Electrochemical oxidation as a strategy for wastewater reuse

(versão final após defesa)

Daliany Maria Farinon

Dissertação para obtenção do Grau de Mestre em

Química Industrial

2º ciclo de estudos

Orientadora: Doutora Annabel Dias Barrocas Fernandes
Co-orientadora: Mestre Alexandra Isabel Godinho Afonso

Dezembro de 2024

Declaração de Integridade

Eu, Daliany Maria Farinon, que abaixo assino, estudante com o número de inscrição M12441 do 2º ciclo de Química Industrial da Faculdade de Ciências, declaro ter desenvolvido o presente trabalho e elaborado o presente texto em total consonância com o **Código de Integridades da Universidade da Beira Interior**.

Mais concretamente afirmo não ter incorrido em qualquer das variedades de Fraude Académica, e que aqui declaro conhecer, que em particular atendi à exigida referenciação de frases, extratos, imagens e outras formas de trabalho intelectual, e assumindo assim na íntegra as responsabilidades da autoria.

Universidade da Beira Interior, Covilhã 13/12/2024

DALIANY MARIA FARINON
13/12/2024 15:45:36

Acknowledgments

To the Research Unit of Fiber Materials and Environmental Technologies (FibEnTech-UBI) through the Project reference UIDB/00195/2020, funded by the Fundação para a Ciência e a Tecnologia, IP/MCTES through national funds (PIDDAC), and DOI: 10.54499/UIDB/00195/2020 (https://doi.org/10.54499/UIDB/00195/2020), for the support granted.

To the Lusitano project, reference 01/C05- 229 i09/2024.PC644933224-00000043, funded by the Recovery and Resilience Plan, for the Research Grant BI#5.

To my supervisor, Doutora Annabel Dias Barrocas Fernandes, for the valuable scientific support, friendship, patience, and encouragement she has given me. It has been a huge privilege to work and learn with her.

To Professor Doutora Ana Maria Carreira Lopes, for her continuous guidance and help and for the immense expertise and constructive discussions that were crucial for the success of this work.

To my co-supervisor, Master Alexandra Isabel Godinho Afonso.

To my laboratory colleagues, who were essential in this journey, especially Carlos Yuri, an exceptional person who helped and taught me from the start.

To my family, who, despite the distance, have always been by my side.

And to me, for sticking with it, even in the most difficult times.

Resumo alargado

A crescente escassez de água e os desafios ambientais gerados por efluentes industriais, juntamente com o aumento populacional projetado pelas Nações Unidas, evidencia ainda mais a necessidade da aplicação de tecnologias para reduzir o consumo de água e tratar adequadamente os efluentes industriais, visando evitar a contaminação dos cursos de água e solos, além de viabilizar a reutilização, fomentando a economia circular.

A indústria da produção de azeite e a indústria têxtil são dois exemplos de indústria consumidora intensiva de água e geradora de efluentes com elevada carga poluente. Na indústria da produção de azeite, para produzir 1 kg de azeite extra virgem, são necessários cerca de 3600 L de água, gerando grandes volumes de águas residuais (OMW) altamente poluentes. Na indústria têxtil, o processo de tingimento consome entre 100-180 L de água por kg de fibra processada, originando efluentes com carga poluente elevada e recalcitrante, que é agravada quando o efluente é submetido a processos de tratamento por membranas, originando os concentrados membranares de efluente têxtil (MCTW). Sem tratamento adequado, estes efluentes não podem ser descartados ou reutilizados.

Diversas tecnologias de tratamento, incluindo processos biológicos, químicos e de oxidação avançada, têm sido estudadas. Nas últimas décadas, a oxidação eletroquímica (OE) ganhou destaque pela sua elevada eficiência no tratamento de efluentes com propriedades recalcitrantes, sem a necessidade de reagentes adicionais ou produção de lamas. Na sua forma mais simples, a OE ocorre através de dois elétrodos conectados por um circuito externo. O material dos elétrodos pode variar de acordo com as características do efluente e os objetivos do tratamento.

No presente estudo, foi aplicada a OE no tratamento de OMW e MCTW. O tratamento do OMW teve como objetivo reduzir a carga orgânica e a toxicidade do efluente, para reutilização em agricultura hidropónica. O tratamento do MCTW visou a geração de espécies reativas de cloro, como o hipoclorito, para reutilização como agente anti-incrustante em processos de membranas da própria indústria têxtil. Os efluentes utilizados foram recolhidos em duas indústrias localizadas em Portugal.

No tratamento do OMW, foi utilizado um ânodo de diamante dopado com boro (BDD) e um cátodo de aço inoxidável. A escolha do material de ânodo prendeu-se com a sua elevada eficiência na oxidação da matéria orgânica, reportada na literatura. Os ensaios de tratamento eletroquímico tiveram a duração de 8 horas e foram realizados a três intensidades de corrente distintas, 300, 500 e 700 mA. Resultado das três condições de corrente estudadas, foram obtidos três efluentes tratados, com características diferentes. O consumo energético específico do tratamento variou de acordo com a corrente aplicada, sendo o menor consumo obtido para 300 mA. A remoção da carência química de oxigénio (CQO) foi de, aproximadamente, 83%, 93% e 98% para 300, 500 e 700 mA, respetivamente. O pH dos efluentes tratados resultantes dos processos a 500 e 700 mA apresentaram-se alcalinos, o que não favorece o cultivo hidropónico. No entanto, o índice de biodegradabilidade aumentou consideravelmente para estas correntes. Para os três efluentes tratados, a taxa de adsorção de sódio (SAR) apresentou níves dentro do adequado, mas a condutividade elétrica apresentou valores que poderiam causar danos moderados ao cultivo. Ainda assim, a diluição dos efluentes tratados possibilita a sua reutilização no cultivo hidropónico.

Para o tratamento do MCTW, foi utilizado um ânodo de óxidos metálicos mistos (MMO), uma vez que, de acordo com a literatura, este tipo de material favorece a reação de oxidação do cloro e, consequentemente, a produção de espécies reativas de cloro. Foram realizados ensaios de tratamento eletroquímico com duas amostras distintas: MCTW_1, que consiste no concentrado da ultrafiltração, e MCTW_2, que consiste no concentrado da osmose inversa. Para MCTW_1, os ensaios tiveram a duração de 40 horas, com corrente aplicada de 0.5 A durante as primeiras 32 horas e 2.5 A nas 8 horas finais. Para MCTW_2, os ensaios tiveram a duração de 75 horas, com corrente aplicada de 1 A durante as primeiras 40 horas e 0.75 A nas 35 horas finais. O tratamento eletroquímico dos concentrados têxteis resultou na geração de hipoclorito, alcançando 62% da produção teórica máxima de ClO^- na amostra MCTW_1 e 54% na amostra MCTW_2. A produção de clorato aumentou com a corrente aplicada, que também resultou no aumento do consumo energético do processo. A remoção de CQO foi de 61% para MCTW_1 e 68% para MCTW_2, mostrando que o processo foi mais eficiente para a segunda amostra, devido à maior carga orgânica inicial.

A OE mostrou-se uma técnica promissora para a remoção de compostos orgânicos e produção de efluentes com potencial de reutilização. No caso dos efluentes da indústria de produção de azeite, a corrente de 500 mA foi considerada a mais adequada, de entre as estudadas, para a reutilização do efluente tratado em cultivo hidropónico, embora a sua diluição seja necessária. Para os efluentes têxteis, o tratamento gerou hipoclorito com potencial para reutilização industrial, requerendo o processo otimização para minimizar o consumo energético e a formação de clorato.

Palavras-chave

Economia circular;BDD;MMO;hipoclorito;cultivo hidropónico

Abstract

This study aims to electrochemically oxidize (EO) industrial wastewater, namely olive mill wastewater (OMW) and membrane concentrate of textile wastewater (MCTW), to produce treated effluents that can be reused in hydroponic agriculture (treated OMW) and as an anti-fouling agent in membrane processes (treated MCTW).

OMW treatment was performed using a boron-doped diamond (BDD) anode suitable for mineralizing organic compounds. Three different applied current intensities were studied, 300, 500, and 700 mA. EO removed up to 98% of the chemical oxygen demand (COD). The biodegradability of the treated OMW increased considerably, especially at 500 and 700 mA. The specific energy consumption increased with the applied current intensity. Considering the overall results, the OMW treated at 500 mA was considered the most suitable for hydroponic cultivation. However, it must be diluted in fresh water to adjust pH and electrical conductivity.

MCTW treatment used a mixed metal oxide (MMO) anode, which is prone to generating active chlorine species from chloride oxidation. Two different MCTW samples were studied: ultrafiltration retentate (MCTW_1) and reverse osmosis retentate (MCTW_2). With both samples, hypochlorite (ClO^-) was generated by EO, leading to treated MCTW samples rich in oxidizing agents with potential for industrial reuse. COD removal was 61% for MCTW_1 and 68% for MCTW_2. Further process optimization is required to minimize energy consumption and chlorate formation.

The obtained results showed that EO is a promising process for treating industrial wastewater. It enables the reduction of the pollutant load and the reuse of the treated wastewater in a circular economy approach.

Keywords

Circular economy;BDD;MMO;hypochlorite;hydroponic cultivation

Index

List of Figures

List of Tables

Chapter 1

Introduction

This chapter presents the framework and motivation that led to the development of the study. It also describes the specific objectives and the strategy followed to achieve the main objective. At the end of the chapter, a description of the content of this dissertation is presented.

1.1 Framework

According to the United Nations (UN), the global population is expected to increase from 8 billion persons in 2022 to approximately 9.7 billion in 2050. This, and other trends happening at the same time, will have implications, mostly about water scarcity, for many generations to come [1]. Therefore, it is imperative to seek solutions and improvements to reduce the amount of water required in industrial processes, as well as treatments for the wastewater they produce. An adequately treated wastewater will prevent watercourses and soil contamination in case of disposal, but it will also allow its reuse in the industry itself or other applications, promoting a sustainable and circular economy, which is the aim of this study. In this context, olive oil and textile industries are responsible for extremely high water consumption and the generation of highly toxic wastewater, requiring an effective treatment [2,3].

The olive oil industry consumes about 3600 L of water to produce 1 kg of extra virgin oil (agricultural stage not included), generating 0.5-1.8 m^3 of olive mill wastewater (OMW) per ton of olive oil and, in terms of polluting load, 1 m^3 of OMW is equivalent to 200 m^3 of domestic sewage [4–6]. OMW has high levels of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) and can contain organic and inorganic compounds, many of them recalcitrant, being a very complex phytotoxic wastewater. Therefore, it cannot be discharged or reused without being treated [7].

Regarding the textile industry, known as one of the most intensive water consumers and responsible for the generation of pollutants around the world, the dyeing of 1 kg of fiber requires an average of 100-180 L of water [8]. Just like in the olive oil industry, wastewater from the textile industries has high levels of polluting load, containing recalcitrant compounds and other characteristics that do not allow its disposal or reuse without treatment [9]. This pollutant and recalcitrant load is even more aggravated when the wastewater is submitted to membrane treatment processes, leading to membrane concentrates from textile wastewater (MCTW).

Several treatment technologies have been and continue to be studied to treat these effluents, such as biological, chemical, and other treatments [10–12]. Electrochemical processes have gained space in the scientific field in the last decades. Electrochemical oxidation (EO) has shown high efficiency in the treatment of effluents with recalcitrant properties, achieving high levels of treated water quality without requiring the addition of reagents or resulting in the production of sludge or concentrates [13]. It is possible to select a more effective anode material, considering the characteristics of the wastewater and objectives for the treated wastewater.

1.2 Objective/Strategy

The main objective of this study was to develop strategies for reusing industrial effluents with recalcitrant properties, involving treatment by electrochemical oxidation. To achieve that, a four-step strategy was outlined and applied, comprising:

Step 1) Select two industrial wastewaters with high environmental impact that are difficult to treat: OMW and MCTW;

Step 2) Propose a reuse strategy: (a) OMW – treat by EO under different operating conditions to obtain 3 different quality indexes of treated OMW and evaluate the influence of the quality index on hydroponic lettuce cultivation; (b) MCTW – treat by EO under different operating conditions with the objective of obtaining a solution rich in oxidizing species (hypochlorite, etc.) for reuse in the membrane process of the textile industry itself, aiming to improve it.

Step 3) Carry out the electrochemical treatments and evaluate the influence of different operating conditions;

Step 4) Send treated wastewaters for their respective reuse.

1.3 Dissertation structure

This dissertation is structured into five main chapters. In the first chapter, the work is framed and the motivations for carrying it out are presented. The objective of the work is presented, as well as the strategy followed to achieve it, and a summary of the dissertation structure is made.

In the second chapter, a literature review is made on the electrochemical method used in this work, EO, and its application in the treatment of OMW and MCTW, and on studies already published regarding the reuse of such wastewaters. The fundamentals of electrochemical oxidation are presented to understand better its advantages and limitations in the treatment of OMW and MCTW and the effect of the main variables on process efficiency. It also presents a brief explanation of how the industries function. Regarding the studies already published on reuse, a brief contextualization is carried out, as well as the importance of developing strategies to promote treatment aimed at reuse.

In the third chapter, the characterization of the wastewaters used in this work is presented, as well as a description of the electrochemical oxidation experiments performed and the analytical methods used to monitor them.

The fourth chapter describes the experimental work carried out and the results obtained, as well as discusses the results.

Finally, the fifth chapter presents the main conclusions and perspectives for future work.

Chapter 2

Fundamentals and literature review

This chapter presents a literature review on the industries that generate the wastewaters used in this work and the fundamentals of the electrochemical method used in this study.

2.1 Olive oil industry

The olive tree has an important role in culture, health, and economic levels of society and has coexisted with humans since ancient times [14,15]. Records indicate that olive trees were grown around the Mediterranean basin six millennia ago, being one of the oldest cultivated trees in the world and linked to the emergence of ancient civilizations due to its use in multiple areas of the economic chain [16,17]. Its use in different spheres among the population and the exploring events of important empires, namely The Roman Empire, spread the cultivation of olive trees, extraction, and use of its products, mostly olive oil, throughout Europe [18].

Spread throughout Europe, Oceania, Asia, and Africa, the wild olive or oleaster (*Olea europaea* subsp. *Europaea* var. *sylvestris*) and the 'European' or cultivated olive (*Olea europaea* L. subsp. *europaea* var. *europaea*) are often found coexisting [16,18,19]. The last is considered by some researchers a representative of one big group of diverse plants located in different geographical areas [16,18]. On the other hand, other researchers believe that it is a hybrid among two or more different species [15,18,19].

Regardless of the actual genetic origin of the species, the olive tree had and still has immense cultural and economic importance in the world, and since the knowledge of health benefits of olive oil, such as reducing the incidence of major cardiovascular events, was disclosed, even more attention was drawn to the production of this commodity [20]. To meet the demand, the olive oil industry had to improve its extraction processes to increase production and maintain the oil quality. The European Union (EU) is responsible for approximately 67% of the world's olive oil production and 50% of the consumption of olive oil per year, with Spain, Italy, Greece, and Portugal as the most significant producers [21]. However, larger productions generate more significant amounts of OMW, which is estimated to be around 6×10^6 m^3 worldwide, being 98% produced in the Mediterranean basin [22].

