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Characterization and Primary Treatment of the Effluent from Olive Pomace Oil Extractor Industry

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Abstract

The olive pomace oil is the principal by-product in the olive oil sector. Nonetheless the production uses olive bagasse after the primary extraction, it also produces by-products and effluents that need strategic approach to possibility reuse and a treatment. This study aimed for the characterization of the effluent from an olive pomace oil extractor industry and investigate the application of physicochemical pre-treatments to future water reuse. The physicochemical characterization shows high amounts of BOD and COD for the effluent freshly produced (E1) and effluent collected from storage tanks (E2) in the industrial plant. Other parameters were evaluated: Phosphorus, Organic nitrogen and Ammonia, FOG, Phenolic compounds, Alkalinity, TS, TDS and TSS, and Biodegradability (Zahn-Wellens Test). E2 shows the storage tanks were able to reduce 55% of TS and TDS, 77.5% of COD and 69% of BOD when compared with E1. Comparing with the Portuguese legislation, these effluents cannot be discharge to waterbodies and need treatments, such as coagulation and flocculation as tested in this work. Aluminium Sulphate show to work at best as a coagulant in the minimum concentration 10 g/L and pH 5, RIFLOC F45 (4 mg/L) was used as flocculant. After the treatment, it was observed a remotion of 95.6% of turbidity, 76,4% of COD,76,7% of TSS, and 85.4% of PhC when compared with E2. A sampling campaign was carried out on the Tua river to assess its water quality, and samples were taken at four different points to assess the impact of the effluent discharge, with none of the evaluated parameters presenting values higher than those recommended by the Law-Decree nº236/98 from the Portuguese Legislation.

Keywords: Industrial effluent, wastewater characterization, olive pomace wastewater, water bodies monitoring, coagulation/flocculation.

Acronyms

BOD Biochemical Oxygen Demand.

COD Chemical Oxygen Demand.

ENEAPAI Estratégia Nacional para os Efluentes Agropecuários e Agroindustriais.

ELV Emission Limit Value.

ERV Emission Recommend Value.

EU European Union.

FOG Fats, Oils and Grease.

OMWW Olive Mill Wastewater.

PAA Poly(allylamine).

PAH Poly(allylamine) Hydrochloride.

PDADMAC Polydiallyldimethylammonium Chloride.

PEI Poly(ethylenimine).

PhC Phenolic Compounds.

TDS Total Dissolved Solids.

TS Total Solids.

TSS Total Suspended Solids.

TVS Total Volatile Solids.

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Chapter - 1

Introduction

Since ancient times, the practice of extracting oil from olives has been explored in the Mediterranean region due to the favorable climatic conditions for growing olive trees. Portugal is the fourth biggest olive oil producer, after Spain, Italy, and Greece. The European Commission estimates that around 2 million tons of olive oil are produced in the European Union (EU) every year [1, 2].

Olive oil production is a relevant economic sector, with job creation, maintaining rural populations, its production involves also environmental aspects that cannot be neglected. Mass and energy resources are consumed throughout the stages of the olive oil production chain, from the cultivation and production of olives to the final consumption of the product, as well as produced gaseous, liquid, and solid residues with impacts on ecosystems. As the circular economy principles, these residues can still be part of new industrial processes [1, 3].

The technologies for olive oil extraction became more efficient over the decades, today most extraction occurs in a 2-phases system to reduce the amount of wastewater produced by the traditional and the 3-phase process. The main byproduct, the olive pomace, goes to a second extraction, the remaining oil percentage is removed applying an organic solvent. This olive pomace oil can be refined and used in some countries in the food and cosmetic industries. After the process, the exhausted pomace serves as fuel in the industry, and the wastewaters produced need to be treated to give a destination to water and organics compounds [4].

The present work aims to characterize the wastewater, to design a primary treatment for one olive pomace oil extractor industry, and to study possibilities to reuse the water inside the extraction processes or in the olive groves. Coagulation/flocculation are the processes chosen to treat the wastewater due to the low investment and easy installation and manipulation by the industry.

Chapter - 2

Objectives

The overall aim of this thesis is to study the effluent from an olive pomace oil extractor industry and design the treatment to enable the reuse of the water or the return to a water body as specified by the Law-Decree nº236/98 from the Portuguese Legislation.

2.1 Specific aims

- Physicochemical characterization of the wastewater produced by the olive pomace oil extractor industry.
- Study the possibility of treatment to water reuse in the irrigation of olive groves.
- Study coagulation/flocculation as a pre-treatment for the effluent produced by the olive pomace oil extractor industry.
- Propose alternative treatments for the discharge of effluent into the receiving body and its energy valorization.

Chapter - 3

State of Art

This chapter organizes to explain the olive oil production and the residues produced in this industry, how the olive pomace oil is produced, and the new residues and their environmental impacts. The wastewater characterization and treatments with a focus on filtration systems and coagulation and flocculation techniques who intended to be replicated in our project for the olive oil pomace production. Along, it is important to understand the environmental legislation from Portugal, the parameters of the water, and the possibility of use of the wastewater in olive irrigation, and the valorization of the residues.

3.1 Olive Oil Industry

To be able to talk about the olive pomace oil, the main byproduct of the olive oil industry, first, is necessary to understand how the olive pomace is produced and its characteristics.

3.1.1 Olive Oil Production

Olive oil is one vegetable oil that only needs mechanical processes to be extracted and can be considered the juice from olives. This process has been enhanced for centuries mainly in the Mediterranean region, because of this area's favorable climatic conditions, such as a dry climate and enough hours of sunshine for the growing of olive trees [1, 5]. First, the olive needs some pre-treatments such as removal of leaves and stones, separation, conservation, cleaning, and washing to guarantee a good quality olive oil as a product. Then the olives are milled in a process called malaxation with a hammer or toothed-disc crushers and thermal bathing producing an olive paste. Using a liquid-solid separation process, the olive oil is separated from the olive pomace [1, 4, 6].

At this point, we have at least three methods of separation as shown in the Figure 1: the traditional method, it was largely used until 1960, became replaced for the three-phase extractor and now in the last thirty years has given space to the 2-phases continuous extractor. This technological improvement has an environmental purpose, in the traditional process, the olive paste is sent from the mill to hydraulic presses, where water is added, producing oily wort, dry bagasse, and wastewater, a very pollutant residue [2, 3].

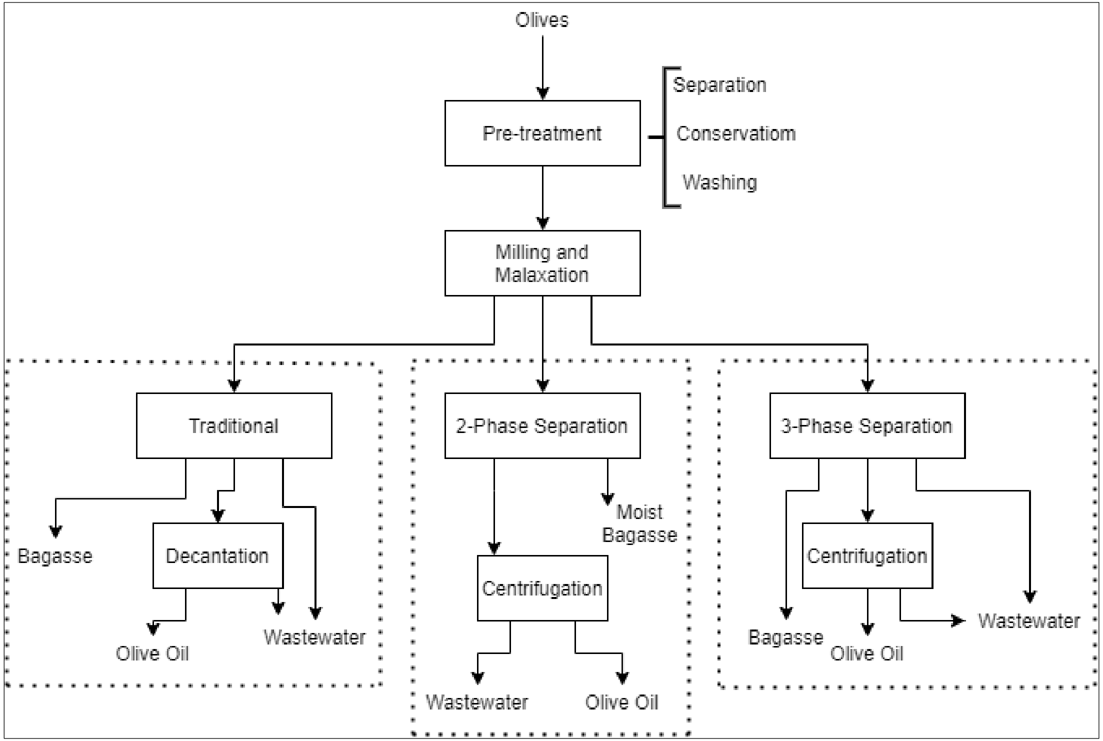


Fig 1: Olive oil production routes.

In the three-phase press, the beaten olive paste goes to the decanter where add heated water, this method also produces three different outputs: oily wort, dry bagasse, and lighting wastewater. In the two-stage process instead, there is no addition of water to the paste, with impacts on a lower production of wastewater, its resulting products are oily wort and moist bagasse [2, 3].

3.1.2 Residues from olive Oil Production

By all the processes present previously, it has as the product virgin olive oil and byproducts. The liquids ones, when present, need to pass several physical, chemical, and biological treatment before having final disposal due to high organic load and hardly degradable. The solid byproducts, the bagasse is sent to an olive pomace oil extraction industry, to extract the small amount of oil remaining in the residue. Bagasse also can be used as solid fuel in the process of obtaining electrical energy, due to its high calorific value [2, 7].

The wastewaters, known as vegetation water, too, are typically composed of water (83 to 94% by weight), organic matter (4 to 16%), and mineral salts. The principal pollutants are lipids, sugars, organics acids, tannins, pectins, lignin, and the high concentration of phenolic compounds (PhC), as well as magnesium, potassium, and phosphate salts [2]. The presence of these pollutants when discharged on water bodies induce coloration, acidification on the water, and loss of transparency. Due to the high concentrations of nutrients and organic compounds (COD close to 220 g/L) being an excellent means for the of microorganisms degrading the water quality by high oxygen consumption, in a process known as eutrophication. For the effects of pollution and toxicity of wastewater, the proportion is 1:100-200 of wastewater to domestic effluent [3, 7].

The olive pomace has different characteristics according to the extraction process, as the presence or not of olive stones, and principally the moisture content. Olive pomace originated by a three-phase extraction have normally 55% moisture and the olive pomace from a two-phase extraction has 80% moisture according to Brito [3]. The dry matter of olive pomace originated from pieces of skin, pulp, stone, and olive kernel, it is rich in proteins, crude fiber, sugars, minerals, polyphenols as some organic acids, and polyalcohols [7, 8].

As shown by Figueiredo *et al.* (2015) in Table 1 the production of olive pomace is 3 to 5 times bigger than the olive oil, evidencing the importance of the olive pomace oil industry even when the oil content in the bagasse is around 8 to 10%. This oil, after processes, to reduce any percentage of remaining solvent and impurities can be used for edible purposes, cosmetics, and biodiesel production [1, 4].

Table 1: Byproducts per liter of olive oil [1].

Method	Output	Production (kg/L olive oil)
3 phases	Olive Oil Bagasse	0.9 2.99
2 phases	Olive Oil Bagasse	0.9 4.34
Traditional	Olive Oil Bagasse	0.9 3.65

Wet pomace obtained by two-phase centrifugal, as explains Petrakis (2006), is not always used in the industry for solvent extraction because of the high percentage of moisture and need a long process of drying increasing the costs and difficulty in handling and storage [6].

Ferraz (2012) also warns about the caramelization due to the sugar presents on this type of pomace, hamper the drying operation, and to a certain extent, there may be a risk of fire. The alternative to the solvent extraction is the second centrifugation of olive pomace, extracting between 40-60% of the retained residual oil. By this process the stones are so separated from bagasse to be used as fuel in the industry, reducing the residues produced at the end of the process [1, 2, 9].

3.1.3 Olive Pomace Oil Production

According to the traditional method of solvent extraction, the olive pomace needs to be dried to 8% moisture before the addition of an organic solvent, but it reflects a minor part of the olive pomace sold to the second extraction industry. In deterrence the high percentage of water in olive pomace oil some extraction facilities that receive the three types of olive bagasse have chosen to homogenize the moisture content of the pomace to be extracted as show in the Figure 2, mixing the three types of bagasse until they reach a humidity of around 50% before a drying process. This process is important to stop fermentation reaction and preserve the reminiscent oil from hydrolysis and enzymatic deterioration [6, 7].

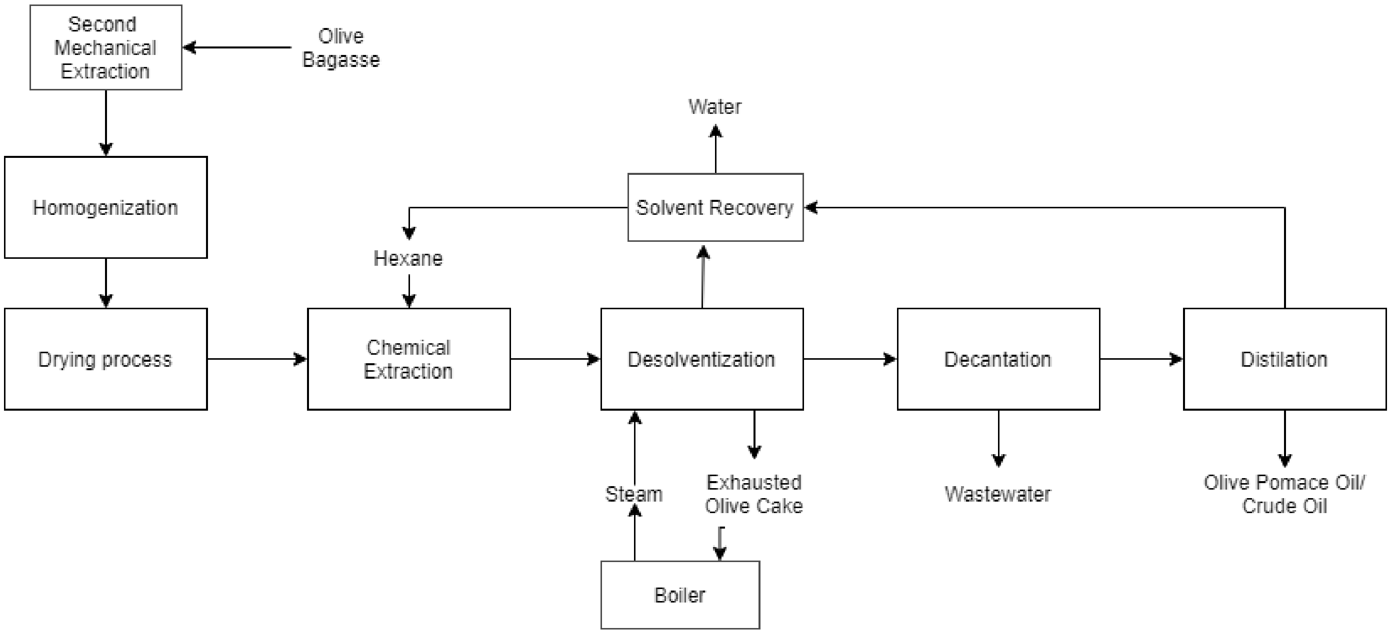


Fig 2: Olive pomace oil production process

After drying, the olive pomace is mixed with a solvent for the extraction of fats. This solvent needs to have no influence on the oil quality and physical properties, also needs a good selectivity and extraction power. As for other vegetable oils, the most used is n-hexane [10].

The solvent/oil mixture is collected from the batch extractors and steam is injected in a desolventizer operation to eliminate the hexane residue from the solids, and the oil/hexane mixture will be distilled to recover solvent. The olive pomace oil obtained, also called crude pomace oil, differs from the virgin olive oil, it is more acid, has a dark green coloration due to its high chlorophyll content and unpleasant odor and taste, needing a refining procedure to become edible [6, 10].

The byproducts generated are biomass composed of stones and fat-free solids (or exhausted olive cake), and residual wastewater. The exhausted olive pomace can have the pulp separated from the rest and destinate to animal feed, the residue remaining is used as a fuel, reducing the fuel demand for steam production of the installation [6, 10, 11].

3.1.4 Treatment and Valorization of Olive Mill Wastewater

Using the Circular Economy concept, which aims to use and transform waste from industry into materials to be used again in production processes, thereby improving the efficiency of company operations while reducing costs and environmental impacts [12], it is notable the effort that the sector of olive oil production has developed research and improvements that have been done to integrate the concepts of circular economy and cleaner production. Some of the most prominent aspects that affect the sector are the use of solid waste for the co-generation of energy and the extraction of economically interesting compounds, such as phenolic compounds, from wastewater, and the biofuels production, and Ceramic building materials [13–15].

To be able to recover phenolic compounds as tyrosol, different processes are being used continuous-flow adsorption/desorption methods, extraction using hydrophobic ionic liquids, an integrated process including fermentation, spray drying, and encapsulation technologies, solar distillation, dark fermentation, enzymatic hydrolysis, and microfiltration- ultrafiltration. To produce solid biofuels, building materials, and even natural dyes for textile dyeing are used impregnation on dry biomasses, fired clay brick production and Brick-making process, dyebath for dyeing wool, respectively [16, 17].

The wastewater treatment is another approach to remained liquids byproducts, it is then essential to treat the wastewater and to determine whether this water can be recycled and reused. Most of the depolluting treatments of Olive Mill Wastewater (OMWW) aim at the destruction of organic matter and phenolic compounds, hence the reduction of chemical oxygen demand and phytotoxicity [4, 9].

Enaime *et al.* (2018) point to the main technologies used in the last years to the treatment of OMWW, applying a range of methods [16]:

- **Physical techniques:** sedimentation, flotation, filtration, and micro-ultrafiltration using membranes, centrifugation, dsorption/desorption methods, able to de- crease COD levels when applied in series.
- **Thermal techniques:** solar distillation, evaporation, combustion, and pyrolysis. These last methods have high energy demands making them unviable.
- **Physicochemical techniques:** neutralization, precipitation, adsorption, advanced oxidation processes (Fenton reaction, wet hydrogen peroxide catalytic oxidation, ozonation, electro-Fenton), lime treatment, electrocoagulation, cloud point extraction (CPE), this process can remove COD, in some cases decrease of the total phenolic content and color.
- **Biological techniques:** anaerobic processes, aerobic processes, enzymatic processes, which can highly (70%) remove COD and phenolic compounds.

3.2 Industrial Wastewater Treatment

Vegetable oil-producing industries are an important food industry, and as many have wastewater with specific characteristics, like color, odor, high Biochemical oxygen de- mand (BOD), and Chemical oxygen demand (COD), oil is also the main pollutant in the wastewaters of the olive oil industry. It is typically a seasonal industry, and therefore there is no regular generation of wastewater throughout the year [18, 19].

The first step to design wastewater treatment is the wastewater characterization, identifying the pollutant compounds present, estimate the volumes and the source of generation, in some cases a corrective action can be proposed to reduce or even eliminate the pollutant levels, this knowledge is also important to evaluate which of the next steps in wastewater treatments are required comparing the data to the specifications requested for the final effluent, obtained in the local legislation or equipment/process demands. Unfortunately, in wastewater treatment, zero production is close to a myth, and the best approach after trying to reduce the pollutant production is to observe valorization opportunities, and if is any, treatment for recycling and reuse before final disposal. The nature of the pollutant is an important point when mixing effluent streams, as nontoxic streams and reusable water are not mixed with toxic materials. Methodical segregation of the streams can reduce costs with wastewater treatments and priority goals such that recycling, and reuse of the water is facilitated [11, 13].

