for this test had an initial COD of 42 g L^{-1}, and the removal percentages were a) 63%, b) 66%, c) 66%, d) 71%, and e) 94%.

As for time, because the removal values in a) and b) were very similar, new tests were needed to determine the best reaction time.

The final pH value of the reaction must be close to neutral (pH 7.0) at the end of the Fenton oxidation reaction or higher to prevent the production of undesirable compounds does not occur (Bracco et al., 2023).

When comparing the COD removal values obtained from the previous assay, it can be observed that the values were close to each other. However, when sodium hydroxide was not added to stop the reaction, sample (b) continued to have a darker color and a less defined solid phase (sludge) than the sample with a final pH of 11 (c).

Dilution tests were performed to minimize excessive use of the reagents. More significant COD removal was expected by diluting the sample and maintaining the amount of hydrogen peroxide and iron sulfate. Moreover, 71% (d) was achieved when diluted 2-fold, and 93% (e) was achieved when diluted 10-fold, compared to 66% (c) without dilution. From these results, it was expected that with the same amount of reagent added to a sample diluted 2-fold, the initial COD removal of 66% would become closer to double this removal, i.e., the total elimination of COD in the sample, directing any residual substance to the semi-solid part (sludge) of the sample.

However, other aspects, such as lighter color and better-defined sludge, demonstrated the direction of the solid particles initially suspended in the sample matrix; with the AOP, they were directed to the bottom of the beaker.

5.1.3 Reaction Time

Reaction time is an important parameter, as the Fenton reaction depends on the contact between hydrogen peroxide and iron to form hydroxyl radicals and, thus, effectively degrade organic matter. It should also be noted that an incorrect choice of reaction time can result in more toxic or degradation-resistant products (Ziembowicz and Kida, 2022). Various reaction times are employed for POA treatments, such as 30 min (Pan & Qian, 2022), 60 min (Domingues et al., 2021), 120 min (Martins et al., 2010), and can even reach 8 hours (A. S. Rodrigues et al., 2022).

The time of reaction was performed by fixing the pH value (3.5), sample volume (100 mL), H_2O_2 volume (6 mL), and Fe^{2+} (1 mL), as shown in Figure 9.

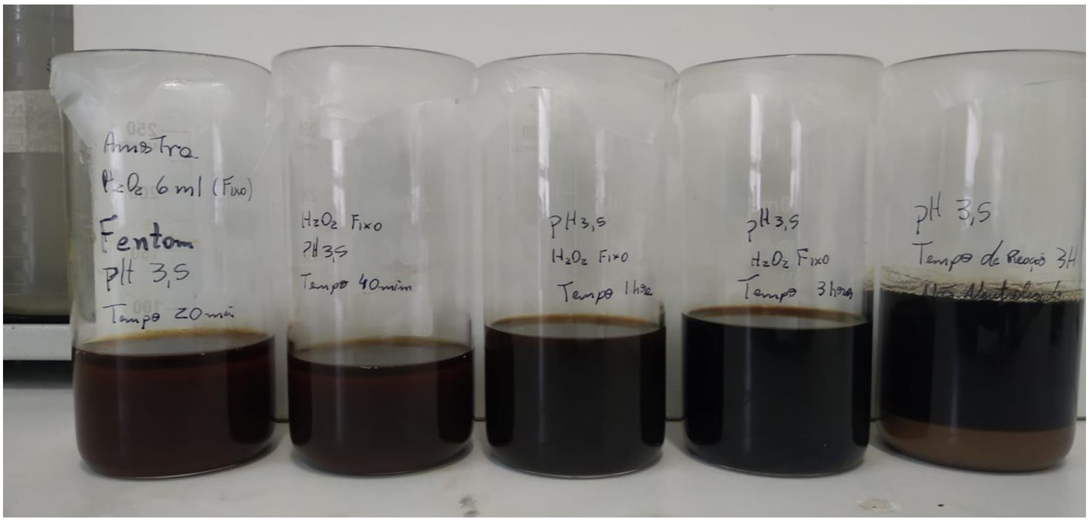

Figure 9: Effect of reaction time on COD removal.

After neutralizing the samples to a pH between 9 and 11 and allowing them to rest for one day, COD removal tests were performed (Figure 10).