2.1.1 Production process

For centuries, the traditional process has been used to extract the oil from the olives, undergoing small changes over time [11,23]. In ancient times, the process consisted of crushing the olives in a stone mortar, adding hot water to the paste formed, and collecting the oil from the surface since it is lighter than water. However, as the demand increased, the Romans introduced presses to the process, which led to the traditional process, improving the extraction system [14]. Therefore, currently, there are two methods of extraction of olive oil: the traditional process

(Figure 1 (a)) and the modern process (Figure 1 (b)), which are mechanical methods that, according to the European Commission Regulation No. 1513/2001 [24], are the only methods allowed to be used for extraction, to preserve the natural organoleptic characteristics [11].

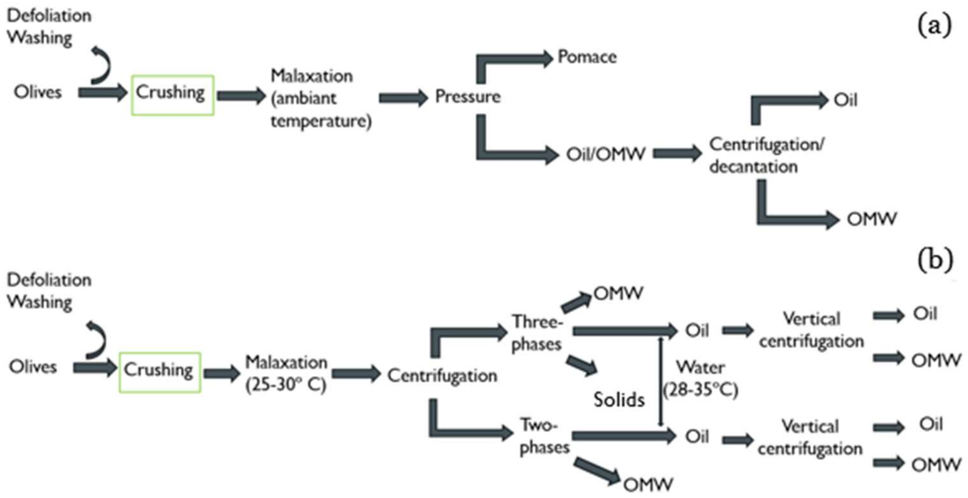

Figure 1. Extraction processes of olive oil: (a) traditional process and (b) modern process. Adapted from [11].

The traditional process (Figure 1 (a)) is a discontinuous process in which the crushing or milling of the olives, aiming to tear apart the plant tissue to liberate the oil contained in the cells, is performed by cylindrical or conical-shaped stone mills that rotate in a granite base [25]. The paste formed is kneaded (malaxation) and then put in fiber disks that, after being placed on top of the other, are pressed by a hydraulic press, compacting the solid phase and allowing the liquid phases to flow in a container (water is added to increase the speed of the flow). These liquid phases are separated by decantation or vertical centrifugation, resulting in the oil itself and OMW [11]. Some advantages of the traditional process, like no metal contamination that can affect color and flavor, reducing oxidative stability, and avoidance or minimization of emulsion formation, contribute to the production of higher quality oil, but nowadays, only small producers still use this system, since it has a low capacity of production and requires large spaces [11,25].

The modern process (Figure 1 (b)) is a continuous process in which the extraction can be performed by a three-phase method or a two-phase method [11,25,26]. The first was developed in 1970 to increase production capacity. This process uses a centrifugation system with a decanter, producing three phases (Figure 2): oil, solid residue, and OMW [11,25]. The disadvantage of this method is the higher water consumption, which generates a higher amount of wastewater [11,26,27]. Hence, to maintain a high production capacity and reduce the generation of wastewater, the manufacturers developed the two-phase (Figure 2) method that delivers only oil and a humid substrate (OMW + pomace) [11,25,27]. This process has the advantage of using less water and, consequently, produces less wastewater [11,28].

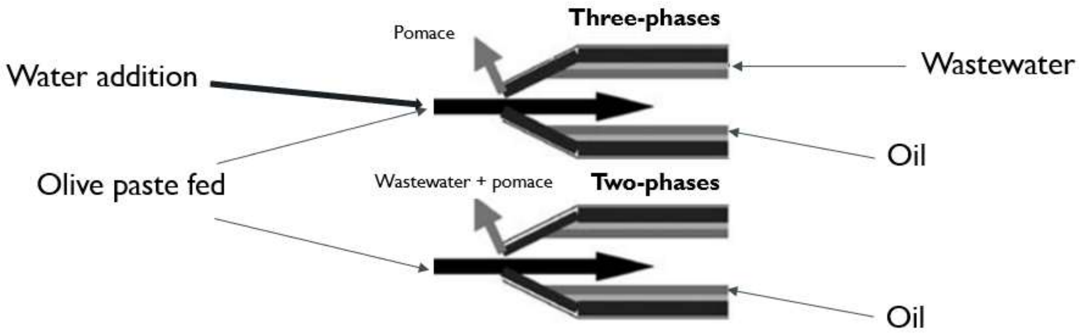

Figure 2. Three and two-phase centrifugation scheme. Adapted from [25].

2.1.2 Characterization and environmental impact of OMW

Each olive oil production process uses different amounts of water, generating different amounts of OMW. Table 2.1 shows the approximate amount of water used, as well as olive oil and OMW produced by each process when 1000 kg of olives are processed.

Table 1. General oil and wastewater quantities produced by each process. Adapted from [26].

Mill type	Olives / kg	Water / L	Olive oil / kg	OMW / L
Traditional	1000	100-200	230.4	650
Three-phase		100-1000	256.4	1200
Two-phase		100-120	247.4	200-300

The characteristics of wastewater from olive oil production depend on several factors, such as olive type and degree of ripeness, but the most important is the extraction technology used [7,10]. In general, OMW is a dark-colored and foul-smelling liquid, being the composition by weight of 83%–96% water, 3.5%–15% organic constituents, and 0.5%–2% mineral compounds, also containing inorganic ions and suspended solids [4,10,29]. Table 2.2 presents the general values for the most commonly analyzed parameters of OMW.

Table 2. General characterization and composition of OMW reported by different researchers.

Parameters	Unit	OMW	References
pH	–	4 – 6	[4,5,26]
EC	mS cm^{-1}	1.5 – 81	[11,30]
COD	g L^{-1}	4 – 356	[5,11,26,31]
BOD_5	g L^{-1}	35 – 132	[26,32]
Potassium	g L^{-1}	2.5 – 6.2	[5,31]
Sodium	mg L^{-1}	1.320 – 2060	[31,33]
Calcium	mg L^{-1}	240 – 780	[5,34]
Magnesium	mg L^{-1}	580 – 2.600	[5,31]
Chloride	mg L^{-1}	4.620	[31]

The high content of organic compounds (aromatic and aliphatic), of which 2-15% are phenolic compounds, including antibacterial substances that make OMW resistant to biodegradation, results in COD and BOD values of 4 to 356 g L^{-1} and 35 to 132 g L^{-1}, respectively, which are strongly linked to environmental pollution [35–38].

2.1.3 Treatment technologies for OMW

Over the years, treatment methods have been developed to reduce the pollutant load of OMW, mitigate environmental damage, enable the reuse of treated effluent, and remove nutrients for further use. Table 3 shows the main treatments described in the literature for OMW treatment.

Table 3. Treatment methods for OMW.

Treatment method	Type	COD removal	Observations	References
Biological	Aerobic Anaerobic Composting	80% 80-85% 52%	OMW has to be diluted and the process can take 90 days to be completed Some methods have a high cost	[39,40]
Thermal	Evaporation Distillation Combustion Pyrolysis	20-80% 20-80% - -	High energy cost	[5,11]
Physicochemical	Centrifugation Neutralization Adsorption Fenton reaction AOPs	21% 30-50% 30-50% 86% 30- 100%	Some methods require pre-treatment, increasing the costs	[22,29,41,42]

The biological treatment uses microorganisms and their mechanisms to break organic compounds and remove nutrients. The choice of microorganisms and their adaptability is essential for satisfactory results since the phenolic compounds, some organic acids, long-chain fatty acids, and polyphenols present in OMW can inhibit the action of some microorganisms [10,11]. The aerobic way uses bioreactors that, with the addition of oxygen and other essential nutrients, promote ideal conditions for the growth of bacteria, fungi, and others, allowing these microorganisms to decompose by oxidation, complex organic compounds, reverting them into simpler molecules that can return to the environment more safely [43,44]. There are also composting and vermicomposting treatments. The first uses aerobic microorganisms in the environment and biomass to produce compost via natural bioxidative activity on organic molecules, performed in mesophilic and thermophilic. The last, function similarly, but uses earthworms as bioxidative agents. The limitations of these treatment methods are the long duration of the process and the attention needed to have an effective treatment [40]. The anaerobic treatment uses limited or no oxygen at all, requires little energy, and in the process of compounds degradation biogas is created, which can be used to produce energy [10,40]. However, it usually requires a pretreatment to reduce the organic load and dilution (due to the inhibitor ingredients) since, for bioconversion to be effective, the OMW must have a balanced level of C/N/P and pH between 6,5-7,5 [10,29].

There are also thermal treatments, the most common of which are combustion, evaporation, distillation, and pyrolysis. Due to the moisture content of OMW, the thermal treatments must be performed indirectly, as in the combustion treatment, olive solid waste can be added to OMW to impregnate lignocellulosic biomass and produce green pellets. Pyrolysis is a promising technique that produces liquid, solid, and gaseous products that can be recovered. The limitations of these methods are the high energy consumption and, consequently, the high cost and the production of toxic gases [5,11].

Physicochemical treatments, such as adsorption, precipitation, lime treatment, Fenton oxidation, and advanced oxidation processes (AOPs), have been studied for the OMW treatment [45]. A combined treatment method using centrifugation and filtration as pre-treatment, to remove total suspended solids, followed by clay adsorption, was reported to remove 70% of COD and 80% of phenolic compounds [42]. A study applied lime coagulation and adsorption on bentonite as OMW pre-treatment, obtaining 99.5% removal of oleic acid, 43% removal of polyphenols, and 55% removal of COD [46]. In a different study, color total removal and 40-70% removal of COD were reported when using lime or ammonium iron sulfate as a coagulant, depending on the dosage of the coagulant employed [47].

AOPs are oxidation processes associated with the production of hydroxyl radicals, promoting the oxidation of pollutants, mainly by these very powerful radicals [29,48]. Some AOPs have been studied for treating OMW, namely Fenton's process, ozonation, and electrochemical oxidation [29,30,49]. Fenton's process promotes the production of oxidative species through the decomposition of H_2O_2 by iron source [48]. Ozonation occurs when ozone interacts with electron-rich molecules, producing hydroxyl radicals [50]. Electrochemical oxidation is based on the electrolysis of the wastewater, and it can be performed using different anode materials, in which the oxidation of pollutants can occur by direct exchange of electrons between the surface of the anode and the pollutant molecules (direct anodic oxidation), or through the reaction of the pollutant molecules with electroactive species generated on the surface of the anode (indirect anodic oxidation) [51,52]. Apart from the anode material, other variables affect the efficiency of the EO process, such as initial COD and current density [29]. Table 4 shows a literature review of the most utilized anode materials, with initial COD from 700 to 250,000 mg L^{-1} and current densities from 150 to 13,500 A m^{-2}.

Table 4. A summary of the main research results previously reported for OMW treatment by electrochemical oxidation using different anode materials.

Anode material	Initial COD / mg L^{-1}	Sample volume / L	Applied Current density or voltage	COD removal / %	Time / h	Ref.
Boron-doped diamond	20500	4	500 A m^{-2}	94	16	[41]
	700	0.6	300 A m^{-2}	≈100	Not informed	[53]
	3000	0.6	30 mA cm^{-2}	≈100	Not informed	[29]
Ti/IrO$_2$	1300	0.11	50 mA cm^{-2}	≈20	7.5	[54]
				60	20	
Ti/Pt	50000	0.8	7.69 mA cm $^{-2}$	23	5	[55]
	65000	0.5	25-35 mA cm^{-2}	40-55	2, 4 and 10	[56]
	250000	15	500 A m^{-2}	93	10	[57]
	42000	0.3	350 A m^{-2}	40	5	[58]
Ti/RuO$_2$	1220	0.11	500 A m^{-2}	52	5	[59]
			150 A m^{-2}	54		
	41000	0.4	13500 A m^{-2}	99.6	7	[60]
Ti/Ta/Pt/Ir	1475	10	5 V	5	2	[61]
			7 V	25		
			9 V	35		
	3060			25		
	5180			15		
	18100	45	14 V	58.9	8	[62]
			16 V	70.8		
			18 V	63.4		
	38100	20		7		
	20200		16 V	39.1	7	
			20 V	45.2		
			24 V	60.2		
Ti/TiRuO$_2$	26750	0.4	≈617 A m^{-2}	≈89	33	[63]
				≈96	21	

Only a few studies presented COD removals higher than 90%. The current intensities (and anodes) used in these studies were 30 (BDD), 300 (BDD), 500 (Ti/Pt), 617 (Ti/TiRuO_2), and 13500 A m^{-2} (Ti/RuO_2). Although metallic anodes are cheaper than BDD, only the latter can achieve high COD removal at a low current density, which highlights the superior efficiency of BDD in removing COD. When using a diamond-based material as boron-doped diamond (BDD) as anode, the organic matter is oxidized by hydroxyl radicals generated at the BDD surface [29]. Total COD removal has been reported when treating OMW with this process [29]. In a case study aiming at the reduction of COD in OMW through EO with BDD anode, it was observed that, during the first hours of EO, the process was kinetically controlled due to the high COD levels of OMW. However, as the COD decreased, the process became diffusively controlled, reducing the EO efficiency. The authors concluded that it is essential to control, as much as possible, the process variables, such as current density, to obtain maximum efficiency with the lowest treatment cost [41].

OMW has a high organic load, which implies high COD levels, and some treatment is required to reduce these levels. Even at safe levels for disposal in water courses, it is possible to recover some nutrients for further use due to the OMW richness in essential elements (carbon, phosphorus, potassium, etc.). [22]. Another option, which has been extensively studied in recent years, is the reuse of treated OMW as a part of a circular economy strategy [5,11,22]. Following this line of thought, and considering that OMW is an agricultural product, a study was carried out in which OMW was pretreated using immediate one-step lime precipitation (IOSLP) followed by carbonation and then used for lettuce cultivation in a hydroponic system [64]. According to the same study, some parameters need to be monitored to guarantee the quality of the water used in the hydroponic system, such as: approximately neutral pH; electrical conductivity (EC, in mS cm^{-1}), which is expressed according to the damage it can cause to the plant (None: <0.75; Some: 0.75–1.5; Moderate: 1.5–3; and Severe: 3–7.5); sodium adsorption ratio (SAR) < 10 (mmol $L^{-1})^{0.5}$ [64,65]. The authors found that, although the size of the plants was smaller than the control ones, indicating that some supplementation might be required, sensorial analysis showed no significant differences between them [64].

Despite the promising features of electrochemical oxidation, especially when using a BDD anode, the use of OMW treated by EO with BDD for hydroponic crop cultivation has never been reported.