Wastewater treatment methodology follows some important steps as a preliminary and primary treatment for the removal of solids and oils if those are required, using a combination of various methods such as filtration, coagulation, and sedimentation. These treatments are size-based separations using physical methods for basic cleanup. They are followed by secondary, and tertiary treatments based on physicochemical methods and/or bio- logical methods and can remove 90% of BOD or COD and TSS from the wastewaters. Tertiary treatment involves the final polishing of the effluent by removing toxic/harmful pollutants to the desired levels [8, 13].

Due to the nonexistence of literature that characterizes the effluents of an extraction industry of olive pomace oil, we will use the data of the characterization of wastewaters generated in the production of olive oil, given the expected similarity between the effluents. Using the data obtained for Enaime et al. (2018), shown in Table 2, the physicochemical characteristics of the olive oil effluents according to different authors, the range of values is justifiable according to which variables are present in the process, such as: the olive variety, the fruit ripeness, the volume of added water, and the extraction process (press or centrifuge) [16].

Table 2: Physicochemical characteristics of olive mill wastewaters [16].

Parameter	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**Range values**
pH	-	5.2	5.1	5.7	5.3	5	4.8	4.8-5.7
Conductivity	mS/cm	5	-	11	24	81	17.5	5-81
COD	g/L	16.5	95	48	156	53	15.	16.5-156
BOD	g/L	-	-	-	-	13.4	37.5	13.4-37.5
Dry residue	g/L	11.5	84.2	-	90	39.4	53.16	11.5-90
PhC	g/L	0.8	4.82	8.8	4.1	8.6	8.9	0.8-8.9
Total nitrogen	g/L	0.06-0.3	-	0.9	-	0.5	-	0.06-0.9

1.Paraskeva *et al.* (2007), 2. Asses *et al.* (2009), 3. Karpouzas *et al.* (2010), 4. El-abbassl *et al.* (2013b), 5. Mekkl *et al.* (2015), 6. Khouft *et al.* (2015).

In some industries, one approach before developing a wastewater treatment facility is the storage of the effluents in lagoons and pools. In these tanks the effluent passes for an aging process, a combination of different process that may occur variating with the wastewater characteristics. The first process is the sedimentation, where the suspended solids is settled by the influence of gravity on the mass and size. The second process common on storage tanks are the evaporation of the water content, in a dewatering process. The third process is a digestion of the organic matter of the effluent by biological agents presents in the effluent or in the local of storage. All the process occurs concomitantly modifying the characteristics of the effluent [19, 22].

The result of the storage and aging process is, in most cases, an effluent with less organic matter and solids, making its treatment easier and cheaper, nonetheless, the sludge resulting of the steeling process needs to be collected and treated as well, and a valorization process may become useful for other industries and process. However, odors may be a problem, depending on the type of sludge involved [19, 22].

Lagoon systems used only for dewatering typically have two treatment cells. Sludge is sent to one lagoon for several months. Then this lagoon is allowed to rest while a second lagoon is filled. Then, the second one rests while the first is used again for biological sludges. The Water Environment Federation suggest solids loadings of 36 to 39 kg/m3/yr. are suggested. If used for storage, sludge lagoons can vary significantly, though depths of 3 to 5 m are typical [19, 22].

Paraskeva and Diamadopoulos (2006) estimate with the use of physicochemical treatment, olive mill wastewater has a decrease between 80 and 95% COD after a combi- nation of physicochemical technologies, including centrifugation, filtration, coagulation- flocculation and adsorption [20].

3.2.1 Coagulation/Flocculation

Coagulation and flocculation are two of the most employed physicochemical methods in effluent treatment, the process is based on invert the electrical repulsion between particles on suspension in the wastewater. To achieve this, coagulant salts are added to the water destabilizing the colloidal particles, reducing, neutralizing, or inverting their electrical charge, and then forming flocs, these flocs tend to sediment, producing a clarified liquid, as show in the Figure 3. Flocculants are also added to promote the agglutination of the already coagulated particles, facilitating the collision between them due to the slow agitation imposed on the water flow, aiming at the formation of flakes with size and specific mass that favor their removal by sedimentation, flotation, or filtration [21].

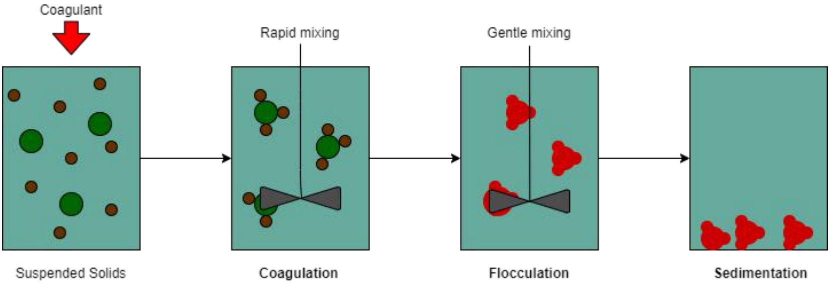


Fig 3: Scheme of coagulation/flocculation process

Typically, inorganic coagulants are aluminium sulphate/chloride, ferric chloride/sulphate, calcium/magnesium oxide, these chemicals are pH sensitive and demand pH control for the operation. The inorganic hydroxides that are formed produce short polymer chains which enhance floc formation [13, 17, 21].

Organic polymers typically are added to aid flocculation and are becoming more widely used as coagulants. Polymers are divided into three main categories: anionic, cationic and non-ionic.. Anionic polymers are often used with metal coagulants, cationic polymers may be used alone, or in combination with alum or ferric coagulants to attract suspended solids and neutralize their surface charge. Polymers are effective over a wider pH range than inorganic coagulants, and can be applied at lower doses [13, 17, 21].

To assess a chemical coagulation treatment usually a jar test is made. Jar tests simulate the conditions of reaction in full scale, allowing them to anticipate the results and choose the best coagulant dosage, pH. Test parameters typically include chemical combination and dose, mixing intensity, and settling time, after that the jar is put under a very slow mixing intensity to allow the particle aggregation, flocculation, and solids to settle to the bottom. The clarification water is analyzed to observe the new concentration of solids, the residue can be removed with filtration or settled systems [13, 21, 22].

Ranade and Bhandari (2014) alerts about the changes wastewater can have during the day, as receiving different quality materials, batch processing, and cleanup activities result in distinct wastewater's characteristics, sometimes changing the treatment protocol, and the operating performance [13, 21].

Coagulation is effective to remove color in wastewaters containing dissolved solids, but the process requires high inorganic chemical dosages producing large volumes of sludge, resulting in a high cost. The use of organic coagulants can reduce the cost due to the lower production of sludge. To provide a better techno-economically feasible operation can be utilized a mix of inorganic and organic coagulants in wastewater treatment [21 - 23].

Domingues *et al.* (2021) studied a similar wastewater (from a pomace olive oil extractor industry) with an organic load of about 50 g/L of COD and high toxicity. The best conditions found for coagulation were double phased addition of a total of 40 mg/L of coagulant polydiallyldimethylammonium chloride (PDADMAC), a highly charged cationic polymer, with results in a 15% of COD removal, after coagulation/flocculation a Fenton reaction (4 g/L of hydrogen peroxide, 2 g/L of iron (II) at pH 3 with 60 min of reaction) achieved about 45 % of COD removal [24].

In Iakovides *et al.* (2014) search, several inorganics [FeCl3, Ca(OH)2, CaO, CaCl2] and organic (PDADMAC, poly(allylamine) hydrochloride (PAH), poly(allylamine) (PAA), poly(ethylenimine) (PEI), Floccan 22-23 coagulants were tested to treat OMWW, either separately or in combination and screened with respect to their removal efficiency. The coupling of calcium hydroxide at 20 g/L, with PDADMAC in a range of 0.75–2.00 g/L led to reductions of 56% COD, 27% TSS, 43% TS and 76% PhC [25].

Vuppala *et al.* (2019) focus was the optimization of coagulation and flocculation was performed focusing on the effect of different pH and coagulant dosage values in OMWW using aluminium sulphate (Alum) and chitosan equal to 400 mg/L and 100 mg/L, respectively, and pH ranging between 3, 4 and 4.5. A 99% reduction of turbidity was observed for both alum and chitosan with 60 minutes of sedimentation [26]. Papaphilippou *et al.* (2012) used iron sulphate as coagulant and FLOCAN 23 (an anionic polyelectrolyte) as flocculant in the doses of 6.67 g/L and 0.287 g/L respectively led to an optimal removal of TSS (97%), COD (72%), and PhC (40%) [27].

Normally a coagulation/flocculation process alone is not a complete solution to wastewater treatment problems, but in the floc formation process, some of the uncharged particles and organics get physically trapped and removed, consequently im- proving the process performance. This allows to increase the biodegradability, for further biological treatment application to definitively treat the effluents [22, 23].

3.3 Portuguese Environmental Legislation

The importance of olive oil production to Portugal can be seen when 97.7% of the total of the olive grove is destined to produce olive oil, and only about 2.3% channeled to the production of table olives [3]. This makes the olive mill wastewaters a problem to be considerate at national levels and with its own legislation.

Environmental legislation is an important factor when designing wastewater treatment, it is necessary to be aware of the laws about industrial effluent disposal and specific legislations to the sector. Laws must also be observed at different levels, as it is common to vary the parameters accepted in national, regional, and municipal legislation [28].

One of most important legislation are the municipal discharge regulations, documents that regulate the discharge of effluent into municipal collectors, each adapted to the reality of the respective municipality. The effluents that may be released into public networks, must respect certain constraints, to ensure that the bodies that make up the treatment system do not affect personnel involved in operations, as well as safeguarding their protection [2, 29].

Each regulation must name the characteristic parameters dated from the respective maximum admission values so that industrial effluents are admitted to a wastewater discharge in a waterbody. In addition to these are described all substances that are prohibited, regardless of their concentrations, the annex XVIII from the decree 236/98 are shown in the Table 3 [28, 29].

Table 3: Parameters of wastewater discharge (ELV) [28].

Parameter	Unit	ELV
pH	Sorensen Scale	6.0 – 9.0
Temperature	ºC	Increase of 3ºC
BOD_5 (20ºC)	mg O_2/L	40
COD	mg O_2/L	150
TSS	mg TSS/L	60
Phenols	mg C_6H_5OH/L	0.5
FOG	mg/L	15
Total Phosphorus	mg P/L	3.0
Ammoniacal Nitrogen	mg NH_4/L	10
Total Nitrogen	mg N/L	15

ELV - Emission Limit Value

Faro Ferraz (2012) points to the importance of the *Estratégia Nacional* *para os Efluentes Agropecuários e Agroindustriais* (ENEAPAI) (National Strategy for Agribusiness and Agro-Industrial Effluents) to build a sustainable strategy for the various sectors of agro-industrial production. It proposes to integrate the specificities and characteristics of each productive sector, the effluents produced by them, and the regions where they operate to design integrated and sustainable solutions for the intervention and resolution of environmental problems caused by the normal activity of the sectors [2].

Other important legislation is the Joint Order No. 626/2000, of 6 June. This order authorizes the application of olive mill wastewater in the irrigation of agricultural soils. In this way, producers have a destination solution for their effluents without major economic costs, valuing a resource considered problematic. It is necessary to request a license for the procedure and respect a list of conditions to avoid problems, such as the prohibition in areas close to water lines and population centers, etc. [2, 30].

The decree-Law No. 208/2008, of 28 October from, transposes Directive 2006/118/EC of 12 December, on the protection of groundwater against pollution and its deterioration. This decree intends to implement measures to prevent and control water pollution groundwater, including criteria for assessing its good chemical status for the identification of significant and persistent trends towards increasing the concentration of pollutants, as well as to define starting points for reversing these trends [30].

The waterbodies monitoring is other important activities of public agencies to observe and evaluate the quality of the water and the security of the environment, preventing problems caused by pollution. On the decree 236/98, it also can be found the ideal and limits for physicochemical and biological parameters for waterbodies characterization as the techniques that should be used to determination. The values and parameters available may change based in the water destinated use as show in the Table 4.

Table 4: Parameters of waterbodies according to their destination (ERV) [28]

Parameter	**Unit**	**ERV for superficial water intended for human consumption**	**ERV for water intended for aquaculture purposes**	**ERV for bathing water**	**ERV for water intended for irrigation**
pH	Sorensen Scale	5.5 – 9.0	6.0 – 9.0	6.0 – 9.0	6.5 – 8.4
Temperature	ºC	22	Increase of 3ºC	-	-
Conductivity	µS/ cm (20ºC)	1000	-	-	-
BOD_5 (20ºC)	mg O_2/L	7	6	-	-

COD	mg O_2/L	30	-	-	-
Dissolved Oxygen	mg/L O_2	-	100% > 7	-	-
Dissolved Oxygen	% Saturation of O_2	-	-	80 – 120	-
TSS	mg TSS/L	-	25	-	60
Phenols	mg C_6H_5OH/L	0.010	(2)	0.005	-
Ammoniacal Nitrogen	mg NH_4/L	2	0.2	(3)	-
Kjeldahl Nitrogen*	mg N/L	3	-	(3)	-
Nitrates	mg NO_3/L	50[1]	-	(3)	50

ERV - Emission Recommended Value

1. ELV
2. Phenolic compounds should not be present in concentrations that alter the taste of the fish.
3. These parameters must be checked by the competent authorities whenever there is a tendency towards the eutrophication of waters.

* Except NO_2 and NO

Chapter - 4

Methodology

To design a wastewater treatment facility for local industry, the components of the effluent must be quantified, in the wastewater characterization step, the data obtained is used to develop potential management strategies and provide a baseline for evaluating the effects of treatment processes, water conservation, or regulations. To develop a pre and primary treatment filtration tests using different media and coagulation tests using commercial coagulants must be carried out.

The Wastewater used was collected on Mirabaga, an olive pomace oil extractor industry, in Mirandela (Portugal), between April and September 2021. The amount of wastewater was delivered to the laboratory and stored as required by the Standards Methods to the analysis and tests. This study was carried out at the Chemical Process Laboratory, at the Instituto Politécnico de Bragança, from September 2020 to September 2021.

Samples from the river close to the industry were also collected on May 19, 2021, to assess its water quality, and eventual influences from the industrial activity to the Tua river.

4.1 Wastewater Characterization

The wastewater characterization 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 [31].

4.1.1 pH and Conductivity

As the wastewater is delivered to the laboratory, a homogeneous sample is used to measure Hydrogen Potential using a HANNA pH meter under magnetic agitation and local temperature of 20ºC. The Conductivity was measured in the same way using a conductivity meter WTW model *Inolar Cond level 1*.

4.1.2 Biochemical Oxygen Demand

The BOD_5 was determined by the standardized respirometric OxiTop method (WTW, Weilheim, Germany). To the sample bottle were added a fresh wastewater volume as recommended by the fabricant and equipped with a magnetic stirrer and NaOH pellets in the headspace, the inoculation was made, when necessary, as the control samples and blanks required by the standard methods. They were placed in an inductive stirring system at 20ºC. After five days, the data was collected and analysed.

4.1.3 Chemical Oxygen Demand

The COD method used was the Colorimetric Method in a Closed Reflux process from the Standards Methods Standard ampules were added 2.5 mL from the sample, 1.5 mL digestion solution, and 3.5 mL sulfuric acid reagent. The samples were digested for 120 minutes at 150 ºC. One blank was digested to confirm good analytical reagents and to determine the blank COD. The calibration curve was made with a Potassium hydrogen phthalate standard solution, diluted to concentrations equivalent to 0 to 1000 COD mg O_2/L. The samples and calibration curve were analysed in a Spectrophotometer JASCO V-530 at 600 nm, obtaining equation 1:

$$y\left(\frac{mg\ O_2}{L}\right) = 3145.1 * x(abs) + 1.1523 \qquad \text{(Equation 1)}$$

4.1.4 Phosphorus

An adaptation of the Standards Methods was used to determine the phosphorus contentment, 50 mL from the sample were added to an Erlenmeyer with 0.5 g of potassium persulfate and put in the autoclave for 60 minutes at 120 ºC and 1 atm. To the flask were added 0.5 g of ascorbic acid. 10 mL of the solution were added to a test tube, 1 mL of a reagent mixture (12.5 mL Sulfuric Acid, 1.25 mL Potassium Sodium Tartrate solution and, 3.75 mL Ammonium Molybdate solution) were added and agitated in a vortex. After the colour development, the sample and the calibration curve were analysed in a Spectrophotometer JASCO V-530 at 882 nm (equation 2):

$$y\left(\frac{mg}{L}\right) = 1.786 * x(abs) - 0.0055 \qquad \text{(Equation 2)}$$

4.1.5 Ammonia

The ammonia content was determined by the direct nesslerization method based on the Standard Methods; a preliminary distillation was necessary for the sample. 500 mL of the sample were previously neutralized and added 25 mL of borate buffer solution and then had the pH adjusted to 9.5 with NaOH solution before distillation. 300 mL of the distillate was received and mixed with 50 mL of boric acid before the volume was completed to 500 mL. One drop of EDTA solution was added to 50 mL of the treated sample and 2 mL of the Nessler reagent. After 10 minutes of colour development, the sample and the calibration curve were read at 410 nm in the Spectrophotometer JASCO V-530 producing the equation 3:

$$y\left(\frac{mg}{L}\right) = 5.0931 * x(abs) + 0.0062 \qquad \text{(Equation 3)}$$

4.1.6 Organic Nitrogen

The Macro-Kjeldahl Method of Standards Methods was applied, and the sample used is the residue from the distillation flask from the ammonia determination. 50mL of the digestion reagent (Sulfuric Acid, Potassium sulphate, and Copper (II) sulphate) were added to the sample, it was digested until the sample became pale green. After cooling, it was diluted to 300 mL with water and 50 mL sodium hydroxide-thiosulfate reagent was added to form an alkaline layer at flask bottom. Connecting the flask to a steamed-out distillation apparatus and swirl flask to ensure complete mixing the sample was distilled until collect 200 mL, and 50 mL of a boric acid solution was used as an absorbent. The organic nitrogen content was determined by the titrimetric method with a standardized solution of 0.02N Sulphuric Acid until the indicator change colour to a pale lavender. A blank was cared for all the process.

4.1.7 Fats, Oils and Grease

The samples were acidified with sulfuric acid to pH 2 or lower for conservation, and the oils and grease were determined by the Soxhlet Extraction Method. Using vacuum filtration equipment, the samples were filtered no more water passes through paper filter. All filter material containing sample fit into an extraction thimble, as any pieces of material remaining with a filter paper soaked in extraction solvent. The thimble was dried in a hot-air oven at 103 °C for 30 min. The extraction flask was weight and add 250 mL extraction solvent, n-hexane. Extract oil and grease in a Soxhlet apparatus, at a rate of 20 cycles/h for 4 h.