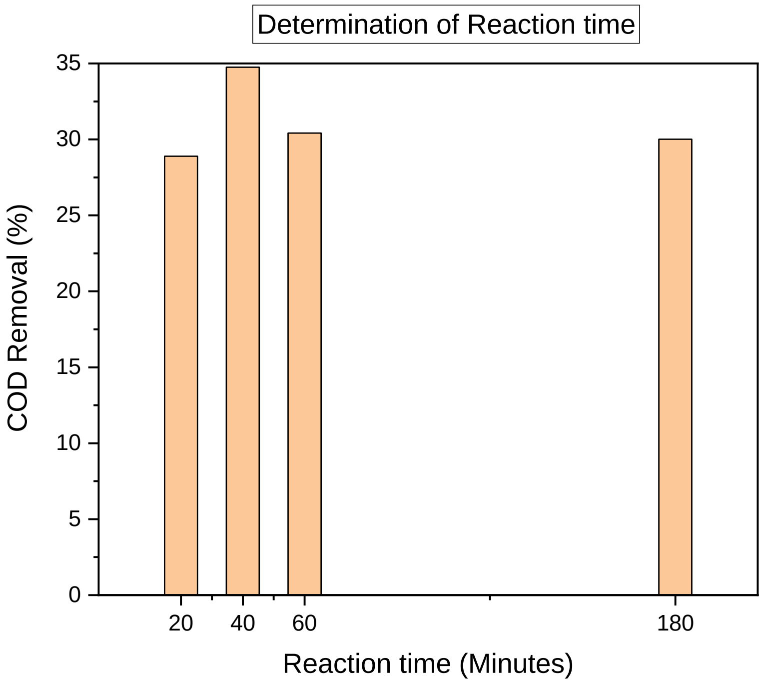

Figure 10: Determination of Reaction time

The removal of organic matter showed the best result at a reaction time of 40 minutes, reaching 35%. Before and after this time, COD removal was not higher than 30%.

5.1.4 Addition of Initial Reaction Temperature

The initial reaction temperature can influence the Fenton reaction, mainly producing ºOH and the byproducts H_2O and O_2. According to research conducted by Rodrigues (2020), this parameter is complex too because at temperatures higher than room temperature; the activation energy is more easily over, whereas, for temperatures lower than 20 °C, this same treatment presents lower removal rates, requiring a longer reaction time.

Therefore, under the same conditions as the previous test, the proposal for the next test was to add a fixed initial temperature of 40ºC and vary the reaction time, thus measuring the COD removal as a response. The following results were obtained using a heating plate and magnetic stirring (Figure 11).

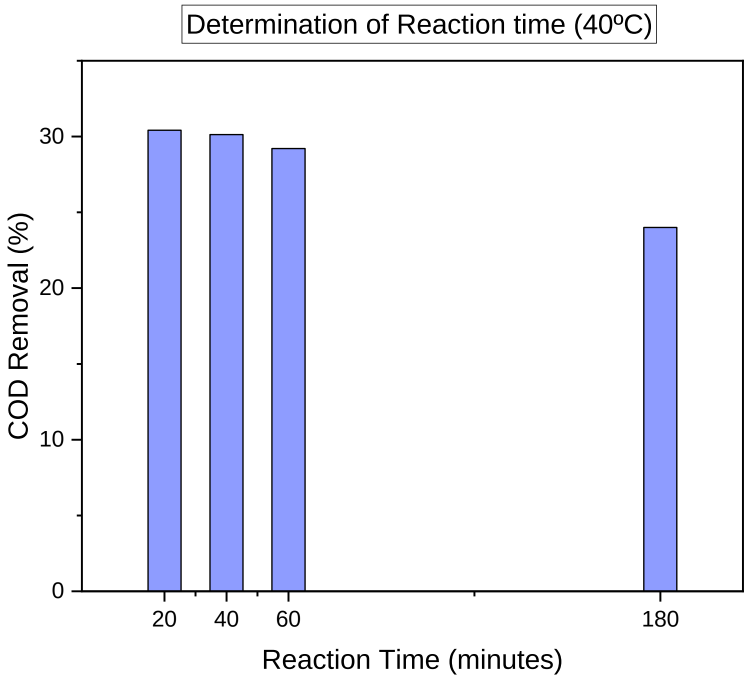

Figure 11: Reaction time and COD removal (40 ºC)

Based on the results of the combination of time and temperature for the Fenton reaction, increasing the temperature did not have a significant positive effect on the COD removal, considering that the removal decreased over time at a fixed temperature of 40 ºC. This phenomenon may be linked to the fact that at higher temperatures, there is an increase in the decomposition of hydrogen peroxide into water, which decreases the formation of radicals responsible for the degradation of organic matter (Ziembowicz & Kida, 2022). Therefore, the choice for the subsequent tests regarding these parameters was 40 minutes for the reaction time, and no initial temperature was added to the reaction.

Finally, as the samples presented varying initial COD and TPC, as shown by the Characterization of Raw Effluent, a BBD experimental design was carried out to determine the ideal quantities for eliminating pollutants in the OPOEI effluent.

5.2 BBD TESTS

Using the R-Studio software version 4.2.2, an RSM experimental design was developed using BBD. For this purpose, the tests outlined in the *Experimental Design BBD* were performed, and the following results were obtained (Table 5).