2.2 Textile industry

The beginning of the textile industry dates back to the end of the 4th millennium BC when it became an essential part of the worldwide economy [66]. Sheep and their wool were the main pieces of this industry, along with cotton and silk. Nonetheless, the expansion of this industry over the years and the importance given to its production boosted research and development of new technologies. In addition to natural fibers, synthetic fibers were developed due to social and economic demands [67]. Differently from natural fibers, synthetic ones are man-made fibers, i.e., they do not occur naturally, and the raw material for their production comes from petroleum, chemicals, or petrochemicals, which are polymerized. More than half of all fiber usage is from synthetic fibers [68].

Being recognized as a primordial activity since it meets one of man's basic needs, the textile industry transforms natural and man-made fibers into yarns and fabrics, fabrics into garments, household items, domestic and technical use [69]. On the other hand, it is also identified as a problematic sector for the environment due to its intensive water consumption (~200 L of water to produce 1 kg of fiber), the elevated organic load, and the recalcitrant properties of the wastewater generated during production. This industry consumes 30 million m^3 of water per year, being 88% discarded as wastewater [70]. China, USA, India, and the EU are the leading textile producers. The most significant textile and clothing production in the EU is in Italy (40%), but also Germany, Spain, France and Portugal are big producers within the EU [71]. More than 65% of the textile production is to meet the demand of the fashion market, followed by technical textile and household products [67].

2.2.1 Production process

Textile industries are classified according to the type of fiber processed, which can be obtained from plants (cellulosic materials), animals (protein fibers), and synthetic fibers (produced artificially). The textile factories are made up of dry and wet processes, with the wet processes the most environmentally hazardous [70]. Figure 3 shows a general flow chart of the production process using natural fibers and the primary pollutants in the wastewater discharge. One or more pretreatment steps might be required, depending on the type of fiber and its posterior use. The objectives of the pretreatment are to remove any undesired content from the natural fibers and provide the required level of fiber property (whiteness of the fabric, absorption, softness, resistance, weight, width, etc.) for further processing of the textile substrate [67,70].

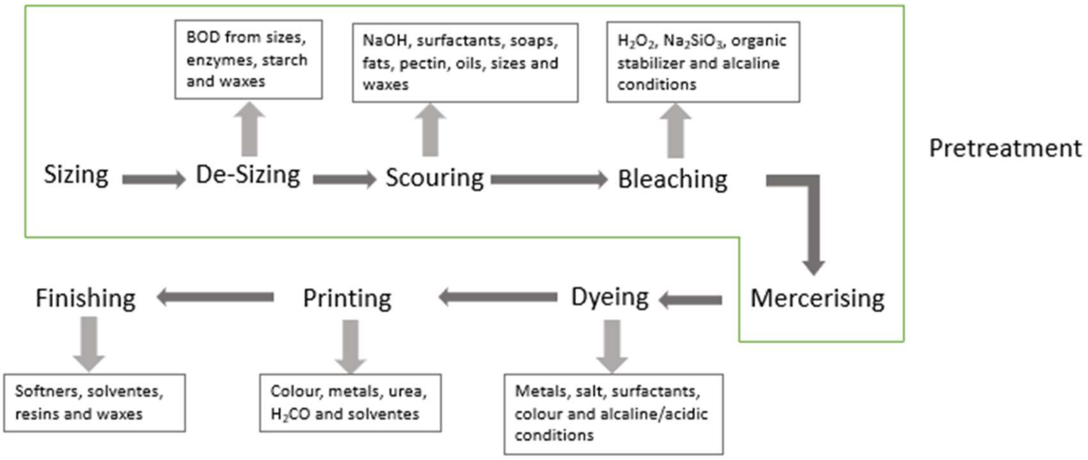

Figure 3. Steps of textile production using natural fibers and the main pollutants discharged during the wet process. Adapted from [52].

Synthetic fibers also generate by-products during their processing due to the use of catalysts and reagents. Some of these by-products are toxic and are discharged in the wastewater.

Figure 4 presents the general steps of synthetic fiber processing and some compounds discharged during this action [72].

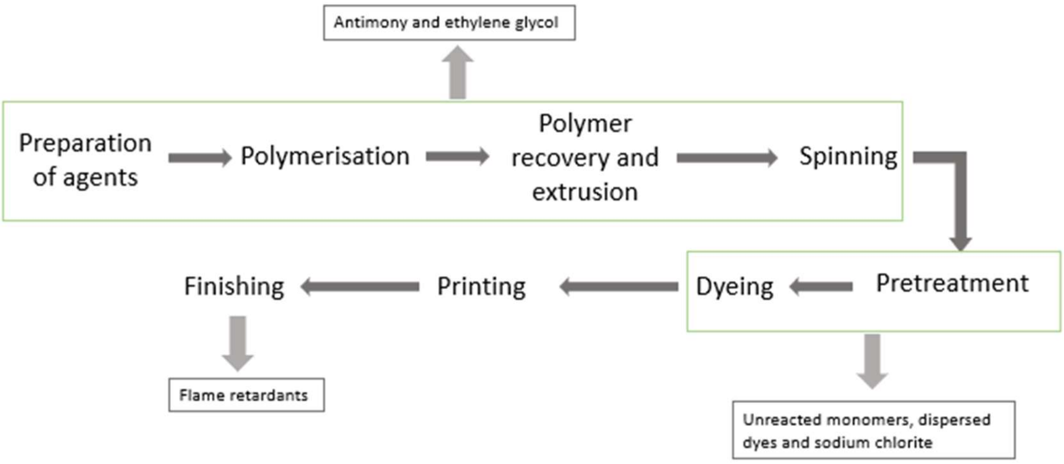

Figure 4. Steps of textile production of synthetic fibers and the main pollutants discharged during the process. Adapted from [54].

2.2.2 Characterization and environmental impact of the textile industry

High water and energy consumption, CO_2 emission, solid waste, and liquid and gaseous effluents make the textile industry one of the most polluting sectors. Concerning energy consumption, this industry consumes 0.5 – 7.5 kWh/kg of product, and in terms of thermal energy, it consumes 11 – 65 MJ/kg of product [73]. More than 8000 chemical products, many of them toxic and harmful, directly or indirectly, to human health, are consumed in this industry. Also, the emission of 3.5 g/kg of product of CO_2, volatile organic compounds, nitrogen oxides, sulfur oxides, CO, and particulate matter, contributes to the greenhouse effect [73]. Still, the textile industry's most concerning environmental hazard aspect is the amount of wastewater produced and its chemical load [74].

The generation of textile wastewater (TWW) can reach 300 L kg^{-1} of produced material, making this industry one of the main producers of wastewater [75]. The contaminants and pollutants contained in TWW threaten environmental protection because of their toxicity and recalcitrant characteristics. TWW qualitative and quantitative characterization varies, depending on the type of fibers used and the desired final product [76,77]. TWW generally has a high COD and salinity, low biodegradability, and variable pH values. TWW with different characteristics can be produced in the same plant due to the variability and quantity of chemical products used [72,76]. Table 4 presents the range of import parameters for TWW.

Table 5. General characterization and composition of textile wastewater reported by different researchers.

Parameters	Unit	Concentration range	References
pH	–	5 – 12.9	[78,79]

EC	mS cm^{-1}	0.739 – 6.8	[77,79,80]
COD	mg L^{-1}	61 – 225084	[77,79]
BOD_5	mg L^{-1}	6 – 2895	[77,78,81]
Chloride	mg L^{-1}	64 – 942	[77–79]

Due to its characteristics, TWW disposal must be preceded by some treatment method to mitigate its environmental impact. The next sub-section will discuss these treatments and provide details about them.

2.2.3 Treatment technologies for TWW

The treatment of TWW has some limitations regarding the possible methods to be used. The biological method is not viable, since the presence of dyes prevents aerobic microbial attack. However, the anaerobic pathway is capable of degrading some dyes; meanwhile, sometimes it produces compounds that are more toxic and more difficult to degrade than the dye itself, making this method not viable as well [82].

Despite their many disadvantages, processes based on physicochemical treatments are the most widely used in the textile industry. Among these processes is coagulation-flocculation, which uses coagulation agents, usually salts of aluminum and iron because of their capability to neutralize negatively charged particles, destabilizing it [83,84]. COD and color removal can reach 72% and 84.7%, respectively. Nevertheless, this process has a high sludge formation, which also requires treatment, as well as high chemical usage and minor mineralization of dyes [83,84].

Adsorption is also used for TWW treatment, which involves transferring a molecule in a fluid bulk to a solid surface. The adsorbent must fit some characteristics to make the process as efficient as possible being the presence of large functional groups, tunable internal architecture, and large surface area essential to achieve that [83]. This process can reduce 90% of the color from TWW, depending on the adsorbent agent used, and it is simple and cheap to perform. Its disadvantages are the need for the disposal of the adsorbent agents, regeneration issues, and low mineralization of dyes [83].

Membrane-based processes, namely microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have been considered the most efficient processes for obtaining water with quality for reuse. Some of these processes achieve COD and color removals of over 90% [85]. Figure 5 shows the porosity of the membrane used in each process, hence, choosing the correct membrane is the key to obtaining an effective treatment. Although membrane processes are very efficient, some disadvantages have been difficult to overcome. Membrane fouling and the production of membrane concentrate from textile wastewater are a concern for the environment and process costs. Several strategies, such as the deposition of different materials on the surface of the membrane to improve anti-adhesive properties, disinfection methods for removing the biofilm from the membrane surface, and optimization of operational parameters, have been investigated to mitigate the membrane fouling problem [86–89].

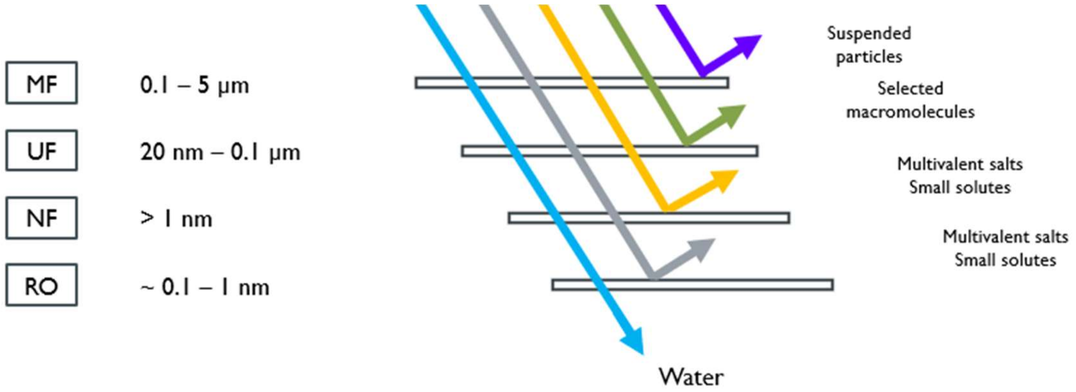

Figure 5. Membrane porosity according to each type. Adapted from [72].

As shown in Figure 5, each membrane has selective permeability, trapping in the system all the compounds that do not permeate it, generating MCTW, which presents high values of COD and salinity, and usually are colored [72,76]. Hence, regardless of the destination given to this concentrate, disposal, or reuse, there must be some prior treatment. In that way, electrochemical treatment, namely the AOPs, are a great and well-known technology, capable of eliminating persistent pollutants, enabling safe disposal, reuse, and/or resource recovery [90,91].

Among the AOPs, ozonation, Fenton's process, and photocatalysis are effective in degrading dyes and decolorizing colored effluents. In this regard, EO has been showing high efficiency in removing organic compounds and color, with the advantage of not requiring the addition of any reagents to generate hydroxyl radicals and not generating any sludge or concentrate [92]. In addition to the production of hydroxyl radicals, reactive chlorine species (RCS, as ClO^-) and sulfate radicals, among others, can be produced using cheaper electrode materials than BDD, such as mixed metals oxide (MMO) anodes [93].

As previously mentioned, other factors influence the efficiency of the EO process. Table 6 presents a compilation of EO studies carried out with TWW with different characteristics and using different anode materials. Only one study showed a removal rate higher than 90%. The current intensity (and anode) used in this study was 20 mA cm^{-2} (BDD), the initial COD was 350 mg L^{-1}, and the EO process lasted 12 hours. However, metallic anodes also performed well. For example, Ti/RuO_2-IrO_2 (similar initial COD) removed 25% of COD in a 10-minute treatment using the same current density.

Table 6. A summary of the main research results previously reported for TWW treatment by electrochemical oxidation using different anode materials.

Anode material	**Initial COD / mg L^{-1}**	**Sample volume / L**	**Applied Current density or voltage**	**COD removal / %**	**Time**	**Ref.**
Ti-TiO$_2$/RuO$_2$ **Ti-TiO$_2$/SnO$_2$** **Ti-TiO$_2$/RuO$_2$-PbO$_2$**	350	0.075	3 A dm^{-2}	>77	150 min	[94]
Ti/CoO$_x$-RuO$_2$-SnO$_2$-Sb$_2$O$_5$	1280	1.0	50 mA cm^{-2}	40.2	2 h	[95]
Ti/SnO$_2$-Sb-Pt	520-1768	0.42	125 mA cm^{-2}	25-59	1-3 h	[96]
Ti/RuO$_2$-IrO$_2$	320 1020	0.50	20 mA cm^{-2}	25 3.82	10 min 40 min	[97]
Ti/IrO$_2$-RuO$_2$-SnO$_2$	Not informed	0.25	20 V	60	9 h	[98]
Ti/Pt	3325	5.0	0,89 A cm^{-2}	86	18 min	[99]
Ti/SnO$_2$-Nb$_2$O$_5$	225	Not informed	1 mA cm^{-2}	83	30 min	[100]
Graphite rod	20840	1.0	8 V	68	60 min	[101]
Ti/PbO$_2$	178	1.2	124 mA cm^{-2}	74	50 min	[102]
BDD	350	0.30	20 mA cm^{-2}	97	12 h	[103]
	2154	5.0	20 mA cm^{-2}	46	6 h	[104]
			40 mA cm^{-2}	61		
			60 mA cm^{-2}	78		
			100 mA cm^{-2}	88		
	1650	0.50	2.8 mA cm^{-2}	84	6 h	[105]

In addition to the good performance in removing COD, metallic anodes produce RCS more easily than BDD. Contrary to hydroxyl radicals, RCS has enough stability to be stored and utilized *ex-situ*. Thus, this study aims to apply EO on MCTW, using MMO electrodes to electrogenerate RCS and remove COD, simultaneously promoting the possibility, in addition to treating the MCTW, of using the treated MCTW (rich in RCS) as a membrane antifouling and disinfectant, aiming to increase the efficiency of the membrane treatment itself [93]. There is no literature on this yet.

2.3 Electrochemical oxidation

Electrochemical oxidation usually occurs in a cell of two electrodes connected by an external circuit (Figure 6).

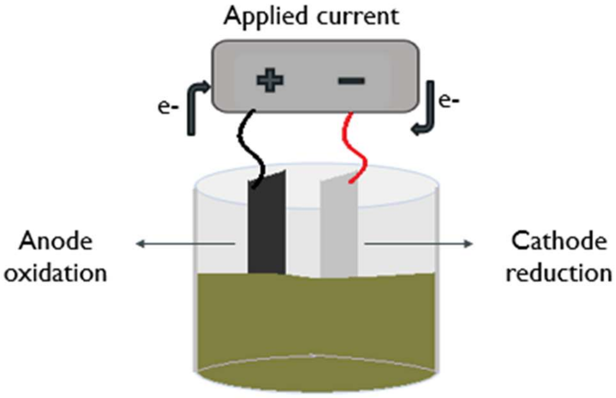

Figure 6. Schematic of an electrochemical cell. Adapted from [77].