The solvent was recovered with distillation and the flasks were to draw the air for 1 minute and let it cool in the desiccator before weighing. Considering the organic solvent is free of residue, the gain in weight of the tared distilling flask is due to oil and grease. The total gain in weight, A, of tared flask, less calculated residue from solvent blank, B, is the amount of oil and grease in the sample, when sample was brought into the laboratory, mark sample bottle at the meniscus for later determination of volume (equation 4).

$$FOG\ (g/L) = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 4)}$$

4.1.8 Aromaticity

To determine the aromaticity of the samples, it was made a calibration curve, in the range of 0 to 200 mg/L of phenol P.A. The sample and the calibration curve were analysed in a Spectrophotometer JASCO V-530 at 254 nm producing the equation 5:

$$y\left(\frac{mg}{L}\right) = 17.62 * x(abs) - 0.4918 \qquad \text{(Equation 5)}$$

4.1.9 Phenolic compounds

To measure the phenolic compounds using the Folin-Ciocalteu method, a calibration curve was built, in the range of 0 to 100 mg/L of phenol as the model compound. In the test-tube were added 0.5 mL of the Folin-Ciocalteu reactant, along with 0.2 mL of the sample (previously diluted) and 8.2 mL of distilled water. The solution was left to rest for 10 minutes. After this, 1 mL of a Na_2CO_3 solution was added and left for 60 minutes to develop colour. The samples were analysed in UV-VIS Spectrophotometer JASCO V-530 at the wavelength of 765 nm producing the equation 6:

$$y\left(\frac{mg}{L}\right) = 1043.6 * x(abs) - 8.2288 \qquad \text{(Equation 6)}$$

4.1.10 Alkalinity

To measure the capacity of the wastewater to neutralize acids the sample was submitted to a Volumetric Titration which sulphuric acid. Fist was added the indicator phenolphthalein to determine simple alkalinity, after the titration, the indicator methyl orange were added and the sample were titrated again, to determine the total alkalinity (equation 7).

$$Alkalinity\ (mg\ CaCO3/L) = \frac{HCl\ volume, mL\ x\ MM[CaCO3]\ x\ 1000}{Sample\ volume, mL} \qquad \text{(Equation 7)}$$

4.1.11 Solids

The Standards Methods was used as a based method for the measurement of total solids, total dissolved solids, total suspended solids, fixed and volatile solids. All the evaporating dishes were cleaned by calcination at 550 °C for 1 hour in a muffle furnace.

A sample volume would yield a residue between 2.5 and 200 mg. Pipet a measured volume of well-mixed sample, during mixing, to a pre weighed dish. First, the samples were evaporated to dryness on a steam bath and then dried in an oven at 103 to 105 °C for at least 1 h, cooled in a desiccator to balance temperature and weight. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight is obtained, or until weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. All samples are made in duplicate. The total solids were obtained by calculating the difference between the last weight (A) obtained and the weight of the dish (B), the value was divided by the sample volume (equation 8).

$$mg\ TS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 8)}$$

To measure the Total Dissolved Solids (TDS) and Total Suspended Solids (TSS), a homogenous sample of the wastewater was filtered in a glass-fiber filter with an applied vacuum. Then, the filter was washed with three successive 10 mL volumes of reagent-grade water, allowing complete drainage between washings, and continuing suction for some minutes after filtration is complete. The filter was weight before use and evaporated for at least 1 h in the oven. The total filtrate (with washings) was transferred to a weighted evaporating dish and evaporated to dryness on a steam bath. The evaporated sample was dried for at least 1 h in an oven at 180 ºC, cooled in a desiccator to balance temperature, and weight. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight is obtained, or until weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. All samples are made in duplicate. The total dissolved solids were obtained by the difference between the last weight obtained (A) and the weight of the dish (B), the value was divided by the sample volume (equation 9). The TSS were obtained by the difference between the last weight obtained from the filter + dish (C) and the initial weight of the filter + dish (D), the value was divided by the sample volume (equation 10).

$$mg\ TDS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 9)}$$

$$mg\ TSS/L\ = \frac{(C-D)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 10)}$$

To measure the Total Volatile Solids (TVS), the residue produced by the Total Dissolved Solids was ignited to constant weight in a muffle furnace at a temperature of 550°C, for 15 to 20 minutes, the ignition is required for 200 mg residue (equation 11).

$$mg\ TVS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 11)}$$

where:

A- weight of residue dish before ignition, mg, B- weight of residue dish or filter after ignition, mg, and

4.1.12 Zahn-Wellens Biodegradability Test

The Zahn-Wellens test was adopted as OECD Guideline 302 B for determining inherent biodegradability in 1981. The reactor containing the test substance (5 mL) and a relatively large amount of activated sludge (16 mL) was added to the reactor and swelled to 2L using distilled water previously added with mineral nutrients is agitated and aerated at 20-25 °C in the dark or in diffuse light for up to 28 days. A blank control reactor, containing activated sludge and mineral nutrients but no test substance, are run in parallel [32].

A fourth reactor containing a control substance was used to validate the results obtained, the substance used was ethylene glycol at a concentration of 0.5 mL/L. The biodegradation process is monitored by determination of COD in filtered samples taken at daily or other time intervals. The ratio of eliminated COD, corrected for the blank, after each time interval, to the initial DOC value is expressed as the percentage biodegradation at the sampling time. The percentage biodegradation is plotted against time to give the biodegradation curve [32].

4.2 Waterbody quality

In order to assess the quality of the water in the river that receives the effluent from the industry after its treatment, samples were collected from four points on the Tua river, to evaluate the variation of the parameters: temperature, conductivity, dissolved oxygen and TDS were measured in situ, pH and turbidity, BOD_5, COD, total phosphorus content, ammonia and organic nitrogen and nitrate content, aromaticity, PhC, alkalinity and TS.

All the characterization used as base the Standard Methods for the Examination of Water and Wastewater (2005) as described in the last topic.

4.2.1 Measurement *in situ*

The parameters temperature, conductivity, dissolved oxygen, and TDS were measurement in the moment of sampling using a Hach HD40d probe.

4.2.2 Turbidity

The turbidity of the samples was measured with an Interface Photometer 7000se from Palintest in the wavelength of 520 nm as required by the equipment.

4.2.3 Nitrates

The nitrates content was measured using the method described in the

Standard Methods for the Examination of Water and Wastewater, to 50 mL clear sample, filtered, if necessary, were add 1 mL HCl solution and mix thoroughly. The absorbance of samples was read in the wavelength of 220 nm. The absorbance was read in the wavelength of 275 nm to determine interference due to dissolved organic matter. The samples were analysed in UV-VIS Spectrophotometer JASCO V-530 at the wavelength of 220 and 275 nm according to the equations 12 and 13:

$$x\ (abs) = abs220 - 2 * abs275 \qquad \text{(Equation 12)}$$

$$y\ \left(\frac{mg}{L}\right) = 4.1024 * x\ (abs) - 0.1298 \qquad \text{(Equation 13)}$$

4.3 Coagulation/Flocculation

In the coagulation process the destabilization of the particles present in the wastewater occurs due to the addition of a chemical product, in adequate quantity and conditions, allowing in a later stage, flocculation, the aggregation of these impurities in larger particles. The coagulation process normally takes last than 1 minute and happens in the fast-mixing unit. However, in the flocculation there is a need for slow agitation, so that shocks occur between the particles, which agglomerate forming flocs, which can be removed by sedimentation, flotation, or rapid filtration.

To determine the optimal process parameters, it is necessary to carry out three steps for each coagulant studied: determination of the minimum coagulant dosage; pH optimization; coagulant dosage optimization. The effects of adding different flocculants can also be assessed for test.

Using 200 mL sample on a magnetic stirrer, small amounts of coagulant were added to effluent at pH 5.0. After each addition, promoting rapid mixing for 1 minute followed by 3 minutes of slow mixing and at least a settling period of 10 minutes. The addition was made until visible formation of a supernatant layer. In the case of coloured effluents, the reduction of turbidity can be used as a parameter to determine the ideal coagulant volume.

To determine the ideal pH for the coagulation, a jar test equipment was applied, in this, six beakers of sample and the minimum dose of coagulant obtained in the first experiment was added. The pH was adjusted between 3 and 8, values adequate to the coagulant chosen (Aluminium Sulphate), using acid or base solutions. A rapid mix (120 rpm) was promoted of each sample for 1 min; followed by a slow stirring (30 rpm) for 3 min and, finally, 15 min of settling. In a sample from the supernatant the turbidity was measure using one turbidimeter MERCK Turbiquant 3000IR to determine which pH presented the higher removal. Due to colour alteration of the effluent analysed the turbidity were measured after the pH adjustment and at the end of the sedimentation time to provide a better removal measurement.

The effluent obtained in the most favourable conditions was submitted to characterization of some important parameters: Solids (TSS, TDS and TS), COD and Phenolic compounds.

Chapter - 5

Characterization

To determine which wastewater treatment is a good option for a specific effluent, it is necessary to perform an extensive characterization encompassing physic and chemical parameters.

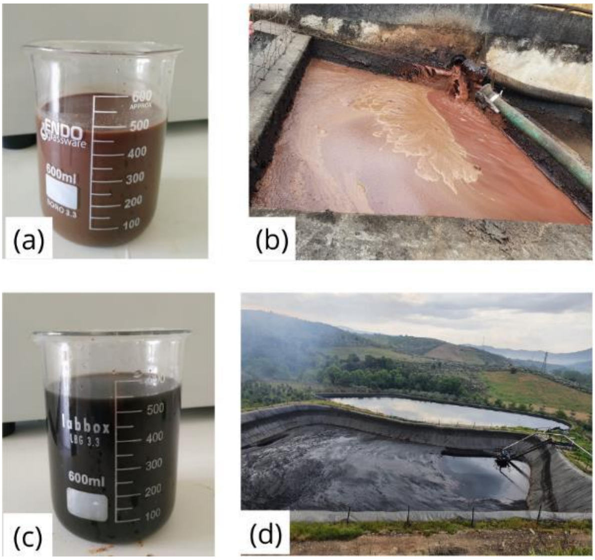


Fig 4: Visual aspect of effluent 1 and 2 and respective collection site

The wastewater was collected at two different locations in the plant. The first is the effluent as it leaves the process of olive pomace oil production, and the place and aspect can be seen in Figure 4 (a, b). The other is from the second storage tank, place and aspect are showed in Figure 4 c) and d).

The visual aspect of the two wastewater is very distinct in colour and turbidity. Effluent 1 is new, have a higher amount of BOD, COD and TSS, resulting in a lighter colouration and higher turbidity when compared to effluent 2, which is older and passes by a decantation process in the pool. An outstanding behaviour presented in effluent E1 and 2 is the absence of an oily layer caused by the separation of the FOG content as normally present in OMWW, it may be due to the smaller content of olive oil, naturally due the second extraction, and the emulsification of the any remaining FOG content.

The parameters choose to be determined: pH, conductivity, Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), phosphorus content, ammonia and organic nitrogen content, oils and grease, aromaticity, phenolic compounds, Alkalinity, and solids. The results for the two effluents are presented in Table 5:

Table 5: Physicochemical characteristics of effluent 1 and 2

Parameter	Unit	Effluent 1	Effluent 2
pH	-	4.21	4.97
Conductivity	mS/cm	9.30	8.80
BOD_5	g O_2/L	48.4 ± 2.1	15.01 ± 1.2
COD	g O_2/L	126.64 ± 7.63	28.52 ± 5.58
Organic nitrogen	g N/L	1.48 ± 0.05	0.21 ± 0.01
Ammoniacal nitrogen	mg N/L	73.13 ± 1.45	19.87 ±0.73
Phosphorus	g P/L	0.54 ± 0.01	0.33 ± 0.01
FOG	g/L	4.62 ± 0.35	2.63 ± 0.11
PhC	g/L	7.82 ± 0.13	1.42 ± 0.14
Aromaticity	g/L	51.66 ± 0.16	11.74 ± 0.5
Alkalinity	g/L	3.77 ± 0	4.71 ± 0.92
TS	g/L	54.97 ± 1.49	23.65 ± 1.46
TDS	g/L	43.57 ± 1.16	19.93 ± 0.49
TSS	g/L	3.28± 0.28	1.28± 0.1
TVS	g/L	45.17 ± 2.60	15.89 ± 1.05

When compared with the Emission Limit Values in the discharge of wastewater present in Decree-Law No. 236/98 of 1st August, all parameters analysed in the characterization of both effluent 1 and 2 are nearly 1000 times above the established limits, what confirms the need to implement a treatment unit for industrial effluents [28].

The polluting power of this effluent can be attributed to the high organic load, observed in the large concentration of BOD_5 and COD, organic nitrogen, and phosphorus content. Ranade and Bhandari (2014) attributed this to the presence of lipids, sugars, tannin, pectin and lignin, the high concentration of phenolic compounds as well as phosphate salts. The high organic load can also be attested by the values of TVS, that are close to TS, showing the most of solids have an organic nature.

The data obtained by Enaime *et al.* (2018) and present in Table 2, shows a similarity on the physicochemical properties of the primary and secondary olive oils extractor industry wastewaters, the pHs, conductivity, solids and nitrogen and phenolic contents are within the range of values proposed in the article. Nonetheless, the organic matter in E1 is superior the range in BOD_5 and COD content, only coming to lower values after aging in the storage tanks.

This proximity of physicochemical parameters to OMWW, makes this effluent a good candidate to reuse in irrigation of olive groves, the legislation only asks for a treatment to ensure pH compatibility, but this action needs monitoring by the competent professionals and apply for a license from the respective regional environmental directorate as described in Joint Order No. 626/20.

The lagoons may be considering a step in the pre-treatment, E2 characterization shows the reduction of 57% of TS, 54,3% of TDS, 61% TSS, 77.5% of COD, 69% of BOD and 81.8% of PhC when compared with the E1, newly produced. This step has the advantage of using the lagoons used by the industry only to stock the effluent, is a cheaper way to have good reductions in the parameters due to sedimentation and digestion of the effluent.

The disadvantage of the use of lagoon is the odour produced by the digestion and evaporation, increasing principally in the summer due the hotter temperatures and the dry climate. The lagoon accumulates the sludge provident from the decantation whereas it has no drainage or withdrawal system, it must be empty after some time and the sludge treated, in most cases using dewatering process as drying before their final disposal in landfills.

The biodegradability of E1 and E2 were measure based in the COD/BOD_5 ratio, and were obtained values of 2.62 and 1.90, respectively. A wastewater is considered easy degradable for a $COD/BOD_5 < 2.5$ and may be degradable with some difficult when $2.5 < COD/BOD_5 < 5$, to higher ratios, biological degradation is not recommendable. It makes E2 a better candidate for a biological treatment then E1 without pre-treatment. Domingues *et al.* (2021) had for the same type of effluent found a much smaller biodegradation ration, on 9% of the organic matter was biodegradable [24]. A higher ratio (26%) indicates a high biodegradable organic compounds fraction, and a biological treatment may be effective as future process in the treatment. In the Figure 5, is observed the Zahn-Wellens test, it shows a similar behaviour to both effluents.

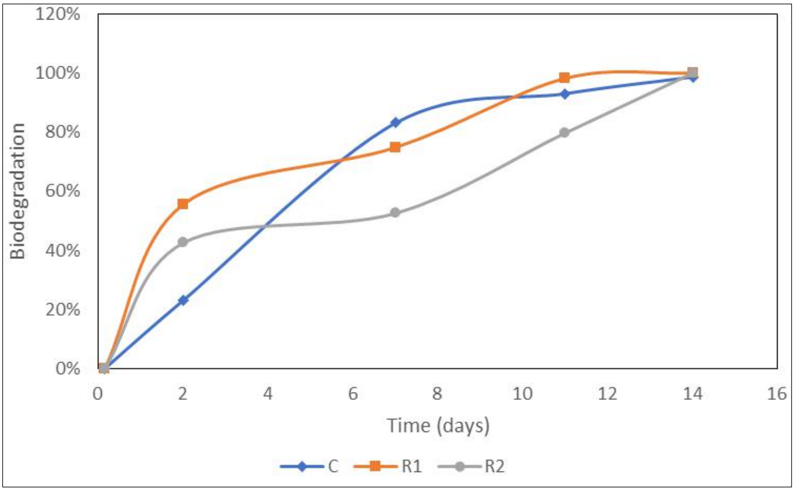


Fig 5: Zahn-Wellens biodegradation test curves

In the Zahn-Wellens test, activated sludge from the local domestic wastewater treatment unit is used to degrade an amount of the two effluents (R1 and R2). The third reactor (C) for control is used to validate the results using ethylene glycol as a control substance to determine the sludge quality and adaptability. A blank reactor with the same conditions as determined for the OECD Guideline (1992) was settled with no biodegradable substance to reduce influences in the COD determination by a colorimetric method due to parallel reactions and variations in the activated sludge. Due to the good adaptability of the activated sludge, in 14 days all the effluents were complete degraded.

However, even with COD/BOD$_5$ ratio that suggest biological treatments where an good option to reduce the pollutant load, the values to BOD and COD were high enough to require primary treatments to reduce the concentrations from g/L to mg/L. Analysing previous works with effluents with a polluting load close to that found in effluents and from nearby matrices, a promising route for treatment is the reduction of solids and organic matter by primary treatments such as coagulation/flocculation and flotation. A biological reactor can be applied as a secondary treatment to digest the remain biomass to acceptable levels, followed by tertiary treatments such as filtering and polishing the effluent until the emission limit values are respected in their entirety [24].

Another crucial aspect is its acidity due to the presence of organic acids, capable of changing the pH of a waterbody if discarded without treatment. The high among of organic and inorganic compounds, that work as nutrients, can destabilize the natural condition on the recipient waterbody, favouring the growth of algae in the process acknowledge as eutrophication. The concentration of phenolic compounds is other potential pollutant in this effluent, these compounds are known to be toxic and inflict severe and long-lasting effects on humans and animals and must have their concentration reduced before reach the waterbody.

An important aspect in the project to design a wastewater treatment facility is to evaluate the quality of the waterbody that is receiving the effluent. To ensure the environmental safety of the river in the point near the factory, the water was collected May 19, 2021. Sampling points selected to monitoring the river water quality is exhibited in Figure 6.

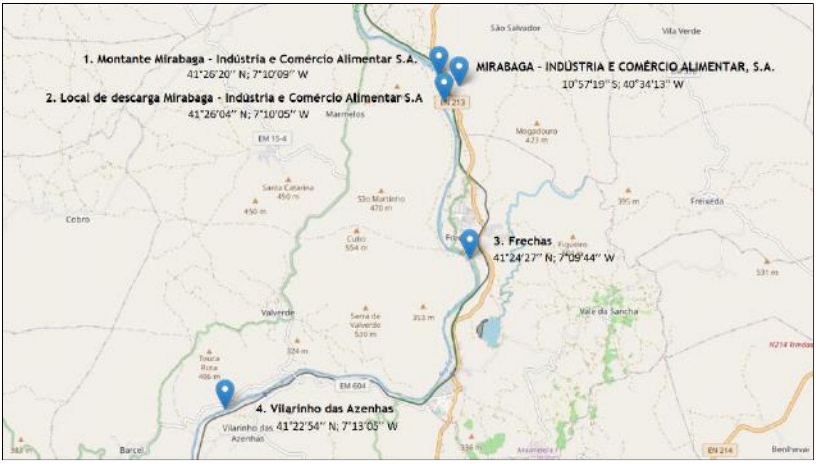


Fig 6: Tua river sampling points

The point 1 corresponds to the upstream sampling point, where the water quality has no influence of the factory studied and, point 2 corresponds the place of wastewater discharge from Mirabaga. Points 3 and 4 were downstream the industrial unit to evaluate the depuration of any pollution charge the factory relies on the river. Point four also corresponds to a pluvial beach accessible to the local population used for recreation and domestics activities.