Table 5: Experimental Results BBD

Test	**Variables**			**Removal (%)**	
	H_2O_2 (mL)*	Fe^{2+} (mL)**	pH	COD	TPC
1	2.9	14.3	3	30.8	62.7
2	29.1	14.3	3	80.5	94.5
3	2.9	58.6	3	53.78	89.1
4	29.1	58.6	3	90.9	> 99
5	2.9	36.4	2	49.33	85.1
6	29.1	36.4	2	88.96	> 99
7	2.9	36.4	4	45.47	81.4
8	29.1	36.4	4	88.48	> 99
9	16.0	14.3	2	71.78	92.4
10	16.0	58.6	2	79.99	96.7
11	16.0	14.3	4	69.25	90.0
12	16.0	58.6	4	82.64	96.7
13	16.0	36.4	3	77.31	94.7
14	16.0	36.4	3	77.12	94.6
15	16.0	36.4	3	77.37	94.8

* Hydrogen peroxide (37%)
** Iron sulfate (50 g L^{-1}).

In this experiment, the highest removal rates for both COD and TPC occurred when a considerable amount of H_2O_2 was added (29.1 mL). This response reflects the need for the amount of this reagent, which was previously calculated in terms of the *COD: H2O2 Ratio H2O2:Fe2+ Ratio*.

These responses may also be associated with the amount of iron added during the tests. For instance, when comparing test 4, which had the highest removal rate for COD and >99% removal rate for TPC, to test 2, which also used 29.1 mL of H_2O_2 but a smaller amount of Fe^{2+}, the removal rate for COD was only 80%, and there was not completely removal of TPC.

The influence of pH on the reaction did not appear relevant for the best removal rates. For example, tests 4 (pH 3), 6 (pH 2), and 8 (pH 4) achieved approximately 90% COD removal and more than 99% TPC removal.

The lower removal results were directly linked to the addition of smaller hydrogen peroxide (2.9 mL) volumes in tests 1, 3, 5, and 7. Among these values, Test 1 was the least efficient for COD and TPC removal, associated with a smaller volume of added Fe^{2+}.

The removal of COD was analyzed using R-Studio to generate contour plots (Figure 12: Contour graphs of COD removal.).

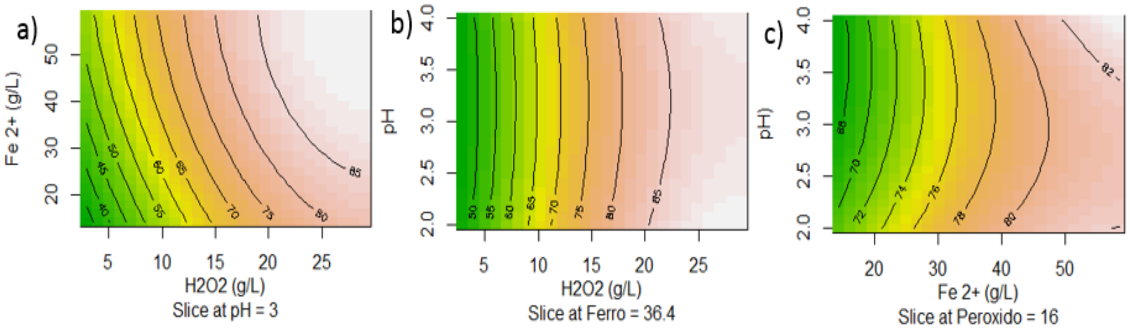

Figure 12: Contour graphs of COD removal.

By analyzing the contour plot "a," which shows the variation of H_2O_2 and Fe^{2+} with the pH fixed at 3, the behavior of the contour lines is linear up to the first removal indices, up to 50%. Above this value, the behavior becomes more curved (nonlinear). In other words, reagent consumption grows unevenly to achieve higher removal indices.

In graph "b," the almost entirely linear behavior indicates that, with the iron fixed, even when the pH varies between 2 and 4, it does not directly interfere with COD removal. In other words, COD removal was directly related to the addition of different volumes of hydrogen peroxide. Although the last contour lines show a curved behavior, the removal results do not change significantly.

Graph "c" presents the relationship between pH and iron when H_2O_2 values are fixed. In this context, the responses obtained showed saddle behavior. Therefore, this graph does not provide the maximum or minimum values possible in this experiment, requiring different amounts of iron and pH for a better response.

Contour plots for COD removal were obtained using R-Studio (Figure 13).