This process is based on the electrolysis of water contained in wastewater, generating hydroxyl radicals (Equation (1)) [51]. The oxidation of pollutants takes place through the transfer of electrons between the surface of the electrodes and the species present in the solution. Hence, it depends on the physical and chemical processes taking place at the interface between the anode and the solution, the diffusion of species to the surface of the anode, and the kinetics with which the species are reduced or oxidized [106].

$$M + H_2O \rightarrow M(\bullet OH) \tag{1}$$

The hydroxyl radical is a highly reactive and non-selective oxidant, capable of promoting the mineralization of a wide range of organic species in effluents, depending on the operating conditions, especially the anode material. Two types of anodes (M) are considered to exist: active and non-active ones. In active anodes, there is a stronger interaction between the hydroxyl radicals and the electrode surface, leading to the formation of a superoxide (MO), as shown in Equation (2), which acts as a mediator in the oxidation of pollutant molecules (R) (Equation (3))

[51,107]. Platinum, IrO_2, and RuO2 are examples of active anodes. The oxidation mechanism mediated by “active anodes” generally leads to the electrochemical conversion of pollutants, in which organic compounds are partially oxidized and transformed into simpler organic products [106,107].

$$M(\bullet OH) \rightarrow MO + H^+ + e^- \tag{2}$$

$$MO + R \rightarrow M + RO \tag{3}$$

The non-active anodes, on the other hand, establish weak interactions between the surface of the anode and hydroxyl radicals, allowing the direct reaction of the pollutant molecules and the radicals adsorbed on the anode surface (Equation (4)). The oxidation mechanism using non-active anodes generally leads to the complete mineralization of organic compounds, producing water, carbon dioxide, and inorganic compounds [51,106,107]. BDD, PbO_2, and SnO_2 are examples of non-active anodes.

$$aM(\bullet OH) + R \rightarrow aM + mCO_2 + nH_2O + (a-2n)H^+ + (a-2n)e^- \tag{4}$$

The studies on the use of BDD anode for wastewater treatment have shown its high efficiency [29,30,106]. Being a non-active electrode, BDD has a high reactivity towards organic compounds due to the weak interaction of hydroxyl radicals with the surface of the electrode, having better use for higher COD values. In addition to the high efficiency of organic matter oxidation, which promotes efficient use of energy, BDD contributes to the decolorization of the wastewater, improving the visual aspect.

The use of MMO as material for active electrodes has been extensively studied [108]. In samples with high concentrations of ions, the oxidation of organic matter and ions occurs simultaneously. Although this type of reaction has slower kinetics, the oxidation of specific ions, namely chlorides, will produce stronger oxidants (e.g., ClO^-), making it possible to reuse the treated wastewater, instead of discharging it.

Chapter 3

Materials and methods

This chapter presents the characterization of the samples used in this work, describes the electrochemical oxidation experiments, and describes the analytical methods used to monitor them.

3.1 Characterization of OMW and MCTW

The OMW sample used in this work was collected from an olive oil mill in Beja, Portugal. This plant uses a two-phase cold extraction system, and the samples were collected during the 2023 campaign, specifically in November. After collection, the samples were transported to the laboratory and stored at -18ºC until they were used, then kept in a refrigerator at 4ºC. Table 5 shows the characterization of the OMW sample used in this study.

Table 7. Characterization of the OMW sample used in this study.

Parameter	**Mean value (± SD)**
Chemical oxygen demand / g L^{-1}	5.90 ± 0.01
Biochemical oxygen demand / g L^{-1}	2.28 ± 0.05
Biodegradability index	0.55
Ecotoxicity (EC_{50}-48h / TU)	2% / 49.8
Dissolved organic carbon / g L^{-1}	0.80 ± 0.03
Dissolved inorganic carbon / mg L^{-1}	18 ± 9
Total suspended solids / g L^{-1}	3.1 ± 0.4
Total dissolved solids / g L^{-1}	2.2 ± 0.1
pH	5.48 ± 0.04
Electrical conductivity / mS cm^{-1}	1.9 ± 0.2
Potassium / mg L^{-1}	196 ± 4
Sodium / mg L^{-1}	172 ± 3
Calcium / mg L^{-1}	151 ± 4
Magnesium / mg L^{-1}	58 ± 1
Chloride / mg L^{-1}	319 ± 6
Sulfate / mg L^{-1}	9.1 ± 0.3

The MCTW samples used in this study came from a textile industry located in Portugal, as part of the project Lusitano running at the Universidade da Beira Interior. The MCTW samples from membrane treatment equipment comprised an ultrafiltration unit followed by a reverse osmosis unit. MCTW_1 corresponds to the retentate from the ultrafiltration unit, and MCTW_2 corresponds to the retentate from reverse osmosis. After collection, the samples were kept in a refrigerator at 4°C until their use. Table 6 presents the characterization of the MCTW samples utilized in this study.

Table 8. Characterization of MCTW samples.

Parameter	MCTW_1	MCTW_2
Chemical oxygen demand / mg L^{-1}	305 ± 3	1045 ± 8
Dissolved organic carbon / mg L^{-1}	80 ± 1	307 ± 3
Dissolved inorganic carbon / mg L^{-1}	79.8 ± 0.4	344 ± 2
pH	7.54 ± 0.04	7.49 ± 0.02
Electrical conductivity / mS cm^{-1}	3.2 ± 0.2	8.1 ± 0.2
Chloride / mg L^{-1}	659 ± 4	1599 ± 6

3.2 Electrochemical experiments

The electrochemical experiments with the OMW sample were carried out in batch mode with stirring (250 rpm), using an anode and cathode placed vertically and parallel to each other, with a distance between them of ~0.5 cm, immersed in 200 mL of solution. Figure 7 shows a picture of the electrochemical cell used. The anode material was BDD, a commercial anode purchased from Neocoat (Switzerland), with a useful area of 10 cm^2. A stainless-steel plate with a similar area of the anode was used as the cathode material.

Three different applied current intensities were studied, 300, 500, and 700 mA. A Multimetrix XA3033, triple output adjustable DC power supply, was used as a power supply. The experiments had a duration of 8 hours, and samples were taken every 2 hours for analytical determinations and experiment monitoring.

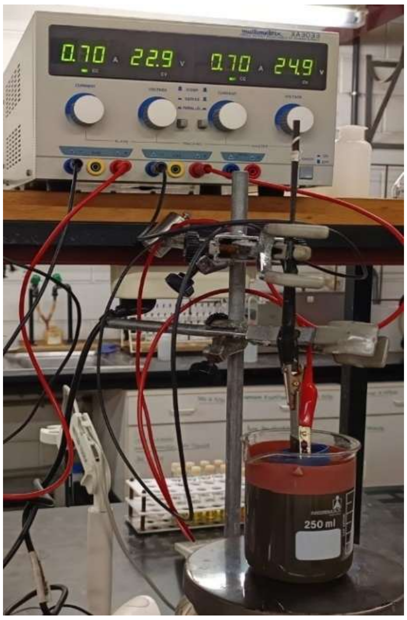

Figure 7. Electrochemical oxidation schematic for OMW tests.

The electrochemical experiments with MCTW samples were carried out in batch mode with recirculation, using a Pan World CO pump, model NH-30PX; an electrochemical cell from APRIA Systems, model PElab c/M-M25, comprised of Ti/IrO_2–RuO_2 anode and cathode with an area of 182.25 cm^2 each; a GW, Lab DC, model GPS-3030D (0–30 V, 0–3 A) as the power supply; and a Multiparameter waterproof meter, model HI98194, from Hanna Instruments for measuring pH, conductivity and oxidation-reduction potential (ORP). Figure 8 shows a picture of the experimental setup. The experimental conditions utilized are presented in Table 7.

Figure 8. Electrochemical oxidation schematic for MCTW tests.

Table 9. Experimental conditions applied in MCTW electrochemical experiments.

Parameter	**MCTW_1**	**MCTW_2**
Sample volume / L	7.5	10
Recirculation flow rate / L h^{-1}	60	60
Experiment duration / h	40	75
Applied current intensity / A	0.5 (32 h) + 2.5 (8 h)	1 (40 h) + 0.75 (35 h)
Sampling interval / h	4	8

3.3 Analytical methods

Several parameters were used to characterize the samples and to follow the electrochemical experiments, namely COD, BOD_5, biodegradability index, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH, EC, ORP, ecotoxicity towards *Daphnia magna* (*D. magna*), chloride (Mohr method), hypochlorite, total suspended solids (TSS), and total dissolved solids (TDS). Also, chloride, chlorate, perchlorate, potassium, sodium, calcium, and magnesium concentrations were determined by ion chromatography (HPLC). In the subsections below, a brief description of the analytical methods and equipment used to determine each parameter is presented.

3.3.1 Chemical oxygen demand

Used to indirectly measure the amount of organic matter present in water and effluents, the COD values are expressed in terms of oxygen concentration, since it represents the amount of oxygen equivalent to the portion of organic matter present in the water or effluent that can be oxidized by a strong chemical oxidant.

As described in the Standard Methods [109]COD was determined by the closed reflux titrimetric method, which involved oxidizing the samples using excess potassium dichromate. Dichromate (a strong oxidizing agent) oxidized the organic matter in the samples, producing H_2O and CO_2 and reducing chrome from hexavalent to trivalent, according to Equation (5).

$$C_nH_aO_b + 8c\,H^+ + Cr_2O_7^{2-} \rightarrow 2cCr^{3+} + \frac{a+8c}{2}H_2O + n\,CO_2 \qquad (5)$$

The samples were digested in a strongly acidic solution, with a silver catalyst to oxidize resistant organic compounds and mercury sulfate to reduce interference from the oxidation of chloride ions. Closed reflux digestion was carried out using a Merck Spectroquant TR 420 thermoreactor for 2 h at 150 °C. After digestion, the unreduced dichromate was titrated with ammoniacal ferrous sulfate (Equation (6)), using ferroin as an indicator.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \qquad (6)$$

The amount of dichromate consumed was calculated based on the amount of unreduced dichromate, which is equivalent to the amount of oxygen needed to oxidize the organic matter. The COD was determined in milligrams of oxygen per liter of sample.

3.3.2 Biochemical oxygen demand and biodegradability index

Although BOD is not a precise quantitative determination, it is widely used as an index of biodegradable organic matter in water or effluent. It is an important parameter for assessing the quality of effluent treatments. BOD represents the amount of oxygen required for microbial metabolism of dissolved organic matter in water and effluent samples. BOD_5 was determined using the respirometric method, according to the Standard Methods [109]. This method provides a direct measurement of the oxygen consumed by microorganisms from an air-enriched environment after 5 days of incubation in a closed container under conditions of constant temperature (20 ± 1 °C) and continuous stirring. The BOD_5 determination tests were carried out using commercially available PolySeed freeze-dried biomass. OxiTop® measuring heads were used, which relate oxygen uptake to the pressure change caused by oxygen consumption at constant volume. Constant temperature and continuous stirring were ensured using a WTW TS 606-G/2-i incubator and a WTW Oxitop IS 12 inductive stirring system, respectively.

The biodegradability index allows one to assess the effluent's suitability for biological degradation. The higher the index, the easier it is to biodegrade. It relates BOD_5 to COD and is given by the ratio of these two parameters (BOD_5/COD).

3.3.3 Dissolved organic and inorganic carbon

The determination of these parameters was performed using a Shimadzu TOC-VCPH carbon analyzer, according to the Standard Methods [109]. Before the samples were analyzed, they were filtered using an LLG Glass microfibre filter of 1.2 µm, meaning that the amounts of inorganic and organic carbon analyzed correspond to the dissolved fractions in the samples.

To determine DIC, the sample is injected, using an automated process, into a reaction chamber, where it is acidified. All the inorganic carbon is converted into CO2, which is quantified in a detector. Its value is given directly in mg C L^{-1}.

On the other hand, DOC determination is an indirect value given by the difference between the DIC and the total carbon (also measured by the analyzer), being its value given directly by the equipment in mg C L^{-1}.

3.3.4 Conductivity, pH, and oxidation-reduction potential

The conductivity and pH measurements were carried out using a Mettler Toledo SevenEasy S30 and a Mettler Toledo SevenEasy S20. Before the measurements, the samples were thermostatized at 20°C.

A Multiparameter waterproof meter, model HI98194, from Hanna Instruments, was used in the EO experiments with MCTW to measure the pH, EC, and ORP.

3.3.5 Ecotoxicity towards *Daphnia magna*

D. magna is a small freshwater crustacean that feeds on green algae, being at the bottom of the food chain and thus playing a key role in the ecosystems' health. Due to its short lifespan, ease of rearing, and reproduction by parthenogenesis, it is widely used as a model species in ecotoxicological tests and is recommended by major international organizations, namely the American Society for Testing and Materials (ASTM), Organization for Economic Cooperation and Development (OECD), and International Organization for Standardization (ISO).

The ecotoxicity towards *Daphnia magna* was evaluated using a Daphtoxkit F microbiotest, DM311023, by measuring the number of immobilized *D. magna* neonates exposed to different sample dilutions. The concentration responsible for 50% of immobilization, EC_{50}, was calculated using the standard data processing method Daphtoxkit F spreadsheet. The toxicity results were also expressed in terms of toxicity units, TU, according to Equation (7) [110].

$$TU = 100 / (\%EC_{50}) \tag{7}$$

3.3.6 Ion chromatography (Cl^-, ClO_3^-, ClO_4^-, K^+, Na^+, Ca^{2+}, and Mg^{2+})

Ions concentration was determined by ion chromatography using a Shimadzu Prominance LC-20A system coupled to a Shimadzu CDD 10Avp conductivity detector. Anions were separated using a Shodex IC I-524A anionic column (4.6 mm ID × 100 mm) at the temperature of 40 °C. An aqueous solution of 2.5 mM phthalic acid and 2.4 mM tris(hydroxymethyl)aminomethane was used as the mobile phase at a flow rate of 1.5 mL min^{-1}. For the determination of cations, an IC YK-421 Shodex cationic column (4.6 mm ID × 100 mm) was used at 40 °C. An aqueous solution of 5.0 mM tartaric acid, 1.0 mM dipicolinic acid, and 24 mM boric acid was used as the mobile phase, at a flow rate of 1.0 mL min^{-1}. For both cases, an injection volume of 10 µL was used. The eluents were prepared with Milli-Q® water (Milli-Qplus185 purification system), filtered through 0.45 µm hydrophilic polypropylene filters, and the samples filtered through syringe filters with a 0.45 µm polypropylene membrane.

3.3.7 Mohr's method (Chloride)

According to the Standard Methods [109], Mohr's method applies to determining chlorides in neutral or slightly alkaline samples (pH between 6 and 9). The indicator (chromate ion) won't work if the medium is too acidic. If it is too alkaline, the silver precipitates as silver hydroxide instead of silver chloride.

