OLIVE POMACE EFFLUENT TREATMENT BY ADSORPTION PROCESS AND PEROXY-ELECTROCOAGULATION

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Final dissertation presented to the Escola Superior de Tecnologia e Gestão of Instituto Politécnico de Bragança to obtain a Master's degree in Chemical Engineering within the scope of the double degree with the Universidade Tecnológica Federal do Paraná.

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Bragança, 2022

DEDICATION

I dedicate this work to my parents, brothers and close friends,
for always helping and supporting my decisions.

ACKNOWLEDGEMENTS

To Prof. Ramiro José Espinheira Martins, for the guidance and support given for the development of this work.

To Prof. Juliana Martins Teixeira de Abreu Pietrobelli, for the guidance and attention for the development of this work and for the teaching and patience.

To the technician of the Chemical Processes Laboratory, Eng. Maria João Almeida Pinto Santos Afonso, for the support given throughout the work.

To Investigator MSc. Chemical Engineer Thais Theomaris dos Santos Grabowski for all support, patience and teachings in every aspect of the research.

To the other Master's students, Luis Felipe do Nascimento Pinheiro and Alexandre Narciso, and the professor Marlei Veiga dos Santos who participated and followed the working group.

To Universidade Tecnológica Federal do Paraná and Instituto Politécnico de Bragança for the opportunity.

To all my friends that I had the opportunity to meet during my journey.

ABSTRACT

The effluent of the olive bagasse oil extraction has a highly toxic nature, due to the high concentration of phenolic compounds (8.13 g L^{-1}), COD (86.41 g O_2 L^{-1}), acid pH (4.84) and low biodegrability (BOD_5/COD = 0.14), making it impossible to apply biological treatments. It is an effluent of dark reddish appearance, with strong odor and difficult to treat. Thus, the aim of this work was to perform the treatment of effluent to reduce the concentration of pollutants and harmful elements to the environment using the method by Adsorption with Activated Carbon (AC) and Peroxy-electrocoagulation (EC) with aluminum electrodes. To evaluate the treatment with both techniques, the physicochemical characterization of the natural effluent and after treatment was performed. The adsorption tests were carried in two stages, at the first stage was evaluated the concentration of AC, agitation time and agitation speed. However, for the second stage, the agitation speed was not considered relevant for the development of effluent treatment, being analyzed only the concentration of AC and agitation time. Based on the Variance Analysis Table (ANOVA) and the Response Surface Methodology (RSM), it was possible to conclude that for adsorption experiments with AC, the adsorbent concentration was the most significant factor of the process. Therefore, with the increase in the amount of AC added to the system, there was greater removal of phenolic compounds and COD. After treatment by adsorption with AC, a reduction of 32.2% of phenolic compounds and 28.4% of COD was obtained. For the peroxy-EC tests, the concentration of hydrogen peroxide (H_2O_2), the current density (DC) and the initial pH were used as parameters. When analyzing the Tables ANOVA and RSM, it was noticed that for the peroxy-EC experiments the parameter with the most significance was the concentration of H_2O_2 added to the system. At the end of the peroxy-EC process, a 90.4% decrease in phenolic compounds and 19.6% of COD was achieved. The adsorption treatment with AC presented insufficient removal of phenolic compounds and organic load (COD), considering the proposed limits for the factors studied. While the peroxy-EC process with aluminum electrodes showed satisfactory decrease in the phenolic compound concentration. However, for both processes, there is space for improvement in the efficiency of the processes. Therefore, future works will be important in the search for adequate treatment for this type of effluent.

Keywords: Adsorption; Chemical oxygen demand; Olive pomace oil; Peroxy-electrocoagulation; Phenolic compounds.

RESUMO

O efluente da extração de óleo de bagaço de azeitona apresenta natureza altamente tóxica, devido a alta concentração de compostos fenólicos (8.13 g L^{-1}), DQO (86.41 g O_2 L^{-1}), pH ácido (4.84) e baixa biodegrabilidade (DBO_5/DQO = 0.14), impossibilitando a aplicação de tratamentos biológicos. É um efluente de aparência avermelhada escura, com forte odor e de difícil tratamento. Assim, o intuito do trabalho foi realizar o tratamento do efluente para reduzir a concentração de elementos poluente e nocivos ao meio ambiente utilizando o método por Adsorção com Carvão Ativado (CA) e por Peroxi-eletrocoagulação (EC) com eletrodos de alumínio. Para avaliar o tratamento com as duas técnicas foi realizado a caracterização físico-química do efluente natural e após tratamento. Os ensaios de adsorção foram realizados em duas etapas, em primeiro momento foi avaliado a concentração de CA, o tempo de agitação e a velocidade de agitação. Entretanto, para a segunda etapa, a velocidade de agitação não foi considerada relevante para o desenvolvimento do tratamento do efluente, sendo analisado somente a concentração de CA e o tempo de agitação. Com base na Tabela de Variância (ANOVA) e a Metodologia de Resposta de Superfície (RSM) foi possível concluir que para os experimentos de adsorção com CA, a concentração do adsorvente apresentou ser o fator mais significativo do processo. Portanto, com o aumento na quantidade de CA adicionado ao sistema ocorreu maior remoção