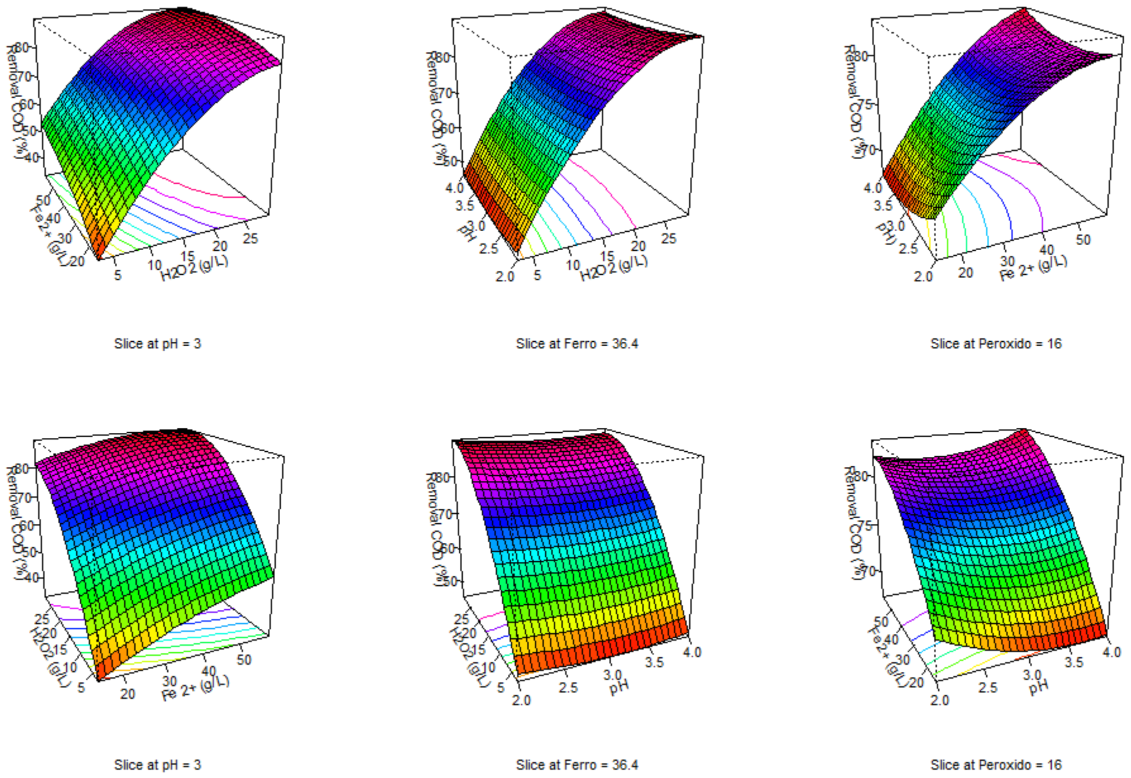

Figure 13: Response Surface Plot for COD removal.

The response surface plot is another way of visualizing COD removal behavior concerning the parameters discussed earlier.

The saddle behavior can be better observed in Figure 13, and graphs that start linearly and end up curved are shown. It was also observed from the graphs that the combination of H_2O_2 and Fe^{2+} parameters was crucial for a higher removal rate.

Contour plots were also generated to remove TPC (Figure 14).

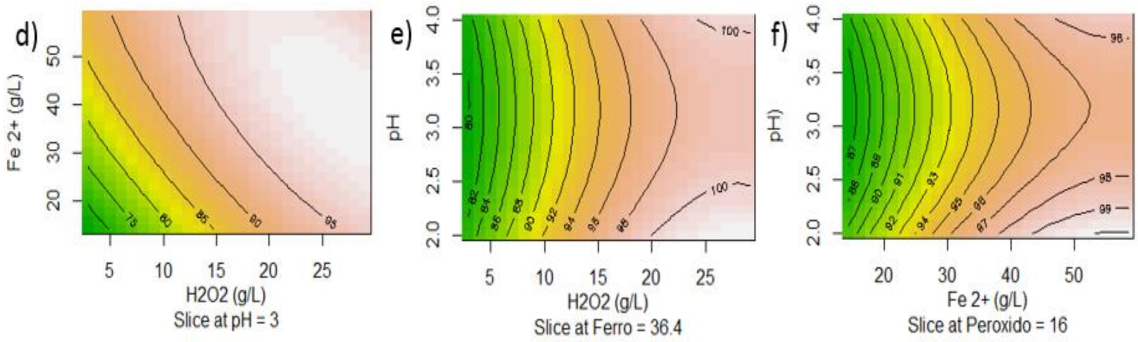

Figure 14: Contour graphs for total phenol compounds (TPC) removal.

In graph "d," the contour lines show a linear behavior in almost the entire area, meaning that the relationship between hydrogen peroxide and iron varies uniformity for the removal of TPC, consistent with what was previously reported, where the highest removal rates occurred when there was a higher addition of hydrogen peroxide and iron to the solution.