For this determination, a suitable sample volume was titrated with a standard solution of silver nitrate, using potassium chromate as the indicator. A blank, where the sample volume was replaced by distilled water, was prepared, and the volume of the titrant was subtracted from the volume used for the sample (the usual volume for the blank was 0.2-0.3 mL). The endpoint of the titration occurred when silver chromate was formed, which gave the solution a brick-red color. The chloride concentration (C / mg L^{-1}) was determined according to Equation (8), where f_{AgNO_3} is the correction factor, C_{AgNO_3} is the titrant concentration, in mol L^{-1}, V_{tit} is the titrant volume, in mL, V_{bl} is the titrant volume used in the blank, in mL and V_{sm} is the sample volume, in mL.

$$C = \frac{f_{AgNO_3} \times C_{AgNO_3} \times (V_{tit} - V_{bl})}{V_{sm}} \times 35453 \qquad (8)$$

3.3.8 Iodometric method (Hypochlorite)

Hypochlorite was determined by iodometric titration following Vogel's Textbook of Quantitative Chemical Analysis [111]. An appropriate sample volume was titrated with a standard sodium thiosulfate solution, using a 2% starch solution as the indicator. In a 125 mL erlenmeyer flask, distilled water was added to a suitable sample volume (5-10 mL) so that the final volume was approximately 50 mL. Approximately 1 g of potassium iodide and 10 mL of glacial acetic acid were added. The erlenmeyer flask was covered with a watch glass for five minutes, after which the solution was quickly titrated with sodium thiosulphate until the brown color (characteristic of iodine) faded. Finally, approximately 2 mL of the indicator solution were added, and the titration continued until the solution was colorless. The hypochlorite concentration (C / mg L^{-1}) was determined according to Equation (9), where $C_{Na_2S_2O_3}$ is the titrant concentration, in mol L^{-1}, $V_{Na_2S_2O_3}$ is the titrant volume, in mL, and V_{sm} is the sample volume, in mL.

$$C = \frac{C_{Na_2S_2O_3} \times V_{Na_2S_2O_3}}{2\, V_{sm}} \times 51452 \qquad (9)$$

3.3.9 Total suspended and dissolved solids

The determination of TSS and TDS was carried out following the Standard Methods [109]. For TSS, the procedure consisted of the preparation of the glass-fiber filter disk (1.2 µm), which was washed, then transferred to a watch glass and dried in an oven at 103-105 °C for over an hour.

After, it was cooled in the desiccator to room temperature and was weighed. Using a pipet, a measured sample volume was transferred onto the glass-fiber filter through vacuum filtration until it was completely drained. The filter was placed back into the watch glass and dried for over an hour at 103-105 °C. After that, it was cooled in the desiccator to room temperature and was weighed. TSS (mg L^{-1}) was determined according to Equation (10), where A is the final weight of filter + dried residue, in mg, B is the weight of the filter, in mg, and V_{sm} is the sample volume, in mL.

$$TSS = \frac{(A-B) \times 1000}{V_{sm}} \tag{10}$$

For TDS, the procedure consisted of using a measured volume of the filtrated sample, obtained above during the TSS procedure, onto a pre-weighed dish, which was dried in an oven at (180 ± 2) °C until constant weight. TDS was determined according to Equation (11), where A is the final weight of dried residue + dish, in mg, B is the weight of the dish, in mg, and V_{sm} is the sample volume, in mL.

$$TDS = \frac{(A-B) \times 1000}{V_{sm}} \tag{11}$$

Chapter 4

Results and discussion

This chapter presents and discusses the results obtained in this study according to the framework proposed in Chapter 1.

4.1 OMW treatment

OMW treatment by EO using a BDD anode was carried out at three applied current intensities, 300, 500, and 700 mA. Figure 9 presents the COD and DOC decays with time for the EO experiments performed. It can be seen that COD and DOC removal occurred, most of the time, at current control, as COD and DOC removal rates increased with applied current. This increase in the removal rates with applied current can be ascribed to the increased formation of hydroxyl radicals and other oxidizing active species that enhanced the oxidation of the organic matter. At 700 mA, after the 4th hour of treatment, the process became completely diffusive controlled, losing efficiency. This behavior was expected, considering the high organic load in the first hours of treatment and its abatement during the EO experiments. After 8 h of EO treatment, COD removals of 82.3%, 92.6%, and 97.6% were achieved at 300, 500, and 700 mA, respectively. As for DOC, 78.4%, 89.8%, and 95.5% removals were attained at 300, 500, and 700 mA, respectively.

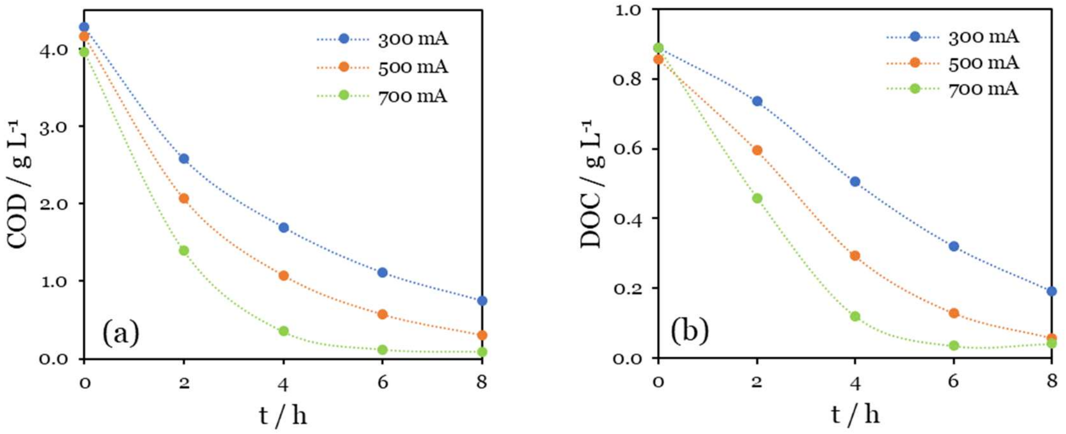

Figure 9. a) COD and b) DOC variation with time for the EO experiments performed with OMW.

A different trend between COD and DOC decay can be observed in the first hours of treatment, which can be ascribed to two factors: i) the incomplete oxidation of some of the organic compounds, which leads to the formation of low molecular mass organic compounds that resist further oxidation, contributing to the decrease in COD, but not a decline in DOC content [112]; ii) the solubilization of suspended matter during the EO treatment. For DOC analyses, samples are previously filtered through 1.2 µm glass microfiber membranes and thus, the suspended solids are not accounted for in the DOC results as they are for the COD results due to the acidic digestion procedure [113]. As the suspended matter is being solubilized during the EO process, it is no longer retained in the filter, thus contributing to DOC concentration. Still, the high DOC removals attained by the EO treatment indicate high mineralization of the organic compounds, in compliance with the reported BDD anode capability to generate large quantities of weakly adsorbed hydroxyl radicals that promote the complete mineralization of the organic compounds [114].

Figure 10 presents the COD and DOC decay with applied electrical charge. For both COD and DOC, the same trend can be observed for the different applied current intensities, indicating similar current efficiencies, which confirms that the experiments took place under current control most of the time.

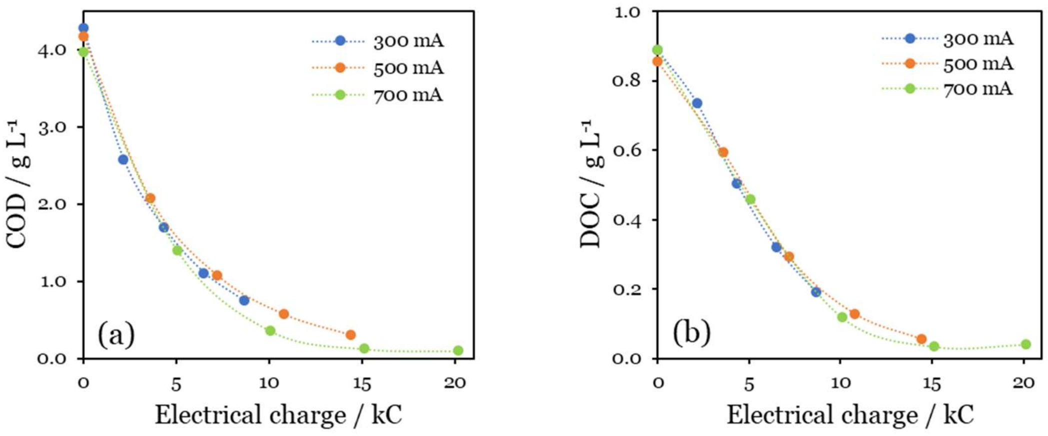

Figure 10. a) COD and b) DOC variation with applied electrical charge for the EO experiments performed with OMW.

The pH variation during the EO experiments is shown in Figure 11 (a). An increase in pH was observed for all applied current intensities studied, being more pronounced with the increase in applied current. According to the literature, this increase results from the suppression of reactions that contribute to the release of H^+ in solution, along with the occurrence of secondary reactions that lead to hydroxide ion formation, which are enhanced by the increase in current intensity and by the decrease of organic matter susceptible to oxidation, as the hydrogen evolution reaction. Although always present, these reactions are enhanced by the increase in applied current [52].

Alongside pH, an increase in DIC during the experiments, more accentuated with the increase in applied current, was observed (Figure 11 (b)). The DIC formation rate was higher during the first hours of treatment, diminishing in the following hours. Indeed, a decrease in DIC concentration during the last hours of experiments was observed at the highest applied current.

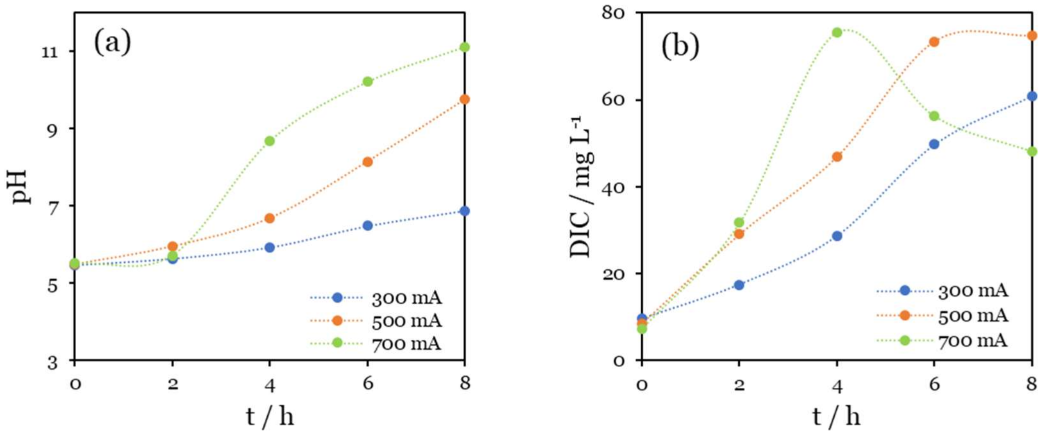

Figure 11. a) pH and b) DIC variation with time for the EO experiments performed with OMW.

The increase in DIC can be ascribed to the organic compounds mineralization (Eqs. (4), (12), and (13)) [113].

$$CO_2 + HO^- \rightleftharpoons HCO_3^- \quad (12)$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad (13)$$

The decrease in DIC concentration observed at 700 mA in the final hours of the treatment can be explained by the occurrence of reactions, such as the one between HCO_3^- and active chlorine species formed from chloride oxidation (Eq. (14)) [115]. Since the decrease in DIC concentration only occurred when pH was higher than 9, it may also be ascribed to the precipitation of calcium carbonate. The stagnation in DIC production at 500 mA in the 2 final hours, when pH has slightly overcome 9, also corroborates this hypothesis.

$$HOCl + HCO_3^- \rightleftharpoons CO_2 + OCl^- + H_2O \quad (14)$$

Figure 12 presents the biodegradability index, given by the BOD_5/COD ratio, and the ecotoxicity towards *D. magna*, expressed as EC_{50}-48h, of the treated OMW samples.

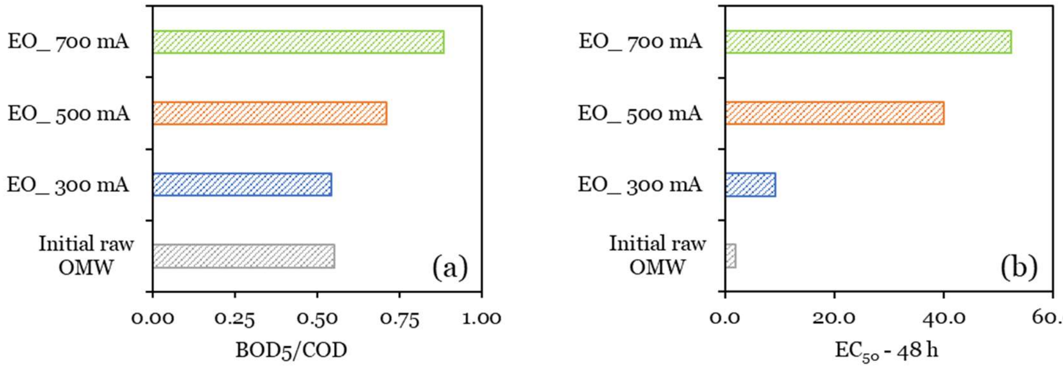

Figure 12. (a) Biodegradability index and (b) ecotoxicity towards Daphnia magna of the OMW samples before and after 8 h of EO treatment at different applied current intensities.

At 300 mA, the biodegradability index remained practically the same as for the initial OMW sample, although an increase in the EC_{50}-48h value was attained. For 500 and 700 mA, a significant increase in both the biodegradability index and EC_{50}-48h was observed.

Table 8 presents the characterization of the OMW samples treated by EO at the different applied current intensities studied.

Table 10. Characterization of the final OMW samples obtained from the EO treatment at different applied current intensities.

Parameter	**Treated OMW**		
	300 mA	**500 mA**	**700 mA**
COD/ g L^{-1}	0.7 ±0.1	0.31 ± 0.04	0.10 ± 0.02
BOD_5 / g L^{-1}	0.36 ± 0.03	0.16 ± 0.03	0.08 ± 0.03
Biodegradability index	0.54	0.71	0.88
Ecotoxicity (EC_{50}-48h / TU)	9.1% / 11	40% / 2.5	52.4% / 1.9
DOC / g L^{-1}	0.19 ± 0.04	0.06 ± 0.01	0.04 ± 0.02
DIC/ mg L^{-1}	61 ± 5	(8 ± 1)×10	(5 ± 1)×10
TSS / g L^{-1}	2.57 ± 0.09	0.625 ± 0.004	0.816 ± 0.001
TDS / g L^{-1}	1.41 ± 0.03	1.53 ± 0.01	1.609 ± 0.004
pH	7 ± 0.2	10 ± 0.3	11 ± 0.2
EC / mS cm^{-1}	1.5 ± 0.1	1.5 ± 0.3	1.9 ± 0.1
Sodium / mg L^{-1}	171 ± 4	169 ± 3	171 ± 4
Calcium / mg L^{-1}	60 ± 2	20 ± 4	38 ± 3
Magnesium / mg L^{-1}	33 ± 2	33 ± 2	24 ± 3
SAR / (mmol $L^{-1})^{0.5}$	4.42	5.51	5.37
E_{sp} / kWh kg_{COD}^{-1}	197	285	462

A significant abatement in the OMW pollutant load was observed for all applied current intensities studied. Still, at the lowest applied current (300 mA), the COD was far from the desirable value for reuse of the treated wastewater in hydroponic culture. Although there was a reduction in the ecotoxicity towards *D. magna*, from 49.8 to 11 TU, the toxicity classification based on toxic units, according to Pablos et al. [110], was kept at the "very toxic" level ($10 < TU < 100$), in agreement with the unaltered biodegradability index. On the other hand, for the treatments performed at 500 and 700 mA, a change in the toxicity classification from "very toxic" to "toxic" ($1 < TU < 10$) was observed, being that, at 700 mA, the value was close to the "non-toxic" level ($TU < 1$). According to the literature, this remaining ecotoxicity can be due to oxidation end-products, such as acetic and propionic acids, that are toxic to *D. magna* [116]. These results agree with the significant increase in the biodegradability index observed at this applied current.