The impact of industrial wastewater disposal is to be seen in point 2, the data shows a raise in parameters COD and BOD_5 when compared with point 1, as noted in Table 6. No effluent characterized previously in this article is released in the waterbody, this alterations in the values were due to the water used to cool the streams out the separation processes and the water recovered in the solvent recuperation process, the effluent pass for a cooling step before being pour in the river.

The waterbody has a good depuration capacity, with the parameters returning lower levels of organic matter as seen in point 3, indicating the factory do not overload the natural ecosystem. In point 4, turbidity, COD, nitrogen content and TSS increased, and can be associated to the human activity present in the area.

The water quality was assured comparing the results with the Portuguese water legislation, Decree-Law No. 236/98 of 1 August (shown in Table 4) considering the maximum recommended value for irrigation and bathing waters, none of the parameters obtained values higher than those allowed, securing the good quality of the waterbody and no negative influence from the factory at time of the sampling.

It is important to emphasize that the quality of the receiving river must be verified at a frequency lower than or equal to that described in the Decree-Law No. 236/98 of 1 August. This monitoring is essential for a good environmental management of the industry and prevention of the pollution of Portuguese waters.

Table 6: Water physicochemical characterization in four locations along the Tua river

Parameter	Unit	Point 1	Point 2	Point 3	Point 4
Temperature[1]	ºC	16.2	18.8	17.3	17.5
Conductivity[1]	µS/cm	47.3	56.5	46.5	45.9
TDS[1]	mg/L	26.9	31	26.3	25.7
Dissolved Oxygen[1]	mg O_2/L %	9.1 95.4	8 87.1	8.78 92.5	8.88 94.1
pH	-	6.4	6.14	6.2	6.17
Turbidity	NTU	12	27	11	14
BOD_5	mg O2/L	< 10	31	< 10	< 10
COD	mg O2/L	14	86	15	24
TSS	mg/L	6.9	28.9	5.2	7.5
TDS	mg/L	61.7	111.3	52.4	49.4
Ammoniacal Nitrogen	mg/L	0.44	0.31	0.27	0.34
Nitrates	mg/L	0.69	0.39	0.09	0.51
Total Phosphorus	mg/L	0.02	0.01	0.02	0.03
PhC	mg/L	< DL	< DL	< DL	< DL
Aromaticity	mg/L	13.2	23.2	13.5	14.8

[1]: parameters measured in the local where the samples were collected

<DL: lower than the method detection limit.

Chapter - 6

Coagulation/Flocculation

Coagulation and flocculation are some of the most extensively used wastewater treatments, due to their simple design and affordable price, producing considerable reductions in physicochemical parameters such as TSS, BOD, COD and PhC. The addition of coagulants, inorganic and organic, associated with agitation is sufficient to destabilize most of the colloids and molecules present in the effluent and form flakes that then are settle by gravity. The result can be observed by the formation and visual separation of the flocs and measured using turbidimeters.

The effluent 2 was chosen for the coagulation process since it has lower levels of COD, BOD and TSS due to the ageing process it passes in the lagoons. The chosen coagulant was alum ($Al_2(SO_4)_3$), based on the coagulation behaviour presented in OMWW coagulation treatments observed by Khouni *et al.* (2020), Vuppala *et al.* (2019), Iakovides *et al.* (2014) [25, 26, 33]. The flocculation was studied to improve the sedimentation, RIFLOC F45 was the flocculant chosen for the test due to it cationic nature, its positives result over OMWW have already been proven, pointed by Domingues *et al.* (2021) and Rattanapan *et al.* (2011) [24, 34].

First, the coagulant concentration was studied with the assistance of a turbidimeter to evaluate the turbidity removal, at pH 5. The settling time was of 20 hours to ensure the complete setting from the flocs formed in the coagulation process. The removal is shown in Figure 7, based on the initial turbidity of E2 (445.03 NTU).

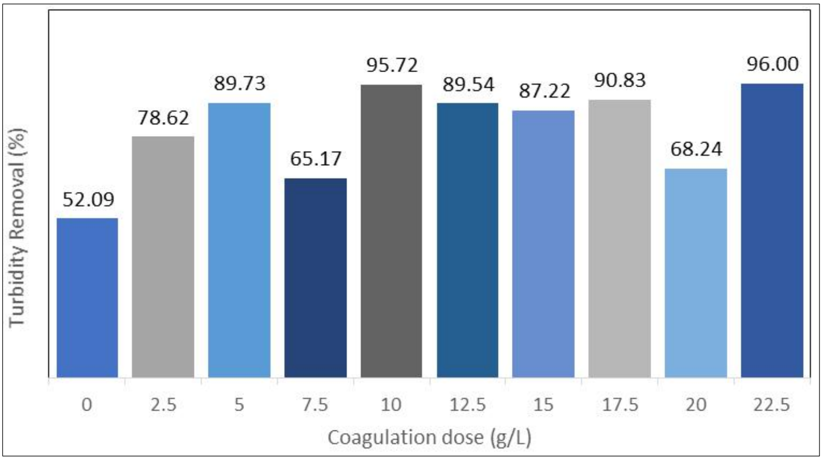


Fig 7: Turbidity removal vs. Aluminium Sulphate dose

The best removal occurs to the alum concentrations of 10, 17.5 and 22.5 g/L, obtaining more than 90% of removal with a settling time of 20h. An anormal behaviour is obtained with concentrations of 7.5 and 20 g/L, the lower turbidity may be caused by the presence of smaller flocs that tend to suspend with any small disturbance in the system.

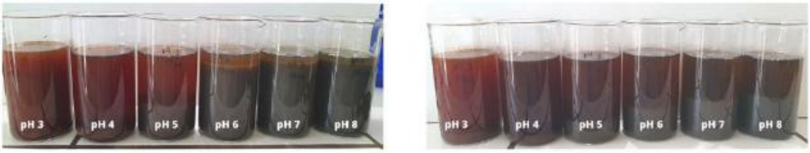
To the alum concentrations that presented better removal values (10, 17.5 and 22.5 g/L) a pH optimization test was made, where the pH was adjusted between 3 and 8 and the turbidity measured at the end 30 and 120 minutes as presented in Table 7.

Table 7: Turbidity removal (%) at pH variation in 10, 17.5 and 22.5 g/L coagulant and resting time of 30 and 120 minutes

$Al_2(SO_4)_3$	10 g/L		17.5 g/L		22.5 g/L
Settling Time	**30 min**	**120 min**	**30 min**	**120 min**	**30 min**
pH 3	0	52	-	7	0
pH 4	21	63	58	76	95
pH 5	77	81	80	89	82
pH 6	-	87	-	69	85
pH 7	-	84	-	90	88
pH 8	-	66	-	92	92

The turbidity was determined only for the samples that formed a large enough supernatant layer (30 mL required by the turbidimeter). The higher pH demonstrated a delay in forming a layer, the dark colour also impairs the visualization of the layer, as visualized in Figure 8. To 22.5 g/L of coagulant the turbidity removal to 30 minutes shown results close to the find to 17.5 g/L and 120 minutes, then the test does not proceed to 120 minutes of sedimentation.

10 g/L, 30 min **10 g/L, 120 min**



17.5 g/L, 30 min **17.5 g/L, 120 min**

22.5 g/L, 30 min

Fig 8: Visual aspect of samples for pH variation in 10, 17.5 and 22.5 g/L coagulant and settling time of 30 and 120 minutes

The best absolute turbidity removal was observed for pH 8 and coagulant concentrations of 17.5 g/L (120 min) and 22.5 g/L (30 min) with removal higher than 91%. Nonetheless, using 10 g/L of coagulant at pH 5 we achieved 77.4% turbidity removal after 30 min and 81% after 120 min, which makes this a standout removal condition to be investigated.

After the optimization of coagulant dosage and pH parameters, the addition of flocculant was evaluated adding RIFLOC F45 in the final concentration of 2 and 4 mg/L, in the conditions of 10 g/L and 17.5 g/L and different pH, as exhibited in Table 8.

Table 8: Turbidity removal for flocculant addition on different coagulant concentration and pH

Coagulant dosage	**pH**	**Flocculant dosage**	**Turbidity removal (%)**	**Flocculant dose**	**Turbidity removal (%)**	
		(mg/L)	**30 min**	**(mg/L)**	**30 min**	**24 h**
10	3	2	35	4	68	81
	4		64		68	72
	5		43		74	91
	6		23		62	90
	7		4		63	92
	8		56		84	95
	9		-		-	98
	10		-		-	98
	11		-		-	99
	12		-		-	98
17.5	3	2	36	4	-	69
	4		76		-	86
	5		79		-	92
	6		68		-	90
	7		62		-	85
	8		45		-	87
	9		-		-	96
	10		-		-	95
	11		-		-	98
	12		-		-	98

Higher pH values were evaluated in this experiment due to an improving trend in turbidity removal from the increase in pH. The addition of flocculant in higher concentrations also shows improvements of at least 30%, discarding the study of smaller coagulant concentrations. The similarities of turbidity removal for different concentrations design the study in a future test of the lower concentration (10 g/L) reducing the treatment cost.

The improvement using flocculant was made by evaluating the removal of TSS, TDS, TS, COD and PhC in the most prominent conditions: 10 g/L at pH 5, due to the proximity of the effluent pH, and pH 8 and 9 due to the higher removal. The reduction results for a resting time of 3 h, much more suitable to a real coagulation process, are shown in Table 9:

Table 9: Turbidity, COD, PhC, and solids removal to the addition of flocculant in different pH (% removal)

pH	Flocculant (mg/L)	Turbidity removal	COD removal	PhC removal	TS removal	TDS removal	TSS removal
5	0	43.	69	0	10	4	66
	4	74	70	28	24	17	98
8	0	0	71	16	0	0	0
	4	0	72	0	4	0	94
9	0	84	68	0	2	0	25
	4	53	73	15	7	0	71

Sedimentation period is an important parameter in coagulation tests to observe the decantation velocity, in the coagulation tanks in wastewater treatment facilities. To obtain results closer to the reality, the resting time was set in 3 hours, by cause of no-good decantation of the samples with pH of 8 and 9 after a resting time of 1h. Although, 3 hours show to be too small amount time interval to obtain good results to solids removal for this samples. Observing the data from pH 5, is clear the improvement of removal levels with the addition of flocculant, producing a TSS removal of 98% after 3 hours of sedimentation.

To pH 5 the influence of flocculant addition is clear to visualize in Figure 9. All the parameters had they removal improved whit the addition of RIFLOC F45, the TSS removal reach almost 98%, 33% superior to the sample without flocculant addition. For turbidity, TS, and TDS parameters the removal was increase 42, 59 and 77%, respectively. To COD removal the improvement was almost despicable (1.6%).

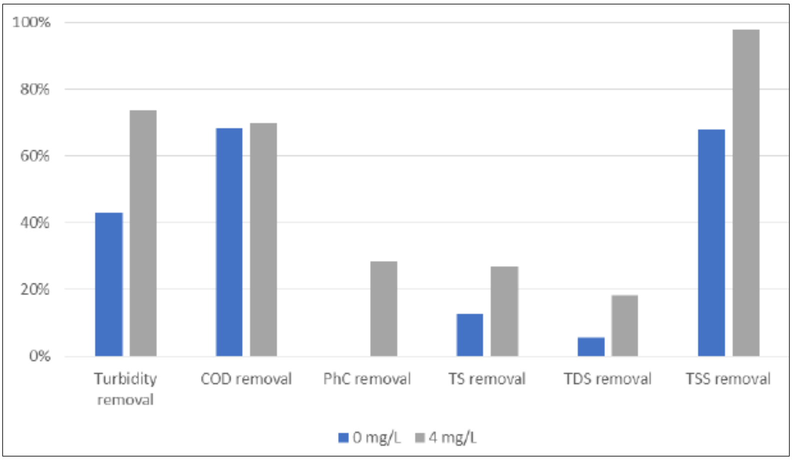


Fig 9: Influence of flocculant addition at pH 5

To ensure the best coagulant concentration, the first test was redone in the optimal pH (5), and the parameters, turbidity, TSS, COD and PhC were determined to evaluate any improvement in the removal levels for these parameters for concentrations close of the minimal dose. The results are shown in Table 10.

Table 10: Turbidity, TSS, COD and PhC removal at pH 5 and different coagulant concentrations (% removal)

Coagulant dosage (g/L)	Turbidity	TSS	COD	PhC
10.0	96	77	76	85
15.0	89	80	73	89
20.0	71	82	76	86
25.0	95	83	79	84
30.0	90	85	76	96

In Figure 10 is observed that the decrease in turbidity is not directly related to the decrease in TSS. This may be due to the dissolved solids reduction with coagulation due to secondary processes. This low ratio, together with the low variation in COD removal, makes the *Alum* concentration of 10 mg/L still the ideal minimum concentration for the process.

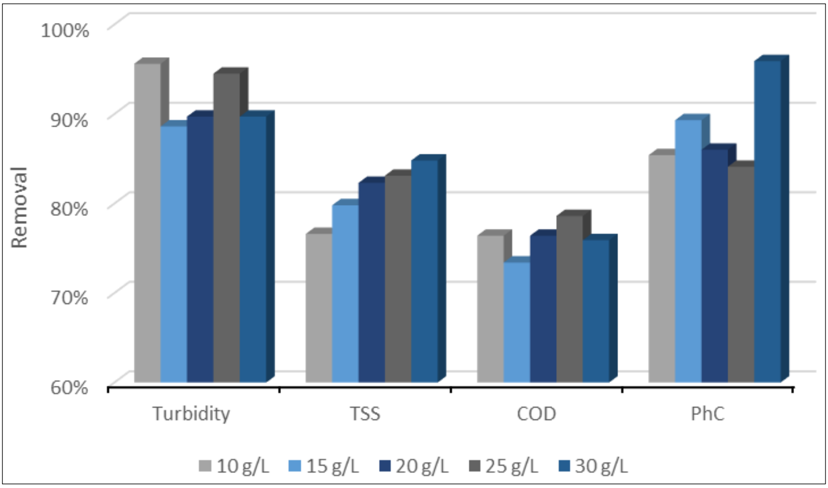


Fig 10: Removal variation for different coagulant concentrations

The best results were obtained for concentration of 30 g/L, which has the best remotion for PhC and TSS, but no statistic relevance was observed in these values. The addition of 2-3 times the concentration of coagulant does not produces a relevant removal in the parameters, making the dosage of 10 g/L of Aluminium Sulphate more interesting, leading to removals of TSS, COD and PhC of 76%, 76% and 85%, respectively.

Despite the good remotion awarded, the clarified effluent still present concentrations of COD, TSS and PhC superior to the maximum allowable values. So, that industrial effluents are admitted to a wastewater discharge in a waterbody, highlighting the fact that coagulation/flocculation process alone is not generally a complete solution to wastewater treatment problems, the reduction of this parameters, however, provides better conditions to a biological treatment, as increasing the biodegradability of the effluent and reducing the volume necessary in a reactor and decanter due to the high sludge formation.

According to other article that apply coagulation/flocculation process in OMWW, two cases are observed, the first when the concentration used are much smaller for the same coagulant, as the one obtained by Vuppala *et al.* (2019), who achieved a reduction of 99% of turbidity, with alum concentration of 400 mg/L plus chitosan (100 mg/L), and removal of 57.16% COD and 62.89% PhC with 800 mg/L of alum [26]. This behaviour may be due to the distinct wastewater composition, the effluent used in this study is the result of chemical extraction and presents they FOG content in emulsification, contrasting with the normal aspect encounter in OMWW where an oily layer is formed in stored effluents and normally is removed in pre-treatments before coagulation/flocculation. This aspect may result in the difference of effluent particles nature in suspension and its interaction with coagulants, demanding higher concentrations.

Using different coagulants, it was found in literature the report of higher concentrations and slow settling velocities, as observed by Iakovides *et al.* (2014) in the study of OMWW coagulation using electrolytes ($FeCl_3$, $Ca(OH)_2$, CaO, $CaCl_2$) and polyelectrolytes (PDADMAC, PAH, PAA, PEI, Floccan 22-23), the best results were obtained with calcium hydroxide at 20 g/L leading to removals of 56% COD, 27% TSS, 43% TS and 76% PhC [25]. Papaphilippou *et al.* (2012), also obtained high removals of TSS (97%), COD (72%), and PhC (40%), using iron sulphate in the concentration of 6.67 g/L associated with flocculant FLOCAN 23-287 mg/L [27]. These concentrations are consistent with the values found in this study, producing even values close to those obtained in the reduction of the studied parameters.

One important observation must be done about the aspect of the solids decanted with the coagulation and flocculation process in the studied conditions. Small and light flakes were produced, which corresponds to inadequate sludge compaction, and under the slightest agitation rise, rising the turbidity of the supernatant as well. The collection of the supernatant must be carefully made with a pump, or a filtration process must be used to obtain a supernatant with the lowest concentration of solids possible. The test of different flocculants is carried out to improve the appearance and weight of the flakes produced in the treatment, facilitating their removal.

Chapter - 7

Conclusions

The concept of Circular Economy is already being applied in the olive oil sector in Portugal, with olive pomace oil as the most prominent product. Nonetheless, the use of by-products from the olive oil production still generates new by-products and effluents, this study aimed for the characterization of the effluent from an olive pomace oil extractor industry and investigate the application of physicochemical pre-treatments to future water reuse.

The fresh effluent (E1) and the effluent from a storage tank (E2) characterisation, by using 14 parameters, demonstrate both effluents have high pollutant load and cannot be released in the river near the factory, due to non-compliance with the limit values for the parameters as stated in Decree-Law No. 236/98 of 1st August, which regulates the emission limit values for wastewater discharge. The Tua river was also analysed to assure the quality of the waterbody and observe any pollution. At the four sampling points, any parameter exceeded the maximum emission values presented in the same legislation, and no pollution from the factory was observed, by the cause, the only effluent from the factory to reach the river is the water used for cooling the extraction process. To provide environmental management to this industrial plant, the waterbody must be monitored as required by current legislation, in the parameters determined by it and sampling frequency required for the maintenance of the quality validated in May 2021.

The lagoons, where the effluent is stored, reveal to be an interesting step for the pre-treatment, reducing TS (57%), TDS (54%), TSS (61%), COD (78%), BOD (69%) and PhC (82%) when compared with the fresh effluent. E2 was submitted to coagulation/flocculation treatment, having the best conditions shown to be 10 g/L of Aluminium Sulphate (coagulant) and 4 mg/L of Rifloc F45 (flocculant), with pH of 5 and a settling period of 3 hours. For these conditions, removals of 96% (turbidity), 76% (COD), 77% (TSS) and 85% (PhC) were achieved, when compared with E2.

The treated effluent can be reused, inside the factory, or in the irrigation of olive groves. To return the water to the waterbody is yet necessary for further treatment, such as biological treatment, as the effluent show before good biodegradability in the Zahn-Welles test.

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Characterization and Primary Treatment of the Effluent from Olive Pomace Oil Extractor Industry

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Abstract

The olive pomace oil is the principal by-product in the olive oil sector. Nonetheless the production uses olive bagasse after the primary extraction, it also produces by-products and effluents that need strategic approach to possibility reuse and a treatment. This study aimed for the characterization of the effluent from an olive pomace oil extractor industry and investigate the application of physicochemical pre-treatments to future water reuse. The physicochemical characterization shows high amounts of BOD and COD for the effluent freshly produced (E1) and effluent collected from storage tanks (E2) in the industrial plant. Other parameters were evaluated: Phosphorus, Organic nitrogen and Ammonia, FOG, Phenolic compounds, Alkalinity, TS, TDS and TSS, and Biodegradability (Zahn-Wellens Test). E2 shows the storage tanks were able to reduce 55% of TS and TDS, 77.5% of COD and 69% of BOD when compared with E1. Comparing with the Portuguese legislation, these effluents cannot be discharge to waterbodies and need treatments, such as coagulation and flocculation as tested in this work. Aluminium Sulphate show to work at best as a coagulant in the minimum concentration 10 g/L and pH 5, RIFLOC F45 (4 mg/L) was used as flocculant. After the treatment, it was observed a remotion of 95.6% of turbidity, 76,4% of COD,76,7% of TSS, and 85.4% of PhC when compared with E2. A sampling campaign was carried out on the Tua river to assess its water quality, and samples were taken at four different points to assess the impact of the effluent discharge, with none of the evaluated parameters presenting values higher than those recommended by the Law-Decree nº236/98 from the Portuguese Legislation.