In graphs "e" and "f," the contour lines have similar behavior, with a slight curve when the removal rate is below 93%, and subsequently, it presents a saddle behavior, which can be seen in the following figure (Figure 13Figure 15).

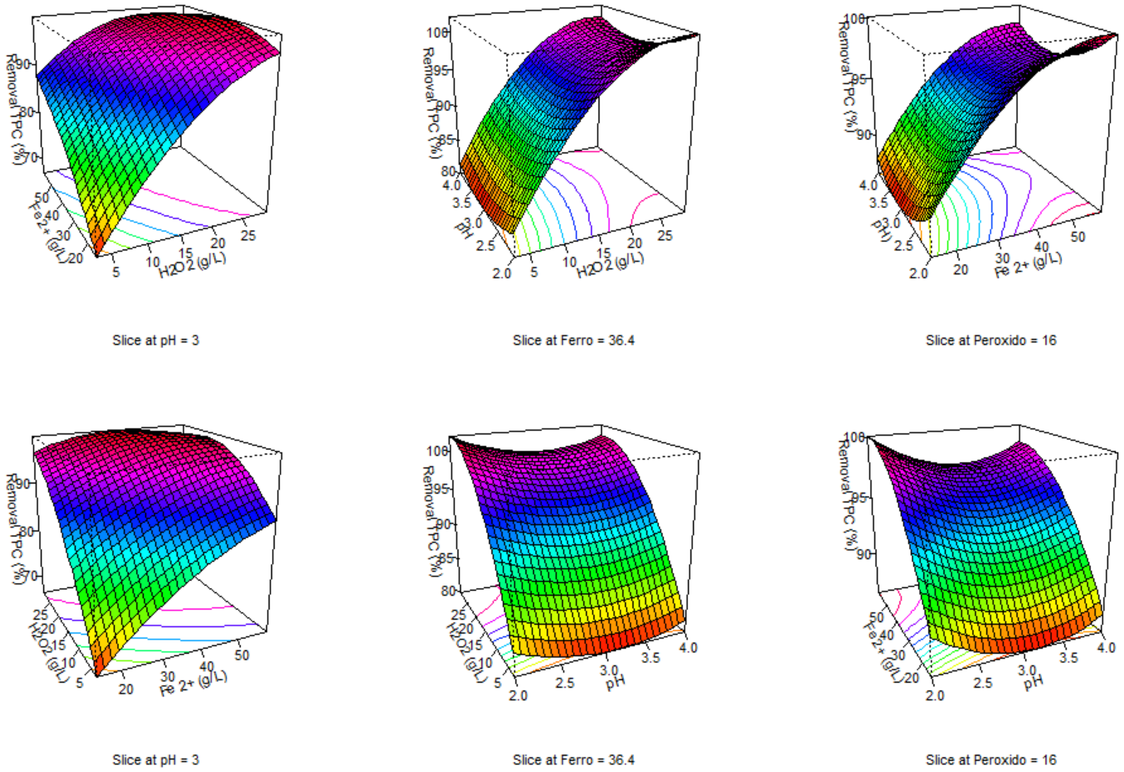

Figure 15: Response Surface Plot for TPC removal.

The removal of TPC when iron was fixed was more significant when the volumes of peroxide were the highest at pH 2 and 4. When peroxide was fixed, the highest TPC removal occurred when the highest volume of iron was added at pH 2.

Other essential factors provided by R-Studio software are related to the sensitivity and statistics of the system, where the polynomial Equation can be adjusted in programming. These data can correlate linear interactions (FO), that is the individual terms, double relationships between variables (TWI), and quadratic term relationships (PQ), based on Equation (13) and modified for reading in the software.

$$\begin{aligned} &\mathrm{FO}\ (x1, x2, x3)\ +\ \mathrm{TWI}\ (x1, x2)\ +\ \mathrm{TWI}\ (x2, x3)\ +\ \mathrm{TWI}\ (x1, x3) \\ &\quad +\ \mathrm{PQ}\ (x1, x2, x3) \end{aligned} \tag{13}$$

The reliability values of response R^2 and the significance value of each variable (p-value) are listed in Table 6.

Table 6. R-Studio’s statistical and sensitivity responses to the BBD test

COD		**TPC**	
R^2	0.9944	R^2	0.946
R^2 – adjusted	0.987	R^2 - adjusted	0.8919
p-value	$3.38 * 10^{-6}$	p-value	0.000614
Individual Variables			
	p-value		p-value
Interception	$8.37*10^{-10}$	Interception	$2.58*10^{-10}$
X1	$1.03*10^{-7}$	X1	$6.01*10^{-5}$
X2	$7.57*10^{-5}$	X2	0.001965
X3	0.49159	X3	0.522817
X1:X2	0.02146	X1:X2	0.012986
X2:X3	0.25071	X2:X3	-
$X1^2$	$5.92*10^{-5}$	$X1^2$	0.015392
$X2^2$	0.04324	$X2^2$	0.122358
$X3^2$	0,24797	$X3^2$	0.234526
FO (x1, x2, x3)	$5.29*10^{-7}$	FO (x1, x2, x3)	0.0001831
TWI (x1, x2)	0.0214639	TWI (x1, x2)	0.0128960
TWI (x2, x3)	0.2507100	TWI (x2, x3)	-
PQ (x1, x2, x3)	0.0003188	PQ (x1, x2, x3)	0.0355497