The enhanced performance of EO treatment at 500 and 700 mA was also noticed in TSS removal. While at 300 mA, TSS removal was meaningless, at the highest currents, it ranged from 74% to 80%, with the highest removal attained at 500 mA. As for TDS, there were no significant removals at any of the currents studied, which is in agreement with the unaltered electrical conductivity. The sodium adsorption ratio was determined using Equation (15). According to the literature [64]. Table 8 shows that the SAR values obtained for all the applied current intensities comply with the range of the ideal SAR for lettuce cultivation.

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{1}{2}\{[Ca^{2+}] + [Mg^{2+}]\}}} \tag{15}$$

The specific energy consumption (E_{sp}), in kWh kg_{COD}^{-1}, was calculated according to Equation (16), where U is the cell voltage, in V, I is the applied current intensity, in A, Δt is the duration of the experiment, in s, V is the volume of the solution, in L, and ΔCOD is the removed COD, in mg L^{-1}, during Δt. Although the efficiency of the EO treatment was not changed by the increase in applied current intensity (Figure 10), the specific energy consumption, and consequently the treatment cost, was higher when operating at higher current. This increase, owing to the increase in the cell potential with applied current, was significantly more pronounced at 700 mA.

$$E_{sp} = \frac{U \times I \times \Delta t}{3.6 \times V \times \Delta COD} \tag{16}$$

After 8 hours of EO treatment with a BDD anode at different applied current intensities, three OMW-treated samples with different quality indexes were obtained. By proving a suitable dilution and nutrient supplementation, these treated samples could be used for hydroponic lettuce growth[64]. Although the sample obtained at 700 mA presented the lowest organic load and the highest biodegradability index and EC_{50}-48h, it had a pH of 11, which is not feasible for use in hydroponics, as a neutral pH is required. Additionally, the high E_{sp} attained at this current impairs the use of this sample at a large-scale process. At 300 mA, the lowest E_{sp} was observed, with the treated sample presenting a neutral pH suitable for hydroponic lettuce growth. Still, the COD was high, as were TSS and ecotoxicity, requiring a substantial sample dilution for its reuse in hydroponics. Finally, the sample resulting from EO at 500 mA, with physicochemical characteristics close to those observed for the sample obtained at 700 mA, but with a much lower E_{sp}. According to a study conducted on hydroponic crops, readily biodegradable organic matter can be utilized in hydroponics as a source of nutrients [64]. Considering this and the overall results obtained, the OMW sample treated at 500 mA seems to be the most suitable for reuse in hydroponics. The three OMW-treated samples were sent to the Instituto Politécnico de Beja in Beja, Portugal, for reuse in hydroponic lettuce cultivation.

4.2 MCTW treatment

This study, performed under the scope of project Lusitano, funded by the Recovery and Resilience Plan, aimed to evaluate the feasibility of using EO to electrogenerate RCS (as ClO^{-}) to be reused as an antifouling agent in membrane technology units for TWW treatment. As shown in Figure 5, the porosity of the membrane varies for each process, directly reflecting the composition of the retentates. This is confirmed by the characterization of MCTW_1 (UF retentate) and MCTW_2 (RO retentate) samples, with an initial COD of, respectively, 305 and 1045 mg L^{-1} (Table 6).

Figure 13 presents the chloride and hypochlorite variation during the EO treatment of MCTW_1 and MCTW_2. Considering the experimental chloride decay obtained, the theoretical hypochlorite formation was calculated, assuming all the chloride was oxidized to hypochlorite. A higher chloride oxidation rate is observed for MCTW_2 compared to MCTW_1, ascribed to the higher initial chloride concentration and applied current intensity in MCTW_2. Consequently, the hypochlorite formation rate was higher in MCTW_2.

For MCTW_1, the increase in applied current intensity from 0.5 to 2.5 A in the last 8 h of treatment enhanced the experimental hypochlorite formation. However, a loss in the efficiency of this process was observed (higher distance between the experimental and theoretical curves). This loss in efficiency can be ascribed to the formation of other chloride species, such as chlorate and perchlorate, which are enhanced at higher applied currents.

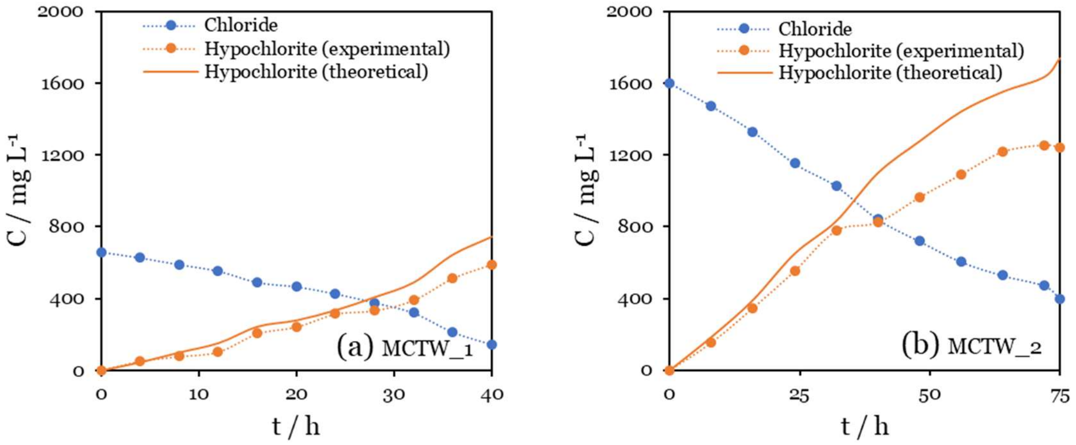

Figure 13. Chloride and hypochlorite variation with time for the EO treatment of (a) MCTW_1 (0.5A_32h + 2.5A_8h) and (b) MCTW_2 (1A_40h + 0.75A_35h).

For MCTW_2, although no significant change was observed in chloride decay with the decrease in the applied current intensity from 1 to 0.75 A, after the 40th hour of treatment, a significant loss in the process efficiency was noticed, with the experimental hypochlorite concentration increasingly lower than the theoretical one. Chlorate formation from hypochlorite (Equation (17)) depends not only on the applied current intensity but also on the hypochlorite concentration, according to Equation (18).

$$ClO^- + 2\,H_2O \rightarrow ClO_3^- + 4\,H^+ + 4\,e^- \tag{17}$$

$$E = E^0 - \frac{RT}{4F}\ln\left(\frac{[ClO_3^-]\times[H^+]^4}{[Cl\ \ ^-]}\right) \tag{18}$$

Equation (18) shows that the required potential to produce chlorate from hypochlorite decreases with increased hypochlorite concentration and pH. Hypochlorite concentration and pH increased in both MCTW_1 and MCTW_2 experiments, meaning chlorate production became favored along the treatment. Therefore, the difference in theoretical and experimental hypochlorite concentration should not be related only to the applied current intensity but also to the pH and the hypochlorite concentration itself, which explains the observed behavior.

Table 9 presents the characterization of the final MCTW_1 and MCTW_2 samples obtained from the EO treatment.

Table 11. Characterization of the final MCTW_1 and MCTW_2 samples obtained from the EO treatment.

Parameter	**Treated MCTW**	
	MCTW_1	**MCTW_2**
COD / mg L^{-1}	118 ± 1	336 ± 2
pH	8.55 ± 0.02	8.96 ± 0.03
EC / mS cm^{-1}	2.8 ± 0.1	7.7 ± 0.3
Chloride / mg L^{-1}	145 ± 2	400 ± 2
Hypochlorite / mg L^{-1}	590 ± 4	1241 ± 3
Chlorate / mg L^{-1}	215 ± 2	412 ± 2
E_{sp} / kWh kg^{-1}	418	56

Although no perchlorate was detected in the treated samples (data not shown), chlorate concentration was much higher in MCTW_2 compared to MCTW_1, which can be ascribed to the longer experiment duration, as explained above (i.e., if chlorate production became easier with time, a longer experiment time will induce a higher chlorate production). ORP can be understood as the activity or strength of redox species in a solution (rigorously, it represents the ability of a solution to accept or donor electrons). Positive ORP values indicate an oxidizing capacity (i.e., ability to donate electrons), and negative ORP values a reducing capacity (i.e., ability to accept electrons). Figure 14 shows the ORP variation during MCTW_1 and MCTW_2 treatment.

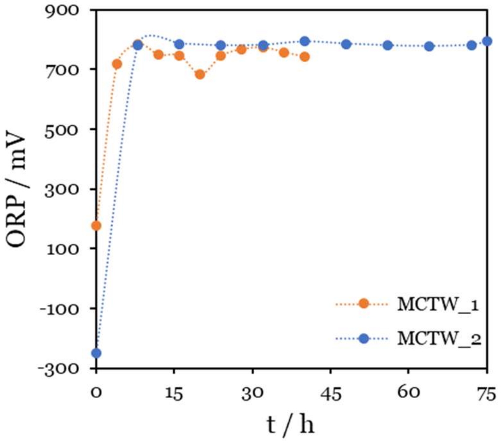

Figure 14. ORP variation with time for the EO treatment of MCTW_1 (0.5A_32h + 2.5A_8h) and MCTW_2 (1A_40h + 0.75A_35h).

MCTW_1 presented a higher initial ORP value than MCTW_2, indicating a solution's reducing capacity. Since ORP is a qualitative method, its variation can be interpreted as a change from a reducing solution to an oxidizing one. Although it can be related to the presence of reducing/oxidizing species in the solution, it should not be related to their concentration. Then, the similar evolution trend along the treatment is just as expected since hypochlorite production occurs in both treatments.

Alongside ORP, pH variation during MCTW_1 and MCTW_2 treatment (Figure 15) showed a similar trend. An increase in pH from 7.5 to 8.5-9 was observed. The redox reactions of aqueous chlorine species are pH dependent, explaining this increase in pH, as hypochlorite predominates from 7.5 to alkaline conditions [117]. This behavior has already been reported in the literature and is related to some conditions that disfavor the production of hydronium ions at the anode by the oxygen evolution reaction [90]. Therefore, the hydrogen evolution reaction, which takes place at the cathode and consumes hydronium ions, raises the pH.

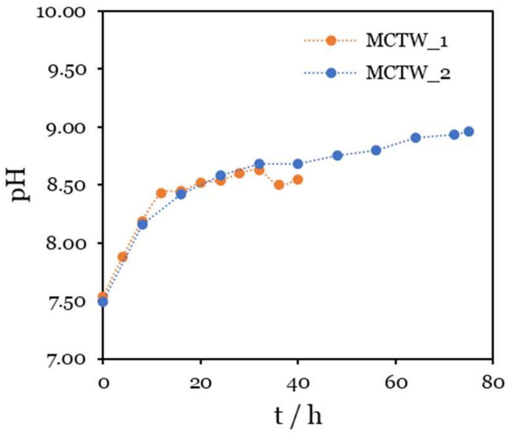

Figure 15. pH variation with time for the EO treatment of MCTW_1 (0.5A_32h + 2.5A_8h) and MCTW_2 (1A_40h + 0.75A_35h).

The COD decay with time for the EO treatment of MCTW_1 and MCTW_2 is presented in Figure 16. A higher COD removal rate can be observed for MCTW_2, probably due to the high initial COD of this sample and the high initial applied current. It can be noticed that the increase in applied current intensity, from 0.5 to 2.5 A, during the last 8 h of MCTW_1 treatment has not significantly affected the COD removal rate, indicating that the process is running at diffusive control, which is consistent with the low initial COD of this sample.

For MCTW_2, the decrease in the applied current after the 40th hour of treatment was performed to save energy since COD had been reduced from 1045 to 478 mg L^{-1} (data not shown). According to the initial chloride concentration of MCTW_1 and MCTW_2, a maximum hypochlorite concentration of 746 and 1740 mg L^{-1} could be produced. Experimental hypochlorite concentration reached 62% (MCTW_1) and 54% (MCTW_2) of the theoretical one. Still, the treated MCTW_2 sample had a much higher hypochlorite concentration than MCTW_1 (Table 9). Also, the specific energy consumption results, calculated from Equation (16) and presented in Table 9, show that the EO treatment is more efficient when using the MCTW_2 sample, presenting a much lower energy consumption (56 kWh kg^{-1}_{COD}) compared to MCTW_1 (418 kWh kg^{-1}_{COD}).

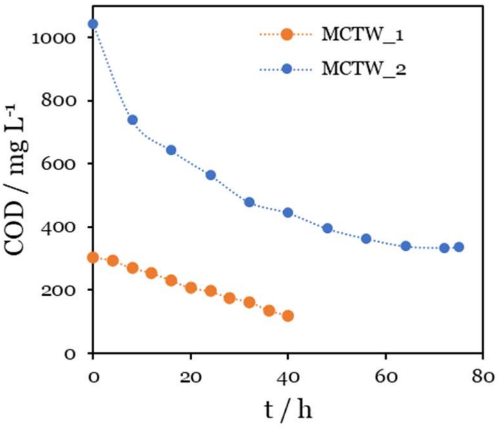

Figure 16. COD decay with time for the EO treatment of MCTW_1 (0.5A_32h + 2.5A_8h) and MCTW_2 (1A_40h + 0.75A_35h).

Although the process can be further optimized, using EO treatment as a tool to electrogenerate RCS (as ClO-) is feasible. Besides promoting the increase in chlorate production, the increase in applied current during MCTW_1 treatment significantly impacted E_{sp}.

The treated MCTW_1 and MCTW_2 samples were sent to the industry for testing in a pilot membrane cell operating with TWW. The obtained results so far have been auspicious.

Chapter 5

Conclusions and future perspectives

The population growth forecasted for the coming years and the increasingly realistic possibility of water shortages worldwide have motivated the study described in this dissertation. The high water consumption and the environmental threat the industrial sector poses highlight the need to develop and apply technologies to reduce water consumption and mitigate environmental impact. As the circular economy is the key that allows these two things to happen simultaneously, the experiments presented in this study aimed to use wastewater from olive oil and textile industries to produce treated wastewater that could be reused.