Keywords: Industrial effluent, wastewater characterization, olive pomace wastewater, water bodies monitoring, coagulation/flocculation.

Acronyms

BOD Biochemical Oxygen Demand.

COD Chemical Oxygen Demand.

ENEAPAI Estratégia Nacional para os Efluentes Agropecuários e Agroindustriais.

ELV Emission Limit Value.

ERV Emission Recommend Value.

EU European Union.

FOG Fats, Oils and Grease.

OMWW Olive Mill Wastewater.

PAA Poly(allylamine).

PAH Poly(allylamine) Hydrochloride.

PDADMAC Polydiallyldimethylammonium Chloride.

PEI Poly(ethylenimine).

PhC Phenolic Compounds.

TDS Total Dissolved Solids.

TS Total Solids.

TSS Total Suspended Solids.

TVS Total Volatile Solids.

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Chapter - 1

Introduction

Since ancient times, the practice of extracting oil from olives has been explored in the Mediterranean region due to the favorable climatic conditions for growing olive trees. Portugal is the fourth biggest olive oil producer, after Spain, Italy, and Greece. The European Commission estimates that around 2 million tons of olive oil are produced in the European Union (EU) every year [1, 2].

Olive oil production is a relevant economic sector, with job creation, maintaining rural populations, its production involves also environmental aspects that cannot be neglected. Mass and energy resources are consumed throughout the stages of the olive oil production chain, from the cultivation and production of olives to the final consumption of the product, as well as produced gaseous, liquid, and solid residues with impacts on ecosystems. As the circular economy principles, these residues can still be part of new industrial processes [1, 3].

The technologies for olive oil extraction became more efficient over the decades, today most extraction occurs in a 2-phases system to reduce the amount of wastewater produced by the traditional and the 3-phase process. The main byproduct, the olive pomace, goes to a second extraction, the remaining oil percentage is removed applying an organic solvent. This olive pomace oil can be refined and used in some countries in the food and cosmetic industries. After the process, the exhausted pomace serves as fuel in the industry, and the wastewaters produced need to be treated to give a destination to water and organics compounds [4].

The present work aims to characterize the wastewater, to design a primary treatment for one olive pomace oil extractor industry, and to study possibilities to reuse the water inside the extraction processes or in the olive groves. Coagulation/flocculation are the processes chosen to treat the wastewater due to the low investment and easy installation and manipulation by the industry.

Chapter - 2

Objectives

The overall aim of this thesis is to study the effluent from an olive pomace oil extractor industry and design the treatment to enable the reuse of the water or the return to a water body as specified by the Law-Decree nº236/98 from the Portuguese Legislation.

2.1 Specific aims

- Physicochemical characterization of the wastewater produced by the olive pomace oil extractor industry.
- Study the possibility of treatment to water reuse in the irrigation of olive groves.
- Study coagulation/flocculation as a pre-treatment for the effluent produced by the olive pomace oil extractor industry.
- Propose alternative treatments for the discharge of effluent into the receiving body and its energy valorization.

Chapter - 3

State of Art

This chapter organizes to explain the olive oil production and the residues produced in this industry, how the olive pomace oil is produced, and the new residues and their environmental impacts. The wastewater characterization and treatments with a focus on filtration systems and coagulation and flocculation techniques who intended to be replicated in our project for the olive oil pomace production. Along, it is important to understand the environmental legislation from Portugal, the parameters of the water, and the possibility of use of the wastewater in olive irrigation, and the valorization of the residues.

3.1 Olive Oil Industry

To be able to talk about the olive pomace oil, the main byproduct of the olive oil industry, first, is necessary to understand how the olive pomace is produced and its characteristics.

3.1.1 Olive Oil Production

Olive oil is one vegetable oil that only needs mechanical processes to be extracted and can be considered the juice from olives. This process has been enhanced for centuries mainly in the Mediterranean region, because of this area's favorable climatic conditions, such as a dry climate and enough hours of sunshine for the growing of olive trees [1, 5]. First, the olive needs some pre-treatments such as removal of leaves and stones, separation, conservation, cleaning, and washing to guarantee a good quality olive oil as a product. Then the olives are milled in a process called malaxation with a hammer or toothed-disc crushers and thermal bathing producing an olive paste. Using a liquid-solid separation process, the olive oil is separated from the olive pomace [1, 4, 6].

At this point, we have at least three methods of separation as shown in the Figure 1: the traditional method, it was largely used until 1960, became replaced for the three-phase extractor and now in the last thirty years has given space to the 2-phases continuous extractor. This technological improvement has an environmental purpose, in the traditional process, the olive paste is sent from the mill to hydraulic presses, where water is added, producing oily wort, dry bagasse, and wastewater, a very pollutant residue [2, 3].

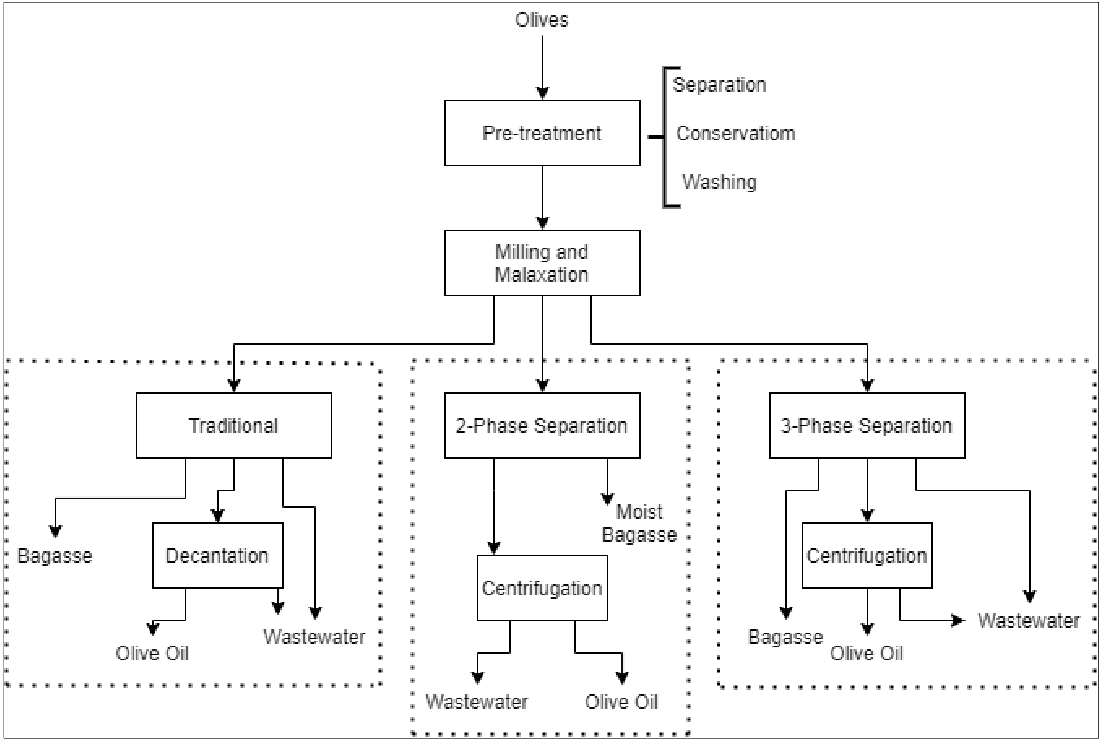


Fig 1: Olive oil production routes.

In the three-phase press, the beaten olive paste goes to the decanter where add heated water, this method also produces three different outputs: oily wort, dry bagasse, and lighting wastewater. In the two-stage process instead, there is no addition of water to the paste, with impacts on a lower production of wastewater, its resulting products are oily wort and moist bagasse [2, 3].

3.1.2 Residues from olive Oil Production

By all the processes present previously, it has as the product virgin olive oil and byproducts. The liquids ones, when present, need to pass several physical, chemical, and biological treatment before having final disposal due to high organic load and hardly degradable. The solid byproducts, the bagasse is sent to an olive pomace oil extraction industry, to extract the small amount of oil remaining in the residue. Bagasse also can be used as solid fuel in the process of obtaining electrical energy, due to its high calorific value [2, 7].

The wastewaters, known as vegetation water, too, are typically composed of water (83 to 94% by weight), organic matter (4 to 16%), and mineral salts. The principal pollutants are lipids, sugars, organics acids, tannins, pectins, lignin, and the high concentration of phenolic compounds (PhC), as well as magnesium, potassium, and phosphate salts [2]. The presence of these pollutants when discharged on water bodies induce coloration, acidification on the water, and loss of transparency. Due to the high concentrations of nutrients and organic compounds (COD close to 220 g/L) being an excellent means for the of microorganisms degrading the water quality by high oxygen consumption, in a process known as eutrophication. For the effects of pollution and toxicity of wastewater, the proportion is 1:100-200 of wastewater to domestic effluent [3, 7].

The olive pomace has different characteristics according to the extraction process, as the presence or not of olive stones, and principally the moisture content. Olive pomace originated by a three-phase extraction have normally 55% moisture and the olive pomace from a two-phase extraction has 80% moisture according to Brito [3]. The dry matter of olive pomace originated from pieces of skin, pulp, stone, and olive kernel, it is rich in proteins, crude fiber, sugars, minerals, polyphenols as some organic acids, and polyalcohols [7, 8].

As shown by Figueiredo *et al.* (2015) in Table 1 the production of olive pomace is 3 to 5 times bigger than the olive oil, evidencing the importance of the olive pomace oil industry even when the oil content in the bagasse is around 8 to 10%. This oil, after processes, to reduce any percentage of remaining solvent and impurities can be used for edible purposes, cosmetics, and biodiesel production [1, 4].

Table 1: Byproducts per liter of olive oil [1].

Method	Output	Production (kg/L olive oil)
3 phases	Olive Oil Bagasse	0.9 2.99
2 phases	Olive Oil Bagasse	0.9 4.34
Traditional	Olive Oil Bagasse	0.9 3.65

Wet pomace obtained by two-phase centrifugal, as explains Petrakis (2006), is not always used in the industry for solvent extraction because of the high percentage of moisture and need a long process of drying increasing the costs and difficulty in handling and storage [6].

Ferraz (2012) also warns about the caramelization due to the sugar presents on this type of pomace, hamper the drying operation, and to a certain extent, there may be a risk of fire. The alternative to the solvent extraction is the second centrifugation of olive pomace, extracting between 40-60% of the retained residual oil. By this process the stones are so separated from bagasse to be used as fuel in the industry, reducing the residues produced at the end of the process [1, 2, 9].

3.1.3 Olive Pomace Oil Production

According to the traditional method of solvent extraction, the olive pomace needs to be dried to 8% moisture before the addition of an organic solvent, but it reflects a minor part of the olive pomace sold to the second extraction industry. In deterrence the high percentage of water in olive pomace oil some extraction facilities that receive the three types of olive bagasse have chosen to homogenize the moisture content of the pomace to be extracted as show in the Figure 2, mixing the three types of bagasse until they reach a humidity of around 50% before a drying process. This process is important to stop fermentation reaction and preserve the reminiscent oil from hydrolysis and enzymatic deterioration [6, 7].

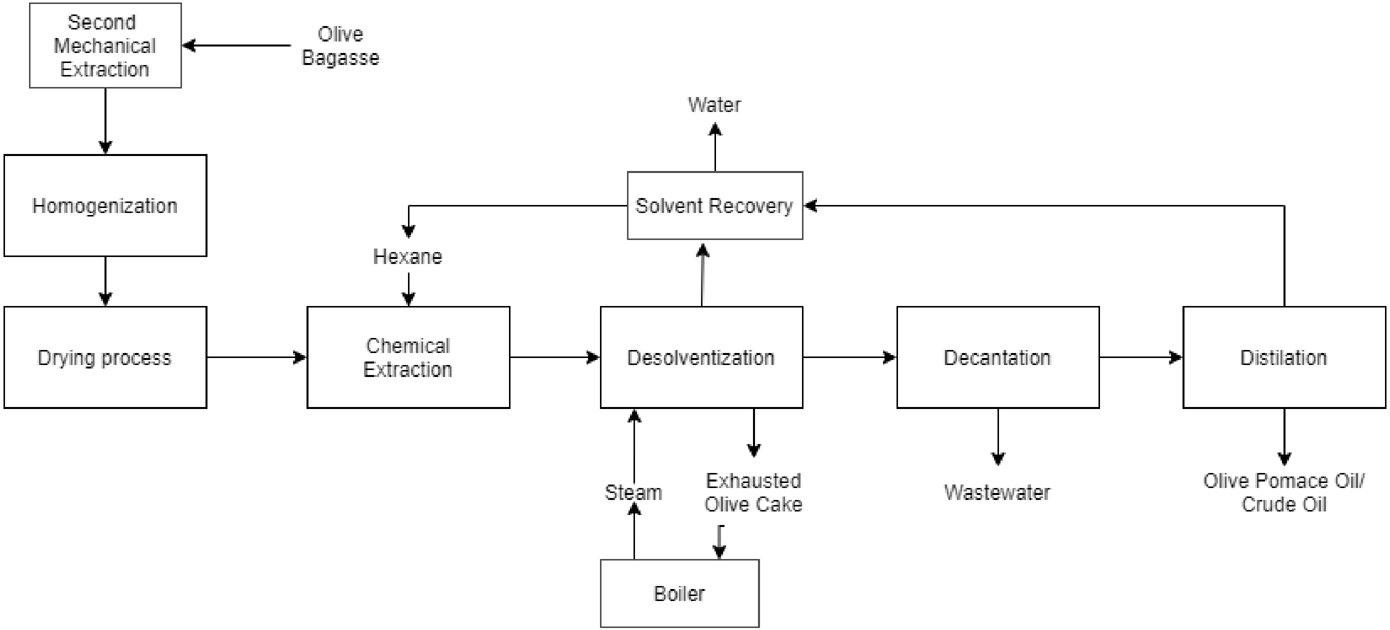


Fig 2: Olive pomace oil production process

After drying, the olive pomace is mixed with a solvent for the extraction of fats. This solvent needs to have no influence on the oil quality and physical properties, also needs a good selectivity and extraction power. As for other vegetable oils, the most used is n-hexane [10].

The solvent/oil mixture is collected from the batch extractors and steam is injected in a desolventizer operation to eliminate the hexane residue from the solids, and the oil/hexane mixture will be distilled to recover solvent. The olive pomace oil obtained, also called crude pomace oil, differs from the virgin olive oil, it is more acid, has a dark green coloration due to its high chlorophyll content and unpleasant odor and taste, needing a refining procedure to become edible [6, 10].

The byproducts generated are biomass composed of stones and fat-free solids (or exhausted olive cake), and residual wastewater. The exhausted olive pomace can have the pulp separated from the rest and destinate to animal feed, the residue remaining is used as a fuel, reducing the fuel demand for steam production of the installation [6, 10, 11].

3.1.4 Treatment and Valorization of Olive Mill Wastewater

Using the Circular Economy concept, which aims to use and transform waste from industry into materials to be used again in production processes, thereby improving the efficiency of company operations while reducing costs and environmental impacts [12], it is notable the effort that the sector of olive oil production has developed research and improvements that have been done to integrate the concepts of circular economy and cleaner production. Some of the most prominent aspects that affect the sector are the use of solid waste for the co-generation of energy and the extraction of economically interesting compounds, such as phenolic compounds, from wastewater, and the biofuels production, and Ceramic building materials [13–15].

To be able to recover phenolic compounds as tyrosol, different processes are being used continuous-flow adsorption/desorption methods, extraction using hydrophobic ionic liquids, an integrated process including fermentation, spray drying, and encapsulation technologies, solar distillation, dark fermentation, enzymatic hydrolysis, and microfiltration- ultrafiltration. To produce solid biofuels, building materials, and even natural dyes for textile dyeing are used impregnation on dry biomasses, fired clay brick production and Brick-making process, dyebath for dyeing wool, respectively [16, 17].

The wastewater treatment is another approach to remained liquids byproducts, it is then essential to treat the wastewater and to determine whether this water can be recycled and reused. Most of the depolluting treatments of Olive Mill Wastewater (OMWW) aim at the destruction of organic matter and phenolic compounds, hence the reduction of chemical oxygen demand and phytotoxicity [4, 9].

Enaime *et al.* (2018) point to the main technologies used in the last years to the treatment of OMWW, applying a range of methods [16]:

- **Physical techniques:** sedimentation, flotation, filtration, and micro-ultrafiltration using membranes, centrifugation, dsorption/desorption methods, able to de- crease COD levels when applied in series.
- **Thermal techniques:** solar distillation, evaporation, combustion, and pyrolysis. These last methods have high energy demands making them unviable.
- **Physicochemical techniques:** neutralization, precipitation, adsorption, advanced oxidation processes (Fenton reaction, wet hydrogen peroxide catalytic oxidation, ozonation, electro-Fenton), lime treatment, electrocoagulation, cloud point extraction (CPE), this process can remove COD, in some cases decrease of the total phenolic content and color.
- **Biological techniques:** anaerobic processes, aerobic processes, enzymatic processes, which can highly (70%) remove COD and phenolic compounds.

3.2 Industrial Wastewater Treatment

Vegetable oil-producing industries are an important food industry, and as many have wastewater with specific characteristics, like color, odor, high Biochemical oxygen de- mand (BOD), and Chemical oxygen demand (COD), oil is also the main pollutant in the wastewaters of the olive oil industry. It is typically a seasonal industry, and therefore there is no regular generation of wastewater throughout the year [18, 19].

The first step to design wastewater treatment is the wastewater characterization, identifying the pollutant compounds present, estimate the volumes and the source of generation, in some cases a corrective action can be proposed to reduce or even eliminate the pollutant levels, this knowledge is also important to evaluate which of the next steps in wastewater treatments are required comparing the data to the specifications requested for the final effluent, obtained in the local legislation or equipment/process demands. Unfortunately, in wastewater treatment, zero production is close to a myth, and the best approach after trying to reduce the pollutant production is to observe valorization opportunities, and if is any, treatment for recycling and reuse before final disposal. The nature of the pollutant is an important point when mixing effluent streams, as nontoxic streams and reusable water are not mixed with toxic materials. Methodical segregation of the streams can reduce costs with wastewater treatments and priority goals such that recycling, and reuse of the water is facilitated [11, 13].

Wastewater treatment methodology follows some important steps as a preliminary and primary treatment for the removal of solids and oils if those are required, using a combination of various methods such as filtration, coagulation, and sedimentation. These treatments are size-based separations using physical methods for basic cleanup. They are followed by secondary, and tertiary treatments based on physicochemical methods and/or bio- logical methods and can remove 90% of BOD or COD and TSS from the wastewaters. Tertiary treatment involves the final polishing of the effluent by removing toxic/harmful pollutants to the desired levels [8, 13].