The data established from R-Studio were satisfactory for the removal of COD, as the reliability of the results presented an R^2 value of 0.9944, that is, reliability higher than 95%, demonstrating that the removal values established by tests 1 to 15 (Table 5) could be modeled by the software.

Based on this analysis, there was a need for only adjustments in the central Equation (13), that is, to eliminate some variables to minimize their interaction with others. In this assay, the variable that had the highest p-value was TWI (x1, x3), which was removed from the central Equation so that the "adjusted R^2" presented a value closer to the obtained R^2 value, as shown in Equation (14).

$$\mathrm{FO}\ (x1, x2, x3)\ +\ \mathrm{TWI}\ (x1, x2)\ +\ \mathrm{TWI}\ (x2, x3)\ +\ \mathrm{PQ}\ (x1, x2, x3) \qquad (14)$$

Another significant observation for the analysis of the experiment's behavior is the level of significance (p-value), where the estimated value for COD removal was less than 0.05, which is above 95% of global significance.

In addition, the significance values can help observe each parameter separately and its iterations, where hydrogen peroxide (X1) presented the lowest p-value, meaning that, compared to the other parameters (X2 and X3), it represents the highest significance for COD removal.

This aspect is also repeated for the relationships between parameters, where (X1:X2) is more significant than (X2:X3), and in quadratic terms, where the p-value presented in $X1^2$ is greater than $X2^2$ and $X3^2$.

In this sense, when comparing the variance between interactions in the COD removal analysis, the behavior of individual factors (FO) was more relevant than that of the double interactions (TWI) and quadratics (PQ).

In the TPC removal analysis, there was also a need for adjustments in Equation 15 to approximate the adjusted R^2 to the real R^2 value and improve the experiment's significance.

$$\mathrm{FO}\ (\mathrm{x1}, \mathrm{x2}, \mathrm{x3})\ +\ \mathrm{TWI}\ (\mathrm{x1}, \mathrm{x2})\ +\ \mathrm{PQ}\ (\mathrm{x1}, \mathrm{x2}, \mathrm{x3}) \qquad (15)$$

The variables removed from the central Equation were TWI (x1, x3) and TWI (x2, x3), both of which had pH (X3) as their least relevant parameter.

Although the TPC removal test presented higher p-values compared to the analysis performed for COD removal, it can be observed that the response behaviors were similar in both analyses; that is, the most significant parameter was hydrogen peroxide, and in the iterations analyses, individual terms were more significant.

Finally, through this methodology, it was possible to establish optimized reagent and pH values for COD removal (H_2O_2 = 27.74 mL, Fe^{2+} = 52.16 mL, and pH = 2.85) and TPC removal (H_2O_2 = 26.68 mL, Fe^{2+} = 40.61 mL, and pH = 3.18).

5.2.1 Optimization of BBD Test.

The best results from the experimental design were used to execute the final tests, which are divided into two sections. In the first test (EXP 1), the best result for the maximum removal of organic matter was established previously by the methodology of

Lucas & Peres (2009). In the second test (EXP 2), the minimum values of the reagents were used to remove >99% of TPC.

Both tests were performed according to previously established experimental conditions. First, the samples were selected, the volume of Fe^{2+} was added, the pH was adjusted, and then the Jar Test was performed. The reaction occurred for over 40 minutes, with the first 5 minutes of fast agitation (150 rpm) and 35 minutes of slow agitation (80 rpm). The sample volume used for these tests was 200 mL to have enough volume for the final characterization (Figure 16).

Figure 16: Optimization tests in the jar test

For this sample volume, in EXP 1, 111 mL of H_2O_2 (373 g L^{-1}) and 208 mL of iron (50 g L^{-1}) were used at pH 2.85, while in EXP 2, 107 mL of H_2O_2 (373 g L^{-1}) and 162 mL of iron (50 g L^{-1}) were used at pH 3.18. All these values of reagents and pH are below the maximum values of the parameters; that is, the "optimized points" by R-Studio are within the proposed response surface previously.

Controlling the reaction temperature is essential for obtaining reliable results after the reaction. Failure to control the temperature can lead to uncontrolled foam formation and matter loss. This phenomenon occurred in previous tests, as the reaction releases heat by adding reactants (Figure 17).