The OMW sample was collected from an olive mill in Beja, Portugal, and used to carry out EO experiments using a BDD anode. Three different current intensities were applied, aiming at the production of treated wastewater with varying levels of quality, to evaluate the feasibility of its reuse in hydroponic lettuce cultivation. It could be seen that, for the range of applied current intensities studied, the process efficiency did not vary significantly with the applied current. The highest COD removals, biodegradability indexes, and EC_{50}-48h values, favorable for OMW reuse in hydroponic cultivation, were achieved at the highest applied currents (500 and 700 mA). However, the final alkaline pH was unsuitable for cultivation, and high E_{sp} values were obtained under these conditions. Contrarywise, the OMW treated at the lowest applied current (300 mA), although presenting a neutral pH and a more acceptable E_{sp} value, presented high ecotoxicity. It is essential to carry out experiments using the treated solutions, with suitable dilution, for hydroponic lettuce cultivation to determine the influence of the treated OMW quality index on the crop's growth.

The MCTW samples were collected from a Portuguese textile industry. Two samples were collected: MCTW_1, a retentate from an ultrafiltration unit, and MCTW_2, a retentate from a reverse osmosis unit. Aiming to evaluate the feasibility of using EO to electrogenerate RCS, namely hypochlorite, and for COD removal, OE experiments were carried out using an MMO electrode. MCTW_1 sample was treated for 40 hours, 32 hours at 0.5 A, and 8 hours at 2.5 A. Although hypochlorite production was not negatively affected by the increase in applied current, this led to an almost fourfold increase in chlorate production and a significant increase in E_{sp}. After 40 hours of EO treatment, hypochlorite concentration reached 62% of the maximum theoretical value, with a COD removal of 61%. MCTW_2 sample was treated for 75 hours, 40 hours at 1 A, and 35 hours at 0.75 A. The reduction in applied current intensity decreased the hypochlorite production rate. Still, hypochlorite concentration reached 54% of the maximum theoretical value, with a COD removal of 68%, at a much lower E_{sp} value than the one observed for MCTW_1. The obtained results allowed to conclude that it is feasible to use EO to electrogenerate hypochlorite and, simultaneously reduce the MCTW organic load.

Overall, it can be concluded that it is feasible for both OMW and MCTW to use EO to generate treated wastewater for reuse. Although the treated wastewater obtained from OMW will require dilution and nutrient supplementation, its use will reduce freshwater consumption during hydroponic lettuce growing. Regarding MCTW, although the process requires further optimization to increase the hypochlorite formation efficiency and decrease the treatment costs, it is possible to obtain a solution rich in hypochlorite and with low COD values, allowing its reuse as an antifouling agent in membrane processes of TWW treatment.

Following the studies carried out, besides optimizing the processes studied, it is suggested that future work broaden the scope of research to other types of industrial effluents with potential for reuse in industrial processes.

References

[1] United Nations, The Sustainable Development Goals Report 2023, (2023). https://www.un.org/sustainabledevelopment/water-and-sanitation/ (accessed April 12, 2024).

[2] S. Elfkih, O. Hadiji, S. Ben Abdallah, O. Boussadia, Water Accounting for Food Security: Virtual Water and Water Productivity in the Case of Tunisian Olive Oil Value Chain, Agriculture 13 (2023) 1205. https://doi.org/10.3390/agriculture13061205.

[3] F. Uddin, Environmental hazard in textile dyeing wastewater from local textile industry, Cellulose 28 (2021) 10715–10739. https://doi.org/10.1007/s10570-021-04228-4.

[4] Z.S. Lee, S.Y. Chin, J.W. Lim, T. Witoon, C.K. Cheng, Treatment technologies of palm oil mill effluent (POME) and olive mill wastewater (OMW): A brief review, Environ Technol Innov 15 (2019) 100377. https://doi.org/10.1016/j.eti.2019.100377.

[5] K. Haddad, M. Jeguirim, B. Jerbi, A. Chouchene, P. Dutournié, N. Thevenin, L. Ruidavets, S. Jellali, L. Limousy, Olive Mill Wastewater: From a Pollutant to Green Fuels, Agricultural Water Source and Biofertilizer, ACS Sustain Chem Eng 5 (2017) 8988–8996. https://doi.org/10.1021/acssuschemeng.7b01786.

[6] G. Banias, C. Achillas, C. Vlachokostas, N. Moussiopoulos, M. Stefanou, Environmental impacts in the life cycle of olive oil: a literature review, J Sci Food Agric 97 (2017) 1686–1697. https://doi.org/10.1002/jsfa.8143.

[7] L.M. Fleyfel, N.K.V. Leitner, M. Deborde, J. Matta, N.H. El Najjar, Olive oil liquid wastes– Characteristics and treatments: A literature review, Process Safety and Environmental Protection 168 (2022) 1031–1048. https://doi.org/10.1016/j.psep.2022.10.035.

[8] T. Hussain, A. Wahab, A critical review of the current water conservation practices in textile wet processing, J Clean Prod 198 (2018) 806–819. https://doi.org/10.1016/j.jclepro.2018.07.051.

[9] F. Uddin, Environmental hazard in textile dyeing wastewater from local textile industry, Cellulose 28 (2021) 10715–10739. https://doi.org/10.1007/s10570-021-04228-4.

[10] S. Shabir, N. Ilyas, M. Saeed, F. Bibi, R.Z. Sayyed, W.H. Almalki, Treatment technologies for olive mill wastewater with impacts on plants, Environ Res 216 (2023) 114399. https://doi.org/10.1016/j.envres.2022.114399.

[11] S. Souilem, A. El-Abbassi, H. Kiai, A. Hafidi, S. Sayadi, C.M. Galanakis, Olive oil production sector: environmental effects and sustainability challenges, in: Olive Mill Waste, Elsevier, 2017: pp. 1–28. https://doi.org/10.1016/B978-0-12-805314-0.00001-7.

[12] A.G.K. Laizer, J.M. Bidu, J.R. Selemani, K.N. Njau, Improving biological treatment of textile wastewater, Water Pract Technol 17 (2022) 456–468. https://doi.org/10.2166/wpt.2021.083.

[13] A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, Review on the electrochemical processes for the treatment of sanitary landfill leachates: Present and future, Appl Catal B 176–177 (2015) 183–200. https://doi.org/10.1016/j.apcatb.2015.03.052.

[14] I.E. Kapellakis, K.P. Tsagarakis, J.C. Crowther, Olive oil history, production and by-product management, Rev Environ Sci Biotechnol 7 (2008) 1–26. https://doi.org/10.1007/s11157-007-9120-9.

[15] R. Mariotti, A. Belaj, R. de la Rosa, R. Muleo, M. Cirilli, I. Forgione, M.C. Valeri, S. Mousavi, Genealogical tracing of Olea europaea species and pedigree relationships of var. europaea using

chloroplast and nuclear markers, BMC Plant Biol 23 (2023) 452. https://doi.org/10.1186/s12870-023-04440-3.

[16] G. Besnard, J.-F. Terral, A. Cornille, On the origins and domestication of the olive: a review and perspectives, Ann Bot 121 (2018) 385–403. https://doi.org/10.1093/aob/mcx145.

[17] G. Di Giacomo, P. Romano, Evolution of the Olive Oil Industry along the Entire Production Chain and Related Waste Management, Energies (Basel) 15 (2022) 465. https://doi.org/10.3390/en15020465.

[18] P. Vossen, Olive Oil: History, Production, and Characteristics of the World's Classic Oils, HortScience 42 (2007) 1093–1100. https://doi.org/10.21273/HORTSCI.42.5.1093.

[19] V. Uylaşer, G. Yildiz, The Historical Development and Nutritional Importance of Olive and Olive Oil Constituted an Important Part of the Mediterranean Diet, Crit Rev Food Sci Nutr 54 (2014) 1092–1101. https://doi.org/10.1080/10408398.2011.626874.

[20] R. Estruch, E. Ros, J. Salas-Salvadó, M.-I. Covas, D. Corella, F. Arós, E. Gómez-Gracia, V. Ruiz-Gutiérrez, M. Fiol, J. Lapetra, R.M. Lamuela-Raventos, L. Serra-Majem, X. Pintó, J. Basora, M.A. Muñoz, J. V. Sorlí, J.A. Martínez, M.A. Martínez-González, Primary Prevention of Cardiovascular Disease with a Mediterranean Diet, New England Journal of Medicine 368 (2013) 1279–1290. https://doi.org/10.1056/NEJMoa1200303.

[21] Europe Union, Agriculture and rural development, 2020. https://agriculture.ec.europa.eu/document/download/cb848d45-397b-4266-ac32-3e2e4394f9cd_en?filename=factsheet-olive-oil_en.pdf&prefLang=pt (accessed May 9, 2024).

[22] P. Foti, F. V. Romeo, N. Russo, A. Pino, A. Vaccalluzzo, C. Caggia, C.L. Randazzo, Olive Mill Wastewater as Renewable Raw Materials to Generate High Added-Value Ingredients for Agro-Food Industries, Applied Sciences 11 (2021) 7511. https://doi.org/10.3390/app11167511.

[23] A. Yüksel Aydar, Emerging Extraction Technologies in Olive Oil Production, in: Technological Innovation in the Olive Oil Production Chain, IntechOpen, 2019. https://doi.org/10.5772/intechopen.81390.

[24] European Comission, Official Journal of the European Communities, 2001. https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=OJ:L:2001:201:TOC.

[25] M. Uceda, G. Beltrán, A. Jiménez, Olive oil extraction and quality, Grasas y Aceites 57 (2006). https://doi.org/10.3989/gya.2006.v57.i1.19.

[26] A. Khdair, G. Abu-Rumman, Sustainable Environmental Management and Valorization Options for Olive Mill Byproducts in the Middle East and North Africa (MENA) Region, Processes 8 (2020) 671. https://doi.org/10.3390/pr8060671.

[27] A.G. Vlyssides, M. Loizides, P.K. Karlis, Integrated strategic approach for reusing olive oil extraction by-products, J Clean Prod 12 (2004) 603–611. https://doi.org/10.1016/S0959-6526(03)00078-7.

[28] C. Bordons, A. Núñez-Reyes, Model based predictive control of an olive oil mill, J Food Eng 84 (2008) 1–11. https://doi.org/10.1016/j.jfoodeng.2007.04.011.

[29] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere 67 (2007) 832–838. https://doi.org/10.1016/j.chemosphere.2006.10.064.

[30] J.M. Ochando-Pulido, S. Pimentel-Moral, V. Verardo, A. Martinez-Ferez, A focus on advanced physico-chemical processes for olive mill wastewater treatment, Sep Purif Technol 179 (2017) 161–174. https://doi.org/10.1016/j.seppur.2017.02.004.

[31] M. Belaqziz, A. El-Abbassi, E.K. Lakhal, E. Agrafioti, C.M. Galanakis, Agronomic application of olive mill wastewater: Effects on maize production and soil properties, J Environ Manage 171 (2016) 158–165. https://doi.org/10.1016/j.jenvman.2016.02.006.

[32] N. Solomakou, A.M. Goula, Treatment of olive mill wastewater by adsorption of phenolic compounds, Rev Environ Sci Biotechnol 20 (2021) 839–863. https://doi.org/10.1007/s11157-021-09585-x.

[33] M. Achak, L. Mandi, N. Ouazzani, Removal of organic pollutants and nutrients from olive mill wastewater by a sand filter, J Environ Manage 90 (2009) 2771–2779. https://doi.org/10.1016/j.jenvman.2009.03.012.

[34] S. Magdich, W. Abid, M. Boukhris, B. Ben Rouina, E. Ammar, Effects of long-term olive mill wastewater spreading on the physiological and biochemical responses of adult Chemlali olive trees (Olea europaea L.), Ecol Eng 97 (2016) 122–129. https://doi.org/10.1016/j.ecoleng.2016.09.004.

[35] M. Antónia Nunes, A.S.G. Costa, S. Bessada, J. Santos, H. Puga, R.C. Alves, V. Freitas, M.B.P.P. Oliveira, Olive pomace as a valuable source of bioactive compounds: A study regarding its lipid- and water-soluble components, Science of The Total Environment 644 (2018) 229–236. https://doi.org/10.1016/j.scitotenv.2018.06.350.

[36] L. Cecchi, M. Bellumori, C. Cipriani, A. Mocali, M. Innocenti, N. Mulinacci, L. Giovannelli, A two-phase olive mill by-product (pâté) as a convenient source of phenolic compounds: Content, stability, and antiaging properties in cultured human fibroblasts, J Funct Foods 40 (2018) 751–759. https://doi.org/10.1016/j.jff.2017.12.018.

[37] A.A. Oladipo, Rapid photocatalytic treatment of high-strength olive mill wastewater by sunlight and UV-induced CuCr2O4@CaFe–LDO, Journal of Water Process Engineering 40 (2021) 101932. https://doi.org/10.1016/j.jwpe.2021.101932.

[38] M. Tufariello, M. Durante, G. Veneziani, A. Taticchi, M. Servili, G. Bleve, G. Mita, Patè Olive Cake: Possible Exploitation of a By-Product for Food Applications, Front Nutr 6 (2019). https://doi.org/10.3389/fnut.2019.00003.

[39] A. Zavra, E. Hatzigiannakis, E.K. Oikonomou, A. Guitonas, Biodegradation of olive mill wastewater by two bacterial strains, Desalination Water Treat 317 (2024) 100180. https://doi.org/10.1016/j.dwt.2024.100180.

[40] P.K. Rose, Mohd.K. Kidwai, P. Kantiwal, Green approaches for the valorization of olive mill wastewater, in: Green Chemistry Approaches to Environmental Sustainability, Elsevier, 2024: pp. 313–336. https://doi.org/10.1016/B978-0-443-18959-3.00011-2.

[41] A. Martínez-Cruz, A. Fernandes, L. Ciríaco, M.J. Pacheco, F. Carvalho, A. Afonso, L. Madeira, S. Luz, A. Lopes, Electrochemical Oxidation of Effluents from Food Processing Industries: A Short Review and a Case-Study, Water (Basel) 12 (2020) 3546. https://doi.org/10.3390/w12123546.

[42] K. Al-Malah, M.O.J. Azzam, N.I. Abu-Lail, Olive mills effluent (OME) wastewater post-treatment using activated clay, Sep Purif Technol 20 (2000) 225–234. https://doi.org/10.1016/S1383-5866(00)00114-3.

[43] H. El Hajjouji, L. El Fels, E. Pinelli, F. Barje, A. El Asli, G. Merlina, M. Hafidi, Evaluation of an aerobic treatment for olive mill wastewater detoxification, Environ Technol 35 (2014) 3052–3059. https://doi.org/10.1080/09593330.2014.930514.

[44] M. Govarthanan, C.-H. Jeon, Y.-H. Jeon, J.-H. Kwon, H. Bae, W. Kim, Non-toxic nano approach for wastewater treatment using Chlorella vulgaris exopolysaccharides immobilized in iron-magnetic nanoparticles, Int J Biol Macromol 162 (2020) 1241–1249. https://doi.org/10.1016/j.ijbiomac.2020.06.227.

[45] R. Sarika, N. Kalogerakis, D. Mantzavinos, Treatment of olive mill effluents, Environ Int 31 (2005) 297–304. https://doi.org/10.1016/j.envint.2004.10.006.

[46] P. Cañizares, L. Martínez, R. Paz, C. Sáez, J. Lobato, M.A. Rodrigo, Treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes, Journal of Chemical Technology & Biotechnology 81 (2006) 1331–1337. https://doi.org/10.1002/jctb.1428.