Due to the nonexistence of literature that characterizes the effluents of an extraction industry of olive pomace oil, we will use the data of the characterization of wastewaters generated in the production of olive oil, given the expected similarity between the effluents. Using the data obtained for Enaime et al. (2018), shown in Table 2, the physicochemical characteristics of the olive oil effluents according to different authors, the range of values is justifiable according to which variables are present in the process, such as: the olive variety, the fruit ripeness, the volume of added water, and the extraction process (press or centrifuge) [16].

Table 2: Physicochemical characteristics of olive mill wastewaters [16].

Parameter	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**Range values**
pH	-	5.2	5.1	5.7	5.3	5	4.8	4.8-5.7
Conductivity	mS/cm	5	-	11	24	81	17.5	5-81
COD	g/L	16.5	95	48	156	53	15.	16.5-156
BOD	g/L	-	-	-	-	13.4	37.5	13.4-37.5
Dry residue	g/L	11.5	84.2	-	90	39.4	53.16	11.5-90
PhC	g/L	0.8	4.82	8.8	4.1	8.6	8.9	0.8-8.9
Total nitrogen	g/L	0.06-0.3	-	0.9	-	0.5	-	0.06-0.9

1.Paraskeva *et al.* (2007), 2. Asses *et al.* (2009), 3. Karpouzas *et al.* (2010), 4. El-abbassl *et al.* (2013b), 5. Mekkl *et al.* (2015), 6. Khouft *et al.* (2015).

In some industries, one approach before developing a wastewater treatment facility is the storage of the effluents in lagoons and pools. In these tanks the effluent passes for an aging process, a combination of different process that may occur variating with the wastewater characteristics. The first process is the sedimentation, where the suspended solids is settled by the influence of gravity on the mass and size. The second process common on storage tanks are the evaporation of the water content, in a dewatering process. The third process is a digestion of the organic matter of the effluent by biological agents presents in the effluent or in the local of storage. All the process occurs concomitantly modifying the characteristics of the effluent [19, 22].

The result of the storage and aging process is, in most cases, an effluent with less organic matter and solids, making its treatment easier and cheaper, nonetheless, the sludge resulting of the steeling process needs to be collected and treated as well, and a valorization process may become useful for other industries and process. However, odors may be a problem, depending on the type of sludge involved [19, 22].

Lagoon systems used only for dewatering typically have two treatment cells. Sludge is sent to one lagoon for several months. Then this lagoon is allowed to rest while a second lagoon is filled. Then, the second one rests while the first is used again for biological sludges. The Water Environment Federation suggest solids loadings of 36 to 39 kg/m3/yr. are suggested. If used for storage, sludge lagoons can vary significantly, though depths of 3 to 5 m are typical [19, 22].

Paraskeva and Diamadopoulos (2006) estimate with the use of physicochemical treatment, olive mill wastewater has a decrease between 80 and 95% COD after a combi- nation of physicochemical technologies, including centrifugation, filtration, coagulation- flocculation and adsorption [20].

3.2.1 Coagulation/Flocculation

Coagulation and flocculation are two of the most employed physicochemical methods in effluent treatment, the process is based on invert the electrical repulsion between particles on suspension in the wastewater. To achieve this, coagulant salts are added to the water destabilizing the colloidal particles, reducing, neutralizing, or inverting their electrical charge, and then forming flocs, these flocs tend to sediment, producing a clarified liquid, as show in the Figure 3. Flocculants are also added to promote the agglutination of the already coagulated particles, facilitating the collision between them due to the slow agitation imposed on the water flow, aiming at the formation of flakes with size and specific mass that favor their removal by sedimentation, flotation, or filtration [21].

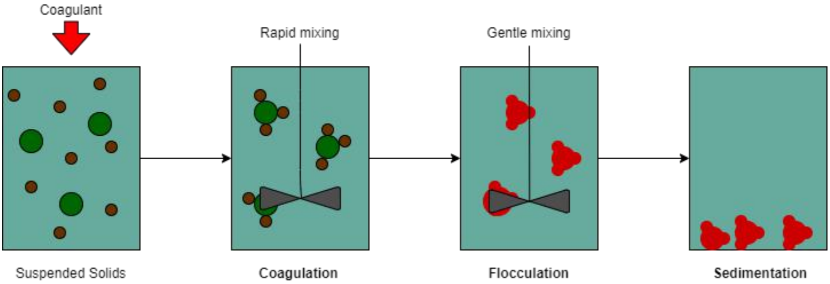


Fig 3: Scheme of coagulation/flocculation process

Typically, inorganic coagulants are aluminium sulphate/chloride, ferric chloride/sulphate, calcium/magnesium oxide, these chemicals are pH sensitive and demand pH control for the operation. The inorganic hydroxides that are formed produce short polymer chains which enhance floc formation [13, 17, 21].

Organic polymers typically are added to aid flocculation and are becoming more widely used as coagulants. Polymers are divided into three main categories: anionic, cationic and non-ionic.. Anionic polymers are often used with metal coagulants, cationic polymers may be used alone, or in combination with alum or ferric coagulants to attract suspended solids and neutralize their surface charge. Polymers are effective over a wider pH range than inorganic coagulants, and can be applied at lower doses [13, 17, 21].

To assess a chemical coagulation treatment usually a jar test is made. Jar tests simulate the conditions of reaction in full scale, allowing them to anticipate the results and choose the best coagulant dosage, pH. Test parameters typically include chemical combination and dose, mixing intensity, and settling time, after that the jar is put under a very slow mixing intensity to allow the particle aggregation, flocculation, and solids to settle to the bottom. The clarification water is analyzed to observe the new concentration of solids, the residue can be removed with filtration or settled systems [13, 21, 22].

Ranade and Bhandari (2014) alerts about the changes wastewater can have during the day, as receiving different quality materials, batch processing, and cleanup activities result in distinct wastewater's characteristics, sometimes changing the treatment protocol, and the operating performance [13, 21].

Coagulation is effective to remove color in wastewaters containing dissolved solids, but the process requires high inorganic chemical dosages producing large volumes of sludge, resulting in a high cost. The use of organic coagulants can reduce the cost due to the lower production of sludge. To provide a better techno-economically feasible operation can be utilized a mix of inorganic and organic coagulants in wastewater treatment [21 - 23].

Domingues *et al.* (2021) studied a similar wastewater (from a pomace olive oil extractor industry) with an organic load of about 50 g/L of COD and high toxicity. The best conditions found for coagulation were double phased addition of a total of 40 mg/L of coagulant polydiallyldimethylammonium chloride (PDADMAC), a highly charged cationic polymer, with results in a 15% of COD removal, after coagulation/flocculation a Fenton reaction (4 g/L of hydrogen peroxide, 2 g/L of iron (II) at pH 3 with 60 min of reaction) achieved about 45 % of COD removal [24].

In Iakovides *et al.* (2014) search, several inorganics [FeCl3, Ca(OH)2, CaO, CaCl2] and organic (PDADMAC, poly(allylamine) hydrochloride (PAH), poly(allylamine) (PAA), poly(ethylenimine) (PEI), Floccan 22-23 coagulants were tested to treat OMWW, either separately or in combination and screened with respect to their removal efficiency. The coupling of calcium hydroxide at 20 g/L, with PDADMAC in a range of 0.75–2.00 g/L led to reductions of 56% COD, 27% TSS, 43% TS and 76% PhC [25].

Vuppala *et al.* (2019) focus was the optimization of coagulation and flocculation was performed focusing on the effect of different pH and coagulant dosage values in OMWW using aluminium sulphate (Alum) and chitosan equal to 400 mg/L and 100 mg/L, respectively, and pH ranging between 3, 4 and 4.5. A 99% reduction of turbidity was observed for both alum and chitosan with 60 minutes of sedimentation [26]. Papaphilippou *et al.* (2012) used iron sulphate as coagulant and FLOCAN 23 (an anionic polyelectrolyte) as flocculant in the doses of 6.67 g/L and 0.287 g/L respectively led to an optimal removal of TSS (97%), COD (72%), and PhC (40%) [27].

Normally a coagulation/flocculation process alone is not a complete solution to wastewater treatment problems, but in the floc formation process, some of the uncharged particles and organics get physically trapped and removed, consequently im- proving the process performance. This allows to increase the biodegradability, for further biological treatment application to definitively treat the effluents [22, 23].

3.3 Portuguese Environmental Legislation

The importance of olive oil production to Portugal can be seen when 97.7% of the total of the olive grove is destined to produce olive oil, and only about 2.3% channeled to the production of table olives [3]. This makes the olive mill wastewaters a problem to be considerate at national levels and with its own legislation.

Environmental legislation is an important factor when designing wastewater treatment, it is necessary to be aware of the laws about industrial effluent disposal and specific legislations to the sector. Laws must also be observed at different levels, as it is common to vary the parameters accepted in national, regional, and municipal legislation [28].

One of most important legislation are the municipal discharge regulations, documents that regulate the discharge of effluent into municipal collectors, each adapted to the reality of the respective municipality. The effluents that may be released into public networks, must respect certain constraints, to ensure that the bodies that make up the treatment system do not affect personnel involved in operations, as well as safeguarding their protection [2, 29].

Each regulation must name the characteristic parameters dated from the respective maximum admission values so that industrial effluents are admitted to a wastewater discharge in a waterbody. In addition to these are described all substances that are prohibited, regardless of their concentrations, the annex XVIII from the decree 236/98 are shown in the Table 3 [28, 29].

Table 3: Parameters of wastewater discharge (ELV) [28].

Parameter	**Unit**	**ELV**
pH	Sorensen Scale	6.0 – 9.0
Temperature	ºC	Increase of 3ºC
BOD_5 (20ºC)	mg O_2/L	40
COD	mg O_2/L	150
TSS	mg TSS/L	60
Phenols	mg C_6H_5OH/L	0.5
FOG	mg/L	15
Total Phosphorus	mg P/L	3.0
Ammoniacal Nitrogen	mg NH_4/L	10
Total Nitrogen	mg N/L	15

ELV - Emission Limit Value

Faro Ferraz (2012) points to the importance of the *Estratégia Nacional* *para os Efluentes Agropecuários e Agroindustriais* (ENEAPAI) (National Strategy for Agribusiness and Agro-Industrial Effluents) to build a sustainable strategy for the various sectors of agro-industrial production. It proposes to integrate the specificities and characteristics of each productive sector, the effluents produced by them, and the regions where they operate to design integrated and sustainable solutions for the intervention and resolution of environmental problems caused by the normal activity of the sectors [2].

Other important legislation is the Joint Order No. 626/2000, of 6 June. This order authorizes the application of olive mill wastewater in the irrigation of agricultural soils. In this way, producers have a destination solution for their effluents without major economic costs, valuing a resource considered problematic. It is necessary to request a license for the procedure and respect a list of conditions to avoid problems, such as the prohibition in areas close to water lines and population centers, etc. [2, 30].

The decree-Law No. 208/2008, of 28 October from, transposes Directive 2006/118/EC of 12 December, on the protection of groundwater against pollution and its deterioration. This decree intends to implement measures to prevent and control water pollution groundwater, including criteria for assessing its good chemical status for the identification of significant and persistent trends towards increasing the concentration of pollutants, as well as to define starting points for reversing these trends [30].

The waterbodies monitoring is other important activities of public agencies to observe and evaluate the quality of the water and the security of the environment, preventing problems caused by pollution. On the decree 236/98, it also can be found the ideal and limits for physicochemical and biological parameters for waterbodies characterization as the techniques that should be used to determination. The values and parameters available may change based in the water destinated use as show in the Table 4.

Table 4: Parameters of waterbodies according to their destination (ERV) [28]

Parameter	**Unit**	**ERV for superficial water intended for human consumption**	**ERV for water intended for aquaculture purposes**	**ERV for bathing water**	**ERV for water intended for irrigation**
pH	Sorensen Scale	5.5 – 9.0	6.0 – 9.0	6.0 – 9.0	6.5 – 8.4
Temperature	ºC	22	Increase of 3ºC	-	-
Conductivity	µS/ cm (20ºC)	1000	-	-	-
BOD_5 (20ºC)	mg O_2/L	7	6	-	-

COD	mg O_2/L	30	-	-	-
Dissolved Oxygen	mg/L O_2	-	100% > 7	-	-
Dissolved Oxygen	% Saturation of O_2	-	-	80 – 120	-
TSS	mg TSS/L	-	25	-	60
Phenols	mg C_6H_5OH/L	0.010	(2)	0.005	-
Ammoniacal Nitrogen	mg NH_4/L	2	0.2	(3)	-
Kjeldahl Nitrogen*	mg N/L	3	-	(3)	-
Nitrates	mg NO_3/L	50[1]	-	(3)	50

ERV - Emission Recommended Value

1. ELV
2. Phenolic compounds should not be present in concentrations that alter the taste of the fish.
3. These parameters must be checked by the competent authorities whenever there is a tendency towards the eutrophication of waters.

* Except NO_2 and NO

Chapter - 4

Methodology

To design a wastewater treatment facility for local industry, the components of the effluent must be quantified, in the wastewater characterization step, the data obtained is used to develop potential management strategies and provide a baseline for evaluating the effects of treatment processes, water conservation, or regulations. To develop a pre and primary treatment filtration tests using different media and coagulation tests using commercial coagulants must be carried out.

The Wastewater used was collected on Mirabaga, an olive pomace oil extractor industry, in Mirandela (Portugal), between April and September 2021. The amount of wastewater was delivered to the laboratory and stored as required by the Standards Methods to the analysis and tests. This study was carried out at the Chemical Process Laboratory, at the Instituto Politécnico de Bragança, from September 2020 to September 2021.

Samples from the river close to the industry were also collected on May 19, 2021, to assess its water quality, and eventual influences from the industrial activity to the Tua river.

4.1 Wastewater Characterization

The wastewater characterization 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 [31].

4.1.1 pH and Conductivity

As the wastewater is delivered to the laboratory, a homogeneous sample is used to measure Hydrogen Potential using a HANNA pH meter under magnetic agitation and local temperature of 20ºC. The Conductivity was measured in the same way using a conductivity meter WTW model *Inolar Cond level 1*.

4.1.2 Biochemical Oxygen Demand

The BOD_5 was determined by the standardized respirometric OxiTop method (WTW, Weilheim, Germany). To the sample bottle were added a fresh wastewater volume as recommended by the fabricant and equipped with a magnetic stirrer and NaOH pellets in the headspace, the inoculation was made, when necessary, as the control samples and blanks required by the standard methods. They were placed in an inductive stirring system at 20ºC. After five days, the data was collected and analysed.

4.1.3 Chemical Oxygen Demand

The COD method used was the Colorimetric Method in a Closed Reflux process from the Standards Methods Standard ampules were added 2.5 mL from the sample, 1.5 mL digestion solution, and 3.5 mL sulfuric acid reagent. The samples were digested for 120 minutes at 150 ºC. One blank was digested to confirm good analytical reagents and to determine the blank COD. The calibration curve was made with a Potassium hydrogen phthalate standard solution, diluted to concentrations equivalent to 0 to 1000 COD mg O_2/L. The samples and calibration curve were analysed in a Spectrophotometer JASCO V-530 at 600 nm, obtaining equation 1:

$$y\,(\frac{mg\ O_2}{L}) = 3145.1 * x(abs) + 1.1523 \qquad \text{(Equation 1)}$$

4.1.4 Phosphorus

An adaptation of the Standards Methods was used to determine the phosphorus contentment, 50 mL from the sample were added to an Erlenmeyer with 0.5 g of potassium persulfate and put in the autoclave for 60 minutes at 120 ºC and 1 atm. To the flask were added 0.5 g of ascorbic acid. 10 mL of the solution were added to a test tube, 1 mL of a reagent mixture (12.5 mL Sulfuric Acid, 1.25 mL Potassium Sodium Tartrate solution and, 3.75 mL Ammonium Molybdate solution) were added and agitated in a vortex. After the colour development, the sample and the calibration curve were analysed in a Spectrophotometer JASCO V-530 at 882 nm (equation 2):

$$y\left(\frac{mg}{L}\right) = 1.786 * x(abs) - 0.0055 \qquad \text{(Equation 2)}$$

4.1.5 Ammonia

The ammonia content was determined by the direct nesslerization method based on the Standard Methods; a preliminary distillation was necessary for the sample. 500 mL of the sample were previously neutralized and added 25 mL of borate buffer solution and then had the pH adjusted to 9.5 with NaOH solution before distillation. 300 mL of the distillate was received and mixed with 50 mL of boric acid before the volume was completed to 500 mL. One drop of EDTA solution was added to 50 mL of the treated sample and 2 mL of the Nessler reagent. After 10 minutes of colour development, the sample and the calibration curve were read at 410 nm in the Spectrophotometer JASCO V-530 producing the equation 3:

$$y\left(\frac{mg}{L}\right) = 5.0931 * x(abs) + 0.0062 \qquad \text{(Equation 3)}$$

4.1.6 Organic Nitrogen

The Macro-Kjeldahl Method of Standards Methods was applied, and the sample used is the residue from the distillation flask from the ammonia determination. 50mL of the digestion reagent (Sulfuric Acid, Potassium sulphate, and Copper (II) sulphate) were added to the sample, it was digested until the sample became pale green. After cooling, it was diluted to 300 mL with water and 50 mL sodium hydroxide-thiosulfate reagent was added to form an alkaline layer at flask bottom. Connecting the flask to a steamed-out distillation apparatus and swirl flask to ensure complete mixing the sample was distilled until collect 200 mL, and 50 mL of a boric acid solution was used as an absorbent. The organic nitrogen content was determined by the titrimetric method with a standardized solution of 0.02N Sulphuric Acid until the indicator change colour to a pale lavender. A blank was cared for all the process.

4.1.7 Fats, Oils and Grease

The samples were acidified with sulfuric acid to pH 2 or lower for conservation, and the oils and grease were determined by the Soxhlet Extraction Method. Using vacuum filtration equipment, the samples were filtered no more water passes through paper filter. All filter material containing sample fit into an extraction thimble, as any pieces of material remaining with a filter paper soaked in extraction solvent. The thimble was dried in a hot-air oven at 103 °C for 30 min. The extraction flask was weight and add 250 mL extraction solvent, n-hexane. Extract oil and grease in a Soxhlet apparatus, at a rate of 20 cycles/h for 4 h.

The solvent was recovered with distillation and the flasks were to draw the air for 1 minute and let it cool in the desiccator before weighing. Considering the organic solvent is free of residue, the gain in weight of the tared distilling flask is due to oil and grease. The total gain in weight, A, of tared flask, less calculated residue from solvent blank, B, is the amount of oil and grease in the sample, when sample was brought into the laboratory, mark sample bottle at the meniscus for later determination of volume (equation 4).

$$FOG\ (g/L) = \frac{(A-B)\ x\ 1000}{sample\ volume{,}mL} \qquad \text{(Equation 4)}$$

4.1.8 Aromaticity

To determine the aromaticity of the samples, it was made a calibration curve, in the range of 0 to 200 mg/L of phenol P.A. The sample and the calibration curve were analysed in a Spectrophotometer JASCO V-530 at 254 nm producing the equation 5:

$$y\left(\frac{mg}{L}\right) = 17.62 * x(abs) - 0.4918 \qquad \text{(Equation 5)}$$

4.1.9 Phenolic compounds

To measure the phenolic compounds using the Folin-Ciocalteu method, a calibration curve was built, in the range of 0 to 100 mg/L of phenol as the model compound. In the test-tube were added 0.5 mL of the Folin-Ciocalteu reactant, along with 0.2 mL of the sample (previously diluted) and 8.2 mL of distilled water. The solution was left to rest for 10 minutes. After this, 1 mL of a Na_2CO_3 solution was added and left for 60 minutes to develop colour. The samples were analysed in UV-VIS Spectrophotometer JASCO V-530 at the wavelength of 765 nm producing the equation 6:

$$y\left(\frac{mg}{L}\right) = 1043.6 * x(abs) - 8.2288 \qquad \text{(Equation 6)}$$

4.1.10 Alkalinity

To measure the capacity of the wastewater to neutralize acids the sample was submitted to a Volumetric Titration which sulphuric acid. Fist was added the indicator phenolphthalein to determine simple alkalinity, after the titration, the indicator methyl orange were added and the sample were titrated again, to determine the total alkalinity (equation 7).

$$Alkalinity\ (mg\ CaCO3/L) = \frac{HCl\ volume{,}mL\ x\ MM[CaCO3]\ x\ 1000}{Sample\ volume{,}mL} \qquad \text{(Equation 7)}$$

4.1.11 Solids

The Standards Methods was used as a based method for the measurement of total solids, total dissolved solids, total suspended solids, fixed and volatile solids. All the evaporating dishes were cleaned by calcination at 550 °C for 1 hour in a muffle furnace.