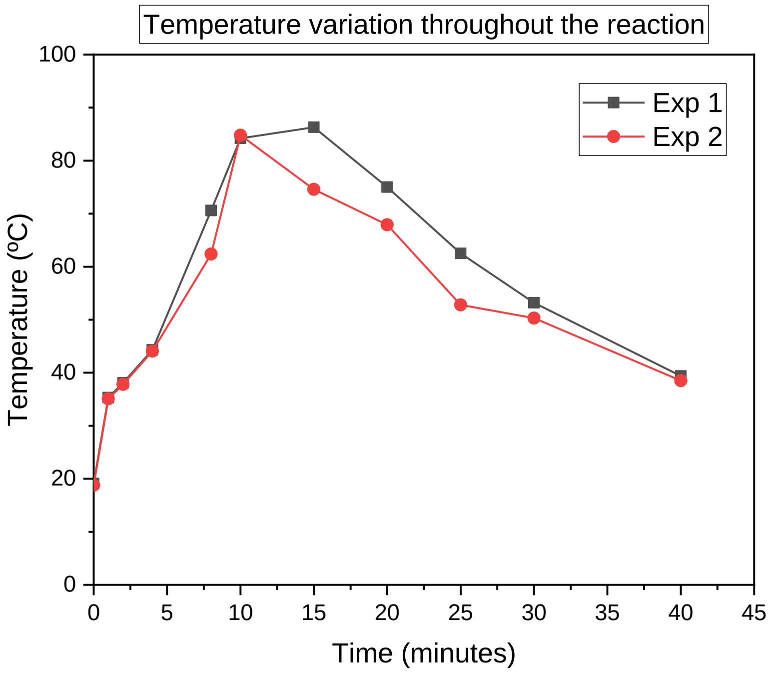

Figure 17: Temperature variation throughout the reaction

Hydrogen peroxide was added with a graduated burette to better control foam formation during the reaction. This step occurred in the first 10 minutes of the reaction, and as predicted, in both tests, the samples showed the same behavior; that is, they presented the highest temperature values (above 80 ºC) when H_2O_2 was added, exemplifying the reaction as exothermic. Initially, the reaction showed changes in coloration and vapor formation, and it was also possible to visualize temperature changes using a simple meter, as shown in Figure 16.

After the reaction ended, the samples were allowed to rest for approximately 10 min to normalize the temperature to room temperature (around 20 °C).

After this time, NaOH, a reagent responsible for stopping the reaction, was added, raising the pH until the sample became basic (pH between 9 and 12). Subsequently, the sample was allowed to rest for 24 h (Figure 18).

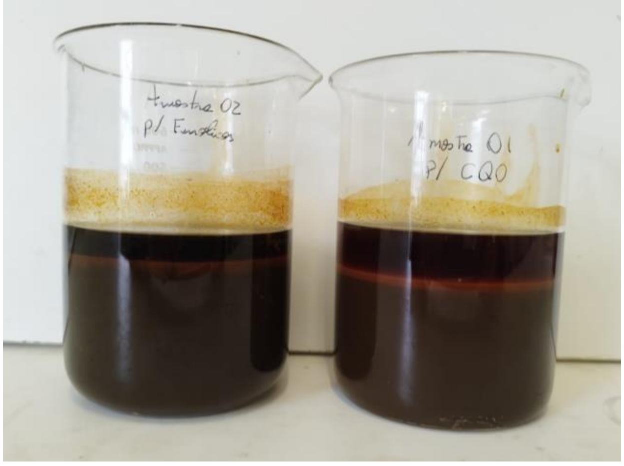

Figure 18: Samples 24 hours after the reaction

After 24 h, the samples settled and separated into two phases. The bottom part of the beaker corresponds to the residual sludge, where most of the solids in these samples were found, whereas the upper part contained the liquid fraction of the samples.

5.3 FINAL CHARACTERIZATION OF THE EFFLUENT AFTER BBD

The final characterization of EXP 1 and EXP 2 was performed using only the sample's liquid part (supernatant). The following parameters were evaluated: COD, BOD_5, TOC, OC, IC, Total Solids (TS), Fixed Solids (FS), Volatile Solids (VS), Total Nitrogen (TN), and TPC.

The results corresponding to EXP 1 and EXP 2 are listed in Table 7.