[47] E. Chatzisymeon, A. Dimou, D. Mantzavinos, A. Katsaounis, Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO2 anode, J Hazard Mater 167 (2009) 268–274. https://doi.org/10.1016/j.jhazmat.2008.12.117.

[48] S. Kul, R. Boncukcuoğlu, A.E. Yilmaz, B.A. Fil, Treatment of Olive Mill Wastewater with Electro-Oxidation Method, J Electrochem Soc 162 (2015) G41–G47. https://doi.org/10.1149/2.0451508jes.

[49] C. Belaid, M. Khadraoui, S. Mseddi, M. Kallel, B. Elleuch, J.F. Fauvarque, Electrochemical treatment of olive mill wastewater: Treatment extent and effluent phenolic compounds monitoring using some uncommon analytical tools, Journal of Environmental Sciences 25 (2013) 220–230. https://doi.org/10.1016/S1001-0742(12)60037-0.

[50] N. Papastefanakis, D. Mantzavinos, A. Katsaounis, DSA electrochemical treatment of olive mill wastewater on Ti/RuO2 anode, J Appl Electrochem 40 (2010) 729–737. https://doi.org/10.1007/s10800-009-0050-9.

[51] U.T. Un, U. Altay, A.S. Koparal, U.B. Ogutveren, Complete treatment of olive mill wastewaters by electrooxidation, Chemical Engineering Journal 139 (2008) 445–452. https://doi.org/10.1016/j.cej.2007.08.009.

[52] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, Electrochemical oxidation of olive oil mill wastewaters, Water Res 39 (2005) 4177–4187. https://doi.org/10.1016/j.watres.2005.07.037.

[53] A. Giannis, M. Kalaitzakis, E. Diamadopoulos, Electrochemical treatment of olive mill wastewater, Journal of Chemical Technology & Biotechnology 82 (2007) 663–671. https://doi.org/10.1002/jctb.1725.

[54] M. Panizza, G. Cerisola, Olive mill wastewater treatment by anodic oxidation with parallel plate electrodes, Water Res 40 (2006) 1179–1184. https://doi.org/10.1016/j.watres.2006.01.020.

[55] A. Afonso, M. Regato, M. Patanita, S. Luz, M.J. Carvalho, A. Fernandes, A. Lopes, A. Almeida, I. Costa, F. Carvalho, Reuse of Pretreated Agro-Industrial Wastewaters for Hydroponic Production of Lettuce, Water (Basel) 15 (2023) 1856. https://doi.org/10.3390/w15101856.

[56] M. Zaman, S.A. Shahid, L. Heng, Guideline for Salinity Assessment, Mitigation and Adaptation Using Nuclear and Related Techniques, Springer International Publishing, Cham, 2018. https://doi.org/10.1007/978-3-319-96190-3.

[57] C. Breniquet, C. Michel, eds., Wool Economy in the Ancient Near East, Oxbow Books, 2014. https://doi.org/10.2307/j.ctvh1djjn.

[58] F. Uddin, Introductory Chapter: Textile Manufacturing Processes, in: Textile Manufacturing Processes, IntechOpen, 2019. https://doi.org/10.5772/intechopen.87968.

[59] M.R.M. Jamir, M.S.A. Majid, A. Khasri, Natural lightweight hybrid composites for aircraft structural applications, in: Sustainable Composites for Aerospace Applications, Elsevier, 2018: pp. 155–170. https://doi.org/10.1016/B978-0-08-102131-6.00008-6.

[60] R. Kant, Textile dyeing industry an environmental hazard, Nat Sci (Irvine) 04 (2012) 22–26. https://doi.org/10.4236/ns.2012.41004.

[61] D.A. Yaseen, M. Scholz, Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review, International Journal of Environmental Science and Technology 16 (2019) 1193–1226. https://doi.org/10.1007/s13762-018-2130-z.

[62] European Commission, Data on the EU textile ecosystem and its competitiveness - Final report, Publications Office of the European Union, Luxembourg, 2021.

[63] C. Stone, F.M. Windsor, M. Munday, I. Durance, Natural or synthetic – how global trends in textile usage threaten freshwater environments, Science of The Total Environment 718 (2020) 134689. https://doi.org/10.1016/j.scitotenv.2019.134689.

[64] E. Ozturk, M. Karaboyacı, U. Yetis, N.O. Yigit, M. Kitis, Evaluation of Integrated Pollution Prevention Control in a textile fiber production and dyeing mill, J Clean Prod 88 (2015) 116–124. https://doi.org/10.1016/j.jclepro.2014.04.064.

[65] European Comission, Integrated pollution prevention and control. Reference document on best available techniques for the textiles industry, 2003.

[66] F. Tisa, A.A. Abdul Raman, W.M.A. Wan Daud, Applicability of fluidized bed reactor in recalcitrant compound degradation through advanced oxidation processes: A review, J Environ Manage 146 (2014) 260–275. https://doi.org/10.1016/j.jenvman.2014.07.032.

[67] K.C.H. Bezerra, T.R. Fiaschitello, G. Labuto, H.S. Freeman, W.D. Fragoso, S.M. da Costa, S.A. da Costa, Reuse of water from real reactive monochromic and trichromic wastewater for new cotton dyes after efficient treatment using H2O2 catalyzed by UV light, J Environ Chem Eng 9 (2021) 105731. https://doi.org/10.1016/j.jece.2021.105731.

[68] N. M. Al-Shuwaiki, B. A. Abid, M. M. Brbooti, Color Removal from Industrial Textile Wastewater Using Chemical Adsorption, Engineering and Technology Journal 31 (2013) 471–489. https://doi.org/10.30684/etj.31.4B.7.

[69] U. Tezcan Un, E. Aytac, Electrocoagulation in a packed bed reactor-complete treatment of color and cod from real textile wastewater, J Environ Manage 123 (2013) 113–119. https://doi.org/10.1016/j.jenvman.2013.03.016.

[70] M.F. Abid, M.A. Zablouk, A.M. Abid-Alameer, Experimental study of dye removal from industrial wastewater by membrane technologies of reverse osmosis and nanofiltration, Iranian J Environ Health Sci Eng 9 (2012) 17. https://doi.org/10.1186/1735-2746-9-17.

[71] H. Patel, R.T. Vashi, Characterization of Textile Wastewater, in: Characterization and Treatment of Textile Wastewater, Elsevier, 2015: pp. 21–71. https://doi.org/10.1016/B978-0-12-802326-6.00002-2.

[72] F.H. Hussein, Chemical Properties of Treated Textile Dyeing Wastewater, Asian Journal of Chemistry 25 (2013) 9393–9400. https://doi.org/10.14233/ajchem.2013.15909A.

[73] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, Toxicol Lett 151 (2004) 203–210. https://doi.org/10.1016/j.toxlet.2003.11.016.

[74] S. Raj, H. Singh, J. Bhattacharya, Treatment of textile industry wastewater based on coagulation-flocculation aided sedimentation followed by adsorption: Process studies in an industrial ecology concept, Science of The Total Environment 857 (2023) 159464. https://doi.org/10.1016/j.scitotenv.2022.159464.

[75] N.H. Torres, B.S. Souza, L.F.R. Ferreira, Á.S. Lima, G.N. dos Santos, E.B. Cavalcanti, Real textile effluents treatment using coagulation/flocculation followed by electrochemical oxidation process and ecotoxicological assessment, Chemosphere 236 (2019) 124309. https://doi.org/10.1016/j.chemosphere.2019.07.040.

[76] B. Keskin, M.E. Ersahin, H. Ozgun, I. Koyuncu, Pilot and full-scale applications of membrane processes for textile wastewater treatment: A critical review, Journal of Water Process Engineering 42 (2021) 102172. https://doi.org/10.1016/j.jwpe.2021.102172.

[77] H. Saleem, A. Saud, N. Munira, P.S. Goh, A.F. Ismail, H.R. Siddiqui, S.J. Zaidi, Improved Forward Osmosis Performance of Thin Film Composite Membranes with Graphene Quantum Dots Derived from Eucalyptus Tree Leaves, Nanomaterials 12 (2022) 3519. https://doi.org/10.3390/nano12193519.

[78] X. Zhang, M. Zhao, H. Yu, J. Wang, W. Sun, Q. Li, X. Cao, P. Zhang, Robust In Situ Fouling Control toward Thin-Film Composite Reverse Osmosis Membrane via One-Step Deposition of a Ternary Homogeneous Metal–Organic Hybrid Layer, ACS Appl Mater Interfaces 14 (2022) 7208–7220. https://doi.org/10.1021/acsami.1c19931.

[79] X. Cheng, Y. Xu, Z. Lei, J. Du, Investigation on operational parameters and membrane fouling performance in treating synthetic aquaculture wastewater via forward osmosis with sucrose as draw solution, Science of The Total Environment 847 (2022) 157573. https://doi.org/10.1016/j.scitotenv.2022.157573.

[80] M.Y. Ashfaq, M.A. Al-Ghouti, Optimization of Polyacrylic Acid Coating on Graphene Oxide-Functionalized Reverse-Osmosis Membrane Using UV Radiation through Response Surface Methodology, Polymers (Basel) 14 (2022) 3711. https://doi.org/10.3390/polym14183711.

[81] C.A. Martínez-Huitle, E.V. dos Santos, D.M. de Araújo, M. Panizza, Applicability of diamond electrode/anode to the electrochemical treatment of a real textile effluent, Journal of Electroanalytical Chemistry 674 (2012) 103–107. https://doi.org/10.1016/j.jelechem.2012.02.005.

[82] F.A. Rodríguez, E.P. Rivero, L. Lartundo-Rojas, I. González, Preparation and characterization of Sb2O5-doped Ti/RuO2-ZrO2 for dye decolorization by means of active chlorine, Journal of Solid State Electrochemistry 18 (2014) 3153–3162. https://doi.org/10.1007/s10008-014-2554-4.

[83] N. MOHAN, N. BALASUBRAMANIAN, C. BASHA, Electrochemical oxidation of textile wastewater and its reuse, J Hazard Mater 147 (2007) 644–651. https://doi.org/10.1016/j.jhazmat.2007.01.063.

[84] F. Orts, A.I. del Río, J. Molina, J. Bonastre, F. Cases, Electrochemical treatment of real textile wastewater: Trichromy Procion HEXL®, Journal of Electroanalytical Chemistry 808 (2018) 387–394. https://doi.org/10.1016/j.jelechem.2017.06.051.

[85] K.V. Radha, V. Sridevi, K. Kalaivani, Electrochemical oxidation for the treatment of textile industry wastewater, Bioresour Technol 100 (2009) 987–990. https://doi.org/10.1016/j.biortech.2008.06.048.

[86] X. Chen, Z. Shen, X. Zhu, Y. Fan, W. Wang, Advanced treatment of textile wastewater for reuse using electrochemical oxidation and membrane filtration, Water SA 31 (2005). https://doi.org/10.4314/wsa.v31i1.5129.

[87] M. Panizza, G. Cerisola, Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation, J Hazard Mater 153 (2008) 83–88. https://doi.org/10.1016/j.jhazmat.2007.08.023.

[88] P.V. Nidheesh, A. Kumar, D. Syam Babu, J. Scaria, M. Suresh Kumar, Treatment of mixed industrial wastewater by electrocoagulation and indirect electrochemical oxidation, Chemosphere 251 (2020) 126437. https://doi.org/10.1016/j.chemosphere.2020.126437.

[89] C.Y. Sousa, A. Fernandes, A. Amaro, M.J. Pacheco, L. Ciríaco, A. Lopes, Electrochemical Recovery of Phosphorus from Simulated and Real Wastewater: Effect of Investigational Conditions on the Process Efficiency, Sustainability 15 (2023) 16556. https://doi.org/10.3390/su152416556.

[90] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, Electrochim Acta 39 (1994) 1857–1862. https://doi.org/10.1016/0013-4686(94)85175-1.

[91] C.A. Martínez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, Chem. Soc. Rev. 35 (2006) 1324–1340. https://doi.org/10.1039/B517632H.

[92] Á. Anglada, A. Urtiaga, I. Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, Journal of Chemical Technology & Biotechnology 84 (2009) 1747–1755. https://doi.org/10.1002/jctb.2214.

[93] W. Wu, Z.-H. Huang, T.-T. Lim, Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water, Appl Catal A Gen 480 (2014) 58–78. https://doi.org/10.1016/j.apcata.2014.04.035.

[94] Preparation of Common Types of Desk Reagents Specified in Standard Methods, (n.d.). https://doi.org/10.2105/SMWW.2882.216.

[95] M.V. Pablos, F. Martini, C. Fernández, M.M. Babín, I. Herraez, J. Miranda, J. Martínez, G. Carbonell, L. San-Segundo, P. García-Hortigüela, J.V. Tarazona, Correlation between physicochemical and ecotoxicological approaches to estimate landfill leachates toxicity, Waste Management 31 (2011) 1841–1847. https://doi.org/10.1016/j.wasman.2011.03.022.

[96] A.I. Vogel, Vogel's Textbook of Quantitative Chemical Analysis, 5th ed., John Wiley & Sons, New York, 1989.

[97] A. Fernandes, M.J. Pacheco, L. Ciríaco, A. Lopes, Anodic oxidation of a biologically treated leachate on a boron-doped diamond anode, J Hazard Mater 199–200 (2012) 82–87. https://doi.org/10.1016/j.jhazmat.2011.10.074.

[98] I. Souli, C. Afonso, A. Lopes, M.J. Pacheco, L. Ciríaco, L. Labiadh, S. Ammar, A. Fernandes, Treatment of fish canning wastewater by electrochemical oxidation process, Journal of Water Process Engineering 56 (2023) 104423. https://doi.org/10.1016/j.jwpe.2023.104423.

[99] A.S. Rodrigues, F. Souiad, A. Fernandes, A. Baía, M.J. Pacheco, L. Ciríaco, Y. Bendaoud-Boulahlib, A. Lopes, Treatment of fruit processing wastewater by electrochemical and activated persulfate processes: Toxicological and energetic evaluation, Environ Res 209 (2022) 112868. https://doi.org/10.1016/j.envres.2022.112868.

[100] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl Catal B 166–167 (2015) 603–643. https://doi.org/10.1016/j.apcatb.2014.11.016.

[101] A. Fernandes, C. Pereira, V. Kozioł, M.J. Pacheco, L. Ciríaco, A. Lopes, Emerging contaminants removal from effluents with complex matrices by electrooxidation, Science of The Total Environment 740 (2020) 140153. https://doi.org/10.1016/j.scitotenv.2020.140153.

[102] A. Baía, A. Lopes, M.J. Nunes, L. Ciríaco, M.J. Pacheco, A. Fernandes, Removal of Recalcitrant Compounds from Winery Wastewater by Electrochemical Oxidation, Water (Basel) 14 (2022) 750. https://doi.org/10.3390/w14050750.

[103] M. Luna-Trujillo, R. Palma-Goyes, J. Vazquez-Arenas, A. Manzo-Robledo, Formation of active chlorine species involving the higher oxide MOx+1 on active Ti/RuO2-IrO2 anodes: A DEMS analysis, Journal of Electroanalytical Chemistry 878 (2020) 114661. https://doi.org/10.1016/j.jelechem.2020.114661.