A sample volume would yield a residue between 2.5 and 200 mg. Pipet a measured volume of well-mixed sample, during mixing, to a pre weighed dish. First, the samples were evaporated to dryness on a steam bath and then dried in an oven at 103 to 105 °C for at least 1 h, cooled in a desiccator to balance temperature and weight. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight is obtained, or until weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. All samples are made in duplicate. The total solids were obtained by calculating the difference between the last weight (A) obtained and the weight of the dish (B), the value was divided by the sample volume (equation 8).

$$mg\ TS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 8)}$$

To measure the Total Dissolved Solids (TDS) and Total Suspended Solids (TSS), a homogenous sample of the wastewater was filtered in a glass-fiber filter with an applied vacuum. Then, the filter was washed with three successive 10 mL volumes of reagent-grade water, allowing complete drainage between washings, and continuing suction for some minutes after filtration is complete. The filter was weight before use and evaporated for at least 1 h in the oven. The total filtrate (with washings) was transferred to a weighted evaporating dish and evaporated to dryness on a steam bath. The evaporated sample was dried for at least 1 h in an oven at 180 ºC, cooled in a desiccator to balance temperature, and weight. The cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight is obtained, or until weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. All samples are made in duplicate. The total dissolved solids were obtained by the difference between the last weight obtained (A) and the weight of the dish (B), the value was divided by the sample volume (equation 9). The TSS were obtained by the difference between the last weight obtained from the filter + dish (C) and the initial weight of the filter + dish (D), the value was divided by the sample volume (equation 10).

$$mg\ TDS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 9)}$$

$$mg\ TSS/L\ = \frac{(C-D)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 10)}$$

To measure the Total Volatile Solids (TVS), the residue produced by the Total Dissolved Solids was ignited to constant weight in a muffle furnace at a temperature of 550°C, for 15 to 20 minutes, the ignition is required for 200 mg residue (equation 11).

$$mg\ TVS/L\ = \frac{(A-B)\ x\ 1000}{sample\ volume, mL} \qquad \text{(Equation 11)}$$

where:

A- weight of residue dish before ignition, mg, B- weight of residue dish or filter after ignition, mg, and

4.1.12 Zahn-Wellens Biodegradability Test

The Zahn-Wellens test was adopted as OECD Guideline 302 B for determining inherent biodegradability in 1981. The reactor containing the test substance (5 mL) and a relatively large amount of activated sludge (16 mL) was added to the reactor and swelled to 2L using distilled water previously added with mineral nutrients is agitated and aerated at 20-25 °C in the dark or in diffuse light for up to 28 days. A blank control reactor, containing activated sludge and mineral nutrients but no test substance, are run in parallel [32].

A fourth reactor containing a control substance was used to validate the results obtained, the substance used was ethylene glycol at a concentration of 0.5 mL/L. The biodegradation process is monitored by determination of COD in filtered samples taken at daily or other time intervals. The ratio of eliminated COD, corrected for the blank, after each time interval, to the initial DOC value is expressed as the percentage biodegradation at the sampling time. The percentage biodegradation is plotted against time to give the biodegradation curve [32].

4.2 Waterbody quality

In order to assess the quality of the water in the river that receives the effluent from the industry after its treatment, samples were collected from four points on the Tua river, to evaluate the variation of the parameters: temperature, conductivity, dissolved oxygen and TDS were measured in situ, pH and turbidity, BOD_5, COD, total phosphorus content, ammonia and organic nitrogen and nitrate content, aromaticity, PhC, alkalinity and TS.

All the characterization used as base the Standard Methods for the Examination of Water and Wastewater (2005) as described in the last topic.

4.2.1 Measurement *in situ*

The parameters temperature, conductivity, dissolved oxygen, and TDS were measurement in the moment of sampling using a Hach HD40d probe.

4.2.2 Turbidity

The turbidity of the samples was measured with an Interface Photometer 7000se from Palintest in the wavelength of 520 nm as required by the equipment.

4.2.3 Nitrates

The nitrates content was measured using the method described in the

Standard Methods for the Examination of Water and Wastewater, to 50 mL clear sample, filtered, if necessary, were add 1 mL HCl solution and mix thoroughly. The absorbance of samples was read in the wavelength of 220 nm. The absorbance was read in the wavelength of 275 nm to determine interference due to dissolved organic matter. The samples were analysed in UV-VIS Spectrophotometer JASCO V-530 at the wavelength of 220 and 275 nm according to the equations 12 and 13:

$$x\ (abs) = abs220 - 2 * abs275 \qquad \text{(Equation 12)}$$

$$y\ \left(\frac{mg}{L}\right) = 4.1024 * x\ (abs) - 0.1298 \qquad \text{(Equation 13)}$$

4.3 Coagulation/Flocculation

In the coagulation process the destabilization of the particles present in the wastewater occurs due to the addition of a chemical product, in adequate quantity and conditions, allowing in a later stage, flocculation, the aggregation of these impurities in larger particles. The coagulation process normally takes last than 1 minute and happens in the fast-mixing unit. However, in the flocculation there is a need for slow agitation, so that shocks occur between the particles, which agglomerate forming flocs, which can be removed by sedimentation, flotation, or rapid filtration.

To determine the optimal process parameters, it is necessary to carry out three steps for each coagulant studied: determination of the minimum coagulant dosage; pH optimization; coagulant dosage optimization. The effects of adding different flocculants can also be assessed for test.

Using 200 mL sample on a magnetic stirrer, small amounts of coagulant were added to effluent at pH 5.0. After each addition, promoting rapid mixing for 1 minute followed by 3 minutes of slow mixing and at least a settling period of 10 minutes. The addition was made until visible formation of a supernatant layer. In the case of coloured effluents, the reduction of turbidity can be used as a parameter to determine the ideal coagulant volume.

To determine the ideal pH for the coagulation, a jar test equipment was applied, in this, six beakers of sample and the minimum dose of coagulant obtained in the first experiment was added. The pH was adjusted between 3 and 8, values adequate to the coagulant chosen (Aluminium Sulphate), using acid or base solutions. A rapid mix (120 rpm) was promoted of each sample for 1 min; followed by a slow stirring (30 rpm) for 3 min and, finally, 15 min of settling. In a sample from the supernatant the turbidity was measure using one turbidimeter MERCK Turbiquant 3000IR to determine which pH presented the higher removal. Due to colour alteration of the effluent analysed the turbidity were measured after the pH adjustment and at the end of the sedimentation time to provide a better removal measurement.

The effluent obtained in the most favourable conditions was submitted to characterization of some important parameters: Solids (TSS, TDS and TS), COD and Phenolic compounds.

Chapter - 5

Characterization

To determine which wastewater treatment is a good option for a specific effluent, it is necessary to perform an extensive characterization encompassing physic and chemical parameters.

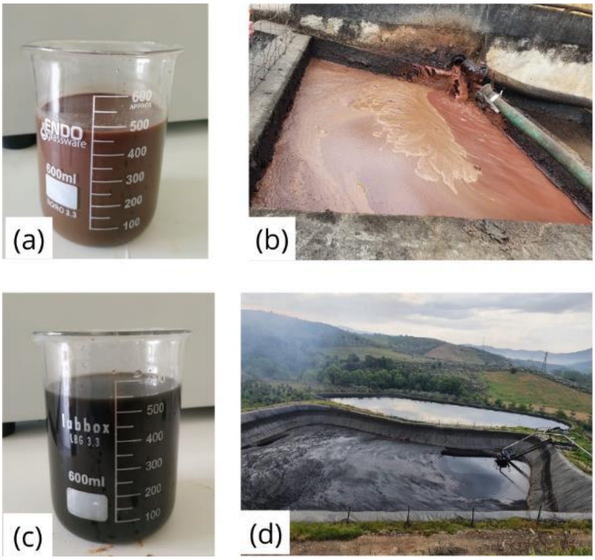


Fig 4: Visual aspect of effluent 1 and 2 and respective collection site

The wastewater was collected at two different locations in the plant. The first is the effluent as it leaves the process of olive pomace oil production, and the place and aspect can be seen in Figure 4 (a, b). The other is from the second storage tank, place and aspect are showed in Figure 4 c) and d).

The visual aspect of the two wastewater is very distinct in colour and turbidity. Effluent 1 is new, have a higher amount of BOD, COD and TSS, resulting in a lighter colouration and higher turbidity when compared to effluent 2, which is older and passes by a decantation process in the pool. An outstanding behaviour presented in effluent E1 and 2 is the absence of an oily layer caused by the separation of the FOG content as normally present in OMWW, it may be due to the smaller content of olive oil, naturally due the second extraction, and the emulsification of the any remaining FOG content.

The parameters choose to be determined: pH, conductivity, Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), phosphorus content, ammonia and organic nitrogen content, oils and grease, aromaticity, phenolic compounds, Alkalinity, and solids. The results for the two effluents are presented in Table 5:

Table 5: Physicochemical characteristics of effluent 1 and 2

Parameter	Unit	Effluent 1	Effluent 2
pH	-	4.21	4.97
Conductivity	mS/cm	9.30	8.80
BOD_5	g O_2/L	48.4 ± 2.1	15.01 ± 1.2
COD	g O_2/L	126.64 ± 7.63	28.52 ± 5.58
Organic nitrogen	g N/L	1.48 ± 0.05	0.21 ± 0.01
Ammoniacal nitrogen	mg N/L	73.13 ± 1.45	19.87 ±0.73
Phosphorus	g P/L	0.54 ± 0.01	0.33 ± 0.01
FOG	g/L	4.62 ± 0.35	2.63 ± 0.11
PhC	g/L	7.82 ± 0.13	1.42 ± 0.14
Aromaticity	g/L	51.66 ± 0.16	11.74 ± 0.5
Alkalinity	g/L	3.77 ± 0	4.71 ± 0.92
TS	g/L	54.97 ± 1.49	23.65 ± 1.46
TDS	g/L	43.57 ± 1.16	19.93 ± 0.49
TSS	g/L	3.28± 0.28	1.28± 0.1
TVS	g/L	45.17 ± 2.60	15.89 ± 1.05

When compared with the Emission Limit Values in the discharge of wastewater present in Decree-Law No. 236/98 of 1st August, all parameters analysed in the characterization of both effluent 1 and 2 are nearly 1000 times above the established limits, what confirms the need to implement a treatment unit for industrial effluents [28].

The polluting power of this effluent can be attributed to the high organic load, observed in the large concentration of BOD_5 and COD, organic nitrogen, and phosphorus content. Ranade and Bhandari (2014) attributed this to the presence of lipids, sugars, tannin, pectin and lignin, the high concentration of phenolic compounds as well as phosphate salts. The high organic load can also be attested by the values of TVS, that are close to TS, showing the most of solids have an organic nature.

The data obtained by Enaime *et al.* (2018) and present in Table 2, shows a similarity on the physicochemical properties of the primary and secondary olive oils extractor industry wastewaters, the pHs, conductivity, solids and nitrogen and phenolic contents are within the range of values proposed in the article. Nonetheless, the organic matter in E1 is superior the range in BOD_5 and COD content, only coming to lower values after aging in the storage tanks.

This proximity of physicochemical parameters to OMWW, makes this effluent a good candidate to reuse in irrigation of olive groves, the legislation only asks for a treatment to ensure pH compatibility, but this action needs monitoring by the competent professionals and apply for a license from the respective regional environmental directorate as described in Joint Order No. 626/20.

The lagoons may be considering a step in the pre-treatment, E2 characterization shows the reduction of 57% of TS, 54,3% of TDS, 61% TSS, 77.5% of COD, 69% of BOD and 81.8% of PhC when compared with the E1, newly produced. This step has the advantage of using the lagoons used by the industry only to stock the effluent, is a cheaper way to have good reductions in the parameters due to sedimentation and digestion of the effluent.

The disadvantage of the use of lagoon is the odour produced by the digestion and evaporation, increasing principally in the summer due the hotter temperatures and the dry climate. The lagoon accumulates the sludge provident from the decantation whereas it has no drainage or withdrawal system, it must be empty after some time and the sludge treated, in most cases using dewatering process as drying before their final disposal in landfills.

The biodegradability of E1 and E2 were measure based in the COD/BOD_5 ratio, and were obtained values of 2.62 and 1.90, respectively. A wastewater is considered easy degradable for a $COD/BOD_5 < 2.5$ and may be degradable with some difficult when $2.5 < COD/BOD_5 < 5$, to higher ratios, biological degradation is not recommendable. It makes E2 a better candidate for a biological treatment then E1 without pre-treatment. Domingues *et al.* (2021) had for the same type of effluent found a much smaller biodegradation ration, on 9% of the organic matter was biodegradable [24]. A higher ratio (26%) indicates a high biodegradable organic compounds fraction, and a biological treatment may be effective as future process in the treatment. In the Figure 5, is observed the Zahn-Wellens test, it shows a similar behaviour to both effluents.

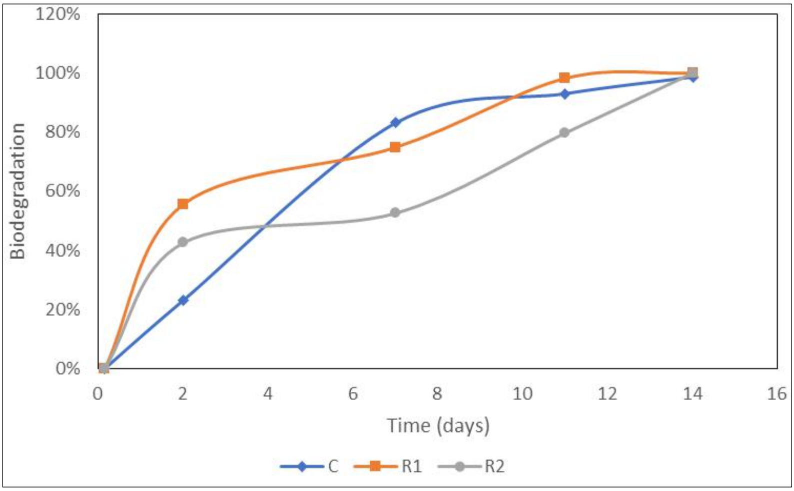


Fig 5: Zahn-Wellens biodegradation test curves

In the Zahn-Wellens test, activated sludge from the local domestic wastewater treatment unit is used to degrade an amount of the two effluents (R1 and R2). The third reactor (C) for control is used to validate the results using ethylene glycol as a control substance to determine the sludge quality and adaptability. A blank reactor with the same conditions as determined for the OECD Guideline (1992) was settled with no biodegradable substance to reduce influences in the COD determination by a colorimetric method due to parallel reactions and variations in the activated sludge. Due to the good adaptability of the activated sludge, in 14 days all the effluents were complete degraded.

However, even with COD/BOD$_5$ ratio that suggest biological treatments where an good option to reduce the pollutant load, the values to BOD and COD were high enough to require primary treatments to reduce the concentrations from g/L to mg/L. Analysing previous works with effluents with a polluting load close to that found in effluents and from nearby matrices, a promising route for treatment is the reduction of solids and organic matter by primary treatments such as coagulation/flocculation and flotation. A biological reactor can be applied as a secondary treatment to digest the remain biomass to acceptable levels, followed by tertiary treatments such as filtering and polishing the effluent until the emission limit values are respected in their entirety [24].

Another crucial aspect is its acidity due to the presence of organic acids, capable of changing the pH of a waterbody if discarded without treatment. The high among of organic and inorganic compounds, that work as nutrients, can destabilize the natural condition on the recipient waterbody, favouring the growth of algae in the process acknowledge as eutrophication. The concentration of phenolic compounds is other potential pollutant in this effluent, these compounds are known to be toxic and inflict severe and long-lasting effects on humans and animals and must have their concentration reduced before reach the waterbody.

An important aspect in the project to design a wastewater treatment facility is to evaluate the quality of the waterbody that is receiving the effluent. To ensure the environmental safety of the river in the point near the factory, the water was collected May 19, 2021. Sampling points selected to monitoring the river water quality is exhibited in Figure 6.

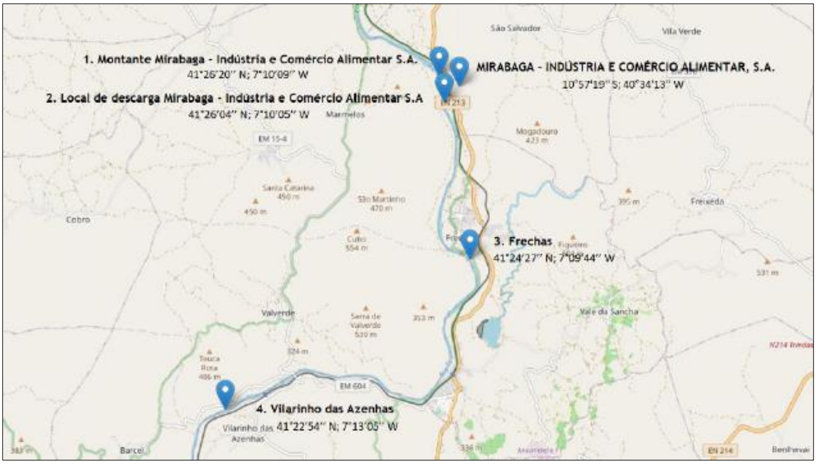


Fig 6: Tua river sampling points

The point 1 corresponds to the upstream sampling point, where the water quality has no influence of the factory studied and, point 2 corresponds the place of wastewater discharge from Mirabaga. Points 3 and 4 were downstream the industrial unit to evaluate the depuration of any pollution charge the factory relies on the river. Point four also corresponds to a pluvial beach accessible to the local population used for recreation and domestics activities.

The impact of industrial wastewater disposal is to be seen in point 2, the data shows a raise in parameters COD and BOD_5 when compared with point 1, as noted in Table 6. No effluent characterized previously in this article is released in the waterbody, this alterations in the values were due to the water used to cool the streams out the separation processes and the water recovered in the solvent recuperation process, the effluent pass for a cooling step before being pour in the river.

The waterbody has a good depuration capacity, with the parameters returning lower levels of organic matter as seen in point 3, indicating the factory do not overload the natural ecosystem. In point 4, turbidity, COD, nitrogen content and TSS increased, and can be associated to the human activity present in the area.