Table 7: Final characterization of EXP 1 and EXP 2

Parameter	Unit	Raw Sample	EXP1	R (%)	EXP2	R (%)
pH		4.42	9,84	-	10.20	-
COD	g L^{-1} O_2	107.71	11,52	89.3	16.06	85.09
BOD_5	g L^{-1} O_2	14.7	4.43	69.86	5.63	61.68
Biodegradability	BOD_5/COD	0.13	0,38		0.35	
TOC	g L^{-1} C	39.38	7,74	80.35	9.01	77.13
OC	g L^{-1} C	39.94	8,02	79.93	9.23	76.88
IC	g L^{-1} C	0.555	0,28	50.25	0.29	58.92
TS	g L^{-1}	69.69	57,66	17.26	59.69	14.35
VS	g L^{-1}	39.77	7,62	80.85	9.01	77.36
FS	g L^{-1}	29.92	50,04	-67.26	50.68	-69.43
TN	mg L^{-1} N	469.7	212,05	54.85	217.4	53.73
TPC	mg L^{-1}	7986.47	0	>99%	29.98	99.62

Analyzing the results obtained in EXP 1, the COD removal was 89.3% for the quantities optimized by the software, which was very close to the maximum removal value obtained by the experimental design. For EXP 2, which used lower quantities of H_2O_2, the COD removal (85%) was expected to be lower than that of EXP 1.

Despite presenting a high value for COD removal, the maximum ELVs allowed by law is 0.15 g L^{-1} O_2. For both analyses, this Fenton reaction alone could not eliminate the necessary amount of organic matter and allow the effluent to be discharged directly into water bodies.

BOD_5 removal for EXP 1 was about 70%, reaching 4.43 g L^{-1} O_2, while in EXP 2, it was 62%, which compared to the ELVs, did not reach (0.04 g L^{-1} O_2). However, the lower the BOD_5 removal, in proportion to the COD, the higher the biodegradability of the sample.

According to Fernandes (2019), biodegradability refers to whether a particular substance or a set of substances can be degraded by biological means, such as aerobic or anaerobic digestion. For this, the BOD_5:COD ratio was used, where when this ratio was higher than 0.5, the effluent was highly biodegradable. Between 0.5 and 0.3, the effluent has good biodegradability, but pretreatment is recommended before making it available for biological treatment. When the effluent is below 0.3, it is poorly biodegradable and may contain recalcitrant and potentially toxic compounds. Thus biological treatment is not recommended.

Therefore, based on the removals established in EXP 1 and EXP 2, the biodegradability index increases from 0.13 to 0.38 and 0.35, respectively, corresponding to possible biological treatment.

The removal percentages of organic matter expressed in the TOC analysis were 80% in EXP 1 and 77% in EXP 2. Most of the case in the sample was organic carbon (OC), which is characteristic of the activity from which the matrix originated.

Analyses of the solid series were carried out according to methodology 2540 of the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2017), where the removal or transformation of solids present in the samples in both experiments was similar. A decrease in volatile solids and an increase in fixed solids reflected the effect of sludge formation and phase separation caused by Fenton reagents in the effluent, which was observed in the experiments.

The other target pollutants in the experiments were TPC, and in EXP 2, the values were optimized for the best TPC removal, and 99.6% removal was obtained. The greater than 99% removal of TPC in EXP 1 shows that adding more reagents makes it possible to eliminate this compound from the effluent. This elimination of this pollutant is essential if there is an interest in subsequently directing conducting biological treatment of the effluent because, as seen earlier, TPCs can function as antimicrobial agents.

6 CONCLUSIONS

The Fenton advanced oxidation process can remove and treat wastewater from the Olive Pomace Oil Extraction Industry. The highest COD and TPC removal efficiencies were approximately 90% and 99%, respectively.

The use of Fenton reagents was determined based on the pollutant concentrations in the sample, mainly COD, because the studied effluents had diverse characteristics. Among the difficulties in applying this technique is that olive pomace oil production is seasonal, resulting in an effluent formed by specific pollutant loads emitted over time, making the analyses challenging, requiring constant adaptation of the methodology, i.e., whenever a new collection is made.

The addition of reactants is crucial for temperature control, as the release of hydroxyl radicals can transform the reaction into an exothermic reaction, reaching 84 °C in this study.

Using BBD, it was possible to establish values for optimal pollutant removal, with hydrogen peroxide as the most effective reagent in the sample oxidation process, followed by iron as the activator of this reaction. The pH was the least influential parameter for the reaction because it was only tested under acidic conditions, as reported in the literature.

It was also possible to improve the characteristics of the final effluent compared with the initial effluent, such as the separation of solids to obtain more defined sludges, which is crucial for more effective water treatment systems, and an increase in biodegradability, which is essential for the disposal of this effluent in subsequent treatment processes.

7 FUTURE WORKS SUGGESTIONS

Suggestions for future work

- Combination and comparison with other OAPs;
- Use of other reagents and catalysts similar to Fenton-like processes;
- Analysis of incorporation of treated effluents into biological reactor systems;
- Ecotoxicological tests;
- Characterization of compounds formed by the reaction;
- Economic viability compared to the removal rate;
- Incorporation into a laboratory-scale effluent treatment system.

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