The water quality was assured comparing the results with the Portuguese water legislation, Decree-Law No. 236/98 of 1 August (shown in Table 4) considering the maximum recommended value for irrigation and bathing waters, none of the parameters obtained values higher than those allowed, securing the good quality of the waterbody and no negative influence from the factory at time of the sampling.

It is important to emphasize that the quality of the receiving river must be verified at a frequency lower than or equal to that described in the Decree-Law No. 236/98 of 1 August. This monitoring is essential for a good environmental management of the industry and prevention of the pollution of Portuguese waters.

Table 6: Water physicochemical characterization in four locations along the Tua river

Parameter	Unit	Point 1	Point 2	Point 3	Point 4
Temperature[1]	ºC	16.2	18.8	17.3	17.5
Conductivity[1]	µS/cm	47.3	56.5	46.5	45.9
TDS[1]	mg/L	26.9	31	26.3	25.7
Dissolved Oxygen[1]	mg O_2/L %	9.1 95.4	8 87.1	8.78 92.5	8.88 94.1
pH	-	6.4	6.14	6.2	6.17
Turbidity	NTU	12	27	11	14
BOD_5	mg O2/L	< 10	31	< 10	< 10
COD	mg O2/L	14	86	15	24
TSS	mg/L	6.9	28.9	5.2	7.5
TDS	mg/L	61.7	111.3	52.4	49.4
Ammoniacal Nitrogen	mg/L	0.44	0.31	0.27	0.34
Nitrates	mg/L	0.69	0.39	0.09	0.51
Total Phosphorus	mg/L	0.02	0.01	0.02	0.03
PhC	mg/L	< DL	< DL	< DL	< DL
Aromaticity	mg/L	13.2	23.2	13.5	14.8

[1]: parameters measured in the local where the samples were collected

<DL: lower than the method detection limit.

Chapter - 6

Coagulation/Flocculation

Coagulation and flocculation are some of the most extensively used wastewater treatments, due to their simple design and affordable price, producing considerable reductions in physicochemical parameters such as TSS, BOD, COD and PhC. The addition of coagulants, inorganic and organic, associated with agitation is sufficient to destabilize most of the colloids and molecules present in the effluent and form flakes that then are settle by gravity. The result can be observed by the formation and visual separation of the flocs and measured using turbidimeters.

The effluent 2 was chosen for the coagulation process since it has lower levels of COD, BOD and TSS due to the ageing process it passes in the lagoons. The chosen coagulant was alum ($Al_2(SO_4)_3$), based on the coagulation behaviour presented in OMWW coagulation treatments observed by Khouni *et al.* (2020), Vuppala *et al.* (2019), Iakovides *et al.* (2014) [25, 26, 33]. The flocculation was studied to improve the sedimentation, RIFLOC F45 was the flocculant chosen for the test due to it cationic nature, its positives result over OMWW have already been proven, pointed by Domingues *et al.* (2021) and Rattanapan *et al.* (2011) [24, 34].

First, the coagulant concentration was studied with the assistance of a turbidimeter to evaluate the turbidity removal, at pH 5. The settling time was of 20 hours to ensure the complete setting from the flocs formed in the coagulation process. The removal is shown in Figure 7, based on the initial turbidity of E2 (445.03 NTU).

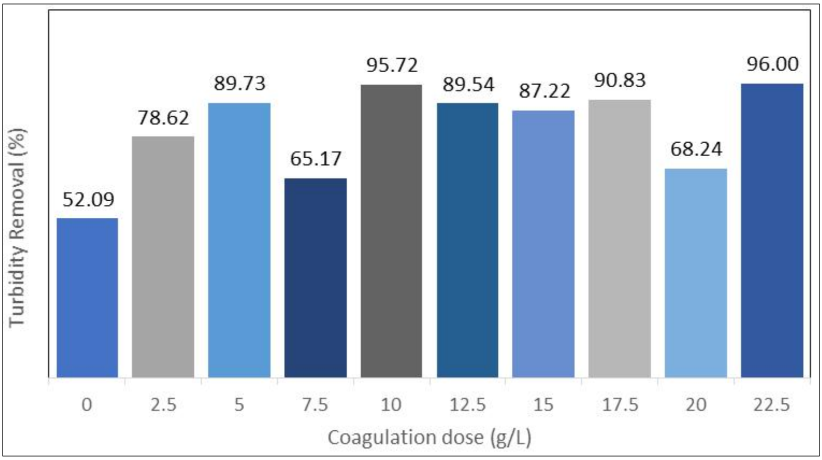


Fig 7: Turbidity removal vs. Aluminium Sulphate dose

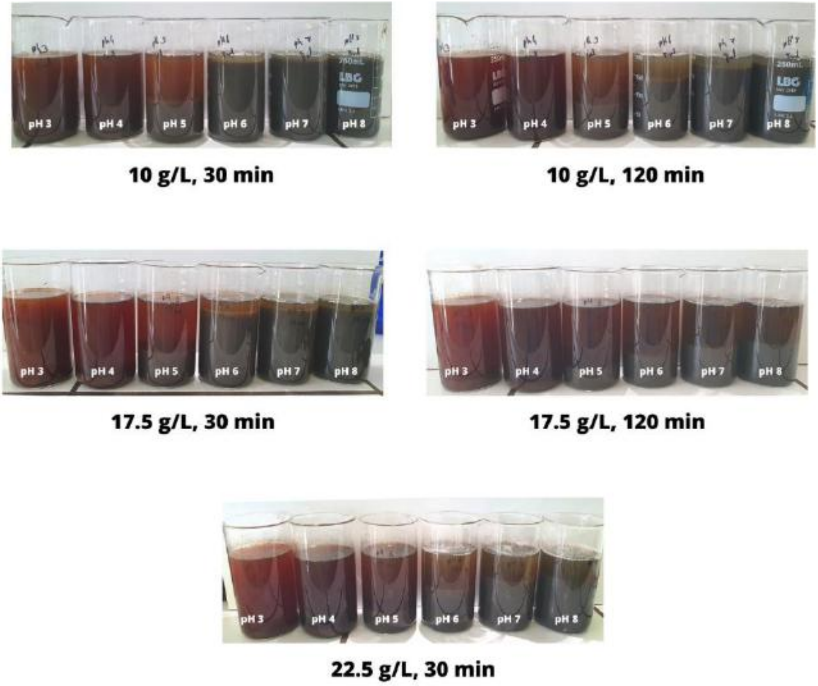
The best removal occurs to the alum concentrations of 10, 17.5 and 22.5 g/L, obtaining more than 90% of removal with a settling time of 20h. An anormal behaviour is obtained with concentrations of 7.5 and 20 g/L, the lower turbidity may be caused by the presence of smaller flocs that tend to suspend with any small disturbance in the system.

To the alum concentrations that presented better removal values (10, 17.5 and 22.5 g/L) a pH optimization test was made, where the pH was adjusted between 3 and 8 and the turbidity measured at the end 30 and 120 minutes as presented in Table 7.

Table 7: Turbidity removal (%) at pH variation in 10, 17.5 and 22.5 g/L coagulant and resting time of 30 and 120 minutes

$Al_2(SO_4)_3$	**10 g/L**		**17.5 g/L**		**22.5 g/L**
Settling Time	**30 min**	**120 min**	**30 min**	**120 min**	**30 min**
pH 3	0	52	-	7	0
pH 4	21	63	58	76	95
pH 5	77	81	80	89	82
pH 6	-	87	-	69	85
pH 7	-	84	-	90	88
pH 8	-	66	-	92	92

The turbidity was determined only for the samples that formed a large enough supernatant layer (30 mL required by the turbidimeter). The higher pH demonstrated a delay in forming a layer, the dark colour also impairs the visualization of the layer, as visualized in Figure 8. To 22.5 g/L of coagulant the turbidity removal to 30 minutes shown results close to the find to 17.5 g/L and 120 minutes, then the test does not proceed to 120 minutes of sedimentation.



10 g/L, 30 min

10 g/L, 120 min

17.5 g/L, 30 min

17.5 g/L, 120 min

22.5 g/L, 30 min

Fig 8: Visual aspect of samples for pH variation in 10, 17.5 and 22.5 g/L coagulant and settling time of 30 and 120 minutes

The best absolute turbidity removal was observed for pH 8 and coagulant concentrations of 17.5 g/L (120 min) and 22.5 g/L (30 min) with removal higher than 91%. Nonetheless, using 10 g/L of coagulant at pH 5 we achieved 77.4% turbidity removal after 30 min and 81% after 120 min, which makes this a standout removal condition to be investigated.

After the optimization of coagulant dosage and pH parameters, the addition of flocculant was evaluated adding RIFLOC F45 in the final concentration of 2 and 4 mg/L, in the conditions of 10 g/L and 17.5 g/L and different pH, as exhibited in Table 8.

Table 8: Turbidity removal for flocculant addition on different coagulant concentration and pH

Coagulant dosage	**pH**	**Flocculant dosage**	**Turbidity removal (%)**	**Flocculant dose**	**Turbidity removal (%)**	
		(mg/L)	**30 min**	**(mg/L)**	**30 min**	**24 h**
10	3	2	35	4	68	81
	4		64		68	72
	5		43		74	91
	6		23		62	90
	7		4		63	92
	8		56		84	95
	9		-		-	98
	10		-		-	98
	11		-		-	99
	12		-		-	98
17.5	3	2	36	4	-	69
	4		76		-	86
	5		79		-	92
	6		68		-	90
	7		62		-	85
	8		45		-	87
	9		-		-	96
	10		-		-	95
	11		-		-	98
	12		-		-	98

Higher pH values were evaluated in this experiment due to an improving trend in turbidity removal from the increase in pH. The addition of flocculant in higher concentrations also shows improvements of at least 30%, discarding the study of smaller coagulant concentrations. The similarities of turbidity removal for different concentrations design the study in a future test of the lower concentration (10 g/L) reducing the treatment cost.

The improvement using flocculant was made by evaluating the removal of TSS, TDS, TS, COD and PhC in the most prominent conditions: 10 g/L at pH 5, due to the proximity of the effluent pH, and pH 8 and 9 due to the higher removal. The reduction results for a resting time of 3 h, much more suitable to a real coagulation process, are shown in Table 9:

Table 9: Turbidity, COD, PhC, and solids removal to the addition of flocculant in different pH (% removal)

pH	Flocculant (mg/L)	Turbidity removal	COD removal	PhC removal	TS removal	TDS removal	TSS removal
5	0	43.	69	0	10	4	66
	4	74	70	28	24	17	98
8	0	0	71	16	0	0	0
	4	0	72	0	4	0	94
9	0	84	68	0	2	0	25
	4	53	73	15	7	0	71

Sedimentation period is an important parameter in coagulation tests to observe the decantation velocity, in the coagulation tanks in wastewater treatment facilities. To obtain results closer to the reality, the resting time was set in 3 hours, by cause of no-good decantation of the samples with pH of 8 and 9 after a resting time of 1h. Although, 3 hours show to be too small amount time interval to obtain good results to solids removal for this samples. Observing the data from pH 5, is clear the improvement of removal levels with the addition of flocculant, producing a TSS removal of 98% after 3 hours of sedimentation.

To pH 5 the influence of flocculant addition is clear to visualize in Figure 9. All the parameters had they removal improved whit the addition of RIFLOC F45, the TSS removal reach almost 98%, 33% superior to the sample without flocculant addition. For turbidity, TS, and TDS parameters the removal was increase 42, 59 and 77%, respectively. To COD removal the improvement was almost despicable (1.6%).

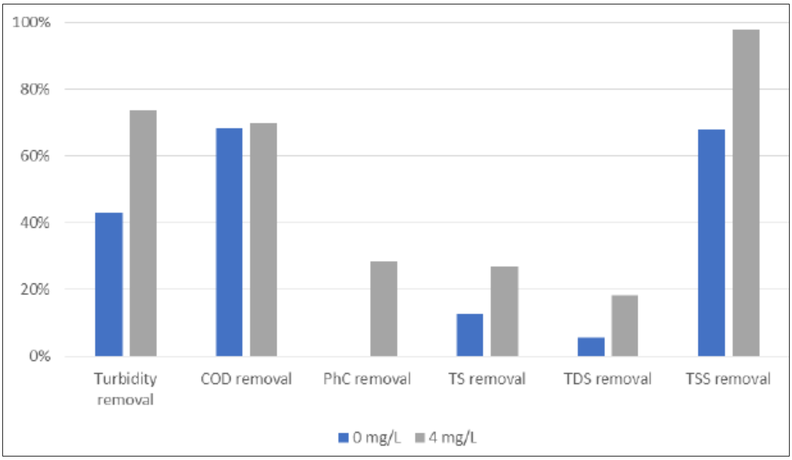


Fig 9: Influence of flocculant addition at pH 5

To ensure the best coagulant concentration, the first test was redone in the optimal pH (5), and the parameters, turbidity, TSS, COD and PhC were determined to evaluate any improvement in the removal levels for these parameters for concentrations close of the minimal dose. The results are shown in Table 10.

Table 10: Turbidity, TSS, COD and PhC removal at pH 5 and different coagulant concentrations (% removal)

Coagulant dosage (g/L)	Turbidity	TSS	COD	PhC
10.0	96	77	76	85
15.0	89	80	73	89
20.0	71	82	76	86
25.0	95	83	79	84
30.0	90	85	76	96

In Figure 10 is observed that the decrease in turbidity is not directly related to the decrease in TSS. This may be due to the dissolved solids reduction with coagulation due to secondary processes. This low ratio, together with the low variation in COD removal, makes the *Alum* concentration of 10 mg/L still the ideal minimum concentration for the process.

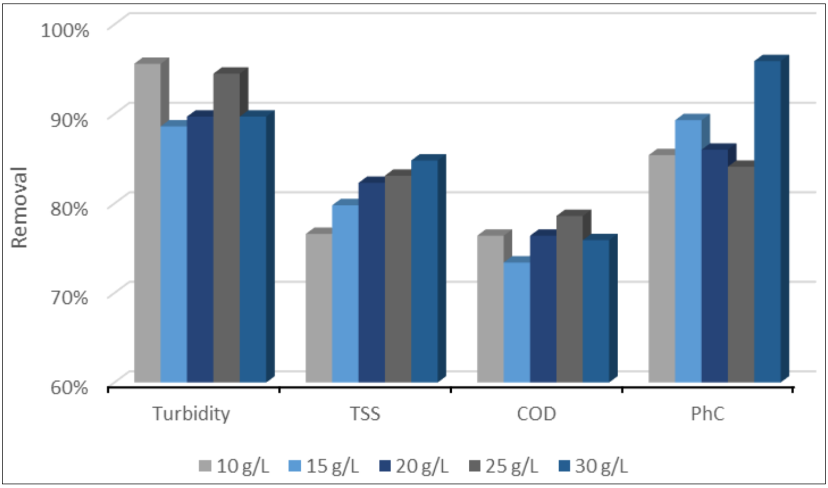


Fig 10: Removal variation for different coagulant concentrations

The best results were obtained for concentration of 30 g/L, which has the best remotion for PhC and TSS, but no statistic relevance was observed in these values. The addition of 2-3 times the concentration of coagulant does not produces a relevant removal in the parameters, making the dosage of 10 g/L of Aluminium Sulphate more interesting, leading to removals of TSS, COD and PhC of 76%, 76% and 85%, respectively.

Despite the good remotion awarded, the clarified effluent still present concentrations of COD, TSS and PhC superior to the maximum allowable values. So, that industrial effluents are admitted to a wastewater discharge in a waterbody, highlighting the fact that coagulation/flocculation process alone is not generally a complete solution to wastewater treatment problems, the reduction of this parameters, however, provides better conditions to a biological treatment, as increasing the biodegradability of the effluent and reducing the volume necessary in a reactor and decanter due to the high sludge formation.

According to other article that apply coagulation/flocculation process in OMWW, two cases are observed, the first when the concentration used are much smaller for the same coagulant, as the one obtained by Vuppala *et al.* (2019), who achieved a reduction of 99% of turbidity, with alum concentration of 400 mg/L plus chitosan (100 mg/L), and removal of 57.16% COD and 62.89% PhC with 800 mg/L of alum [26]. This behaviour may be due to the distinct wastewater composition, the effluent used in this study is the result of chemical extraction and presents they FOG content in emulsification, contrasting with the normal aspect encounter in OMWW where an oily layer is formed in stored effluents and normally is removed in pre-treatments before coagulation/flocculation. This aspect may result in the difference of effluent particles nature in suspension and its interaction with coagulants, demanding higher concentrations.

Using different coagulants, it was found in literature the report of higher concentrations and slow settling velocities, as observed by Iakovides *et al.* (2014) in the study of OMWW coagulation using electrolytes ($FeCl_3$, $Ca(OH)_2$, CaO, $CaCl_2$) and polyelectrolytes (PDADMAC, PAH, PAA, PEI, Floccan 22-23), the best results were obtained with calcium hydroxide at 20 g/L leading to removals of 56% COD, 27% TSS, 43% TS and 76% PhC [25]. Papaphilippou *et al.* (2012), also obtained high removals of TSS (97%), COD (72%), and PhC (40%), using iron sulphate in the concentration of 6.67 g/L associated with flocculant FLOCAN 23-287 mg/L [27]. These concentrations are consistent with the values found in this study, producing even values close to those obtained in the reduction of the studied parameters.

One important observation must be done about the aspect of the solids decanted with the coagulation and flocculation process in the studied conditions. Small and light flakes were produced, which corresponds to inadequate sludge compaction, and under the slightest agitation rise, rising the turbidity of the supernatant as well. The collection of the supernatant must be carefully made with a pump, or a filtration process must be used to obtain a supernatant with the lowest concentration of solids possible. The test of different flocculants is carried out to improve the appearance and weight of the flakes produced in the treatment, facilitating their removal.

Chapter - 7

Conclusions

The concept of Circular Economy is already being applied in the olive oil sector in Portugal, with olive pomace oil as the most prominent product. Nonetheless, the use of by-products from the olive oil production still generates new by-products and effluents, this study aimed for the characterization of the effluent from an olive pomace oil extractor industry and investigate the application of physicochemical pre-treatments to future water reuse.

The fresh effluent (E1) and the effluent from a storage tank (E2) characterisation, by using 14 parameters, demonstrate both effluents have high pollutant load and cannot be released in the river near the factory, due to non-compliance with the limit values for the parameters as stated in Decree-Law No. 236/98 of 1st August, which regulates the emission limit values for wastewater discharge. The Tua river was also analysed to assure the quality of the waterbody and observe any pollution. At the four sampling points, any parameter exceeded the maximum emission values presented in the same legislation, and no pollution from the factory was observed, by the cause, the only effluent from the factory to reach the river is the water used for cooling the extraction process. To provide environmental management to this industrial plant, the waterbody must be monitored as required by current legislation, in the parameters determined by it and sampling frequency required for the maintenance of the quality validated in May 2021.

The lagoons, where the effluent is stored, reveal to be an interesting step for the pre-treatment, reducing TS (57%), TDS (54%), TSS (61%), COD (78%), BOD (69%) and PhC (82%) when compared with the fresh effluent. E2 was submitted to coagulation/flocculation treatment, having the best conditions shown to be 10 g/L of Aluminium Sulphate (coagulant) and 4 mg/L of Rifloc F45 (flocculant), with pH of 5 and a settling period of 3 hours. For these conditions, removals of 96% (turbidity), 76% (COD), 77% (TSS) and 85% (PhC) were achieved, when compared with E2.

The treated effluent can be reused, inside the factory, or in the irrigation of olive groves. To return the water to the waterbody is yet necessary for further treatment, such as biological treatment, as the effluent show before good biodegradability in the Zahn-Welles test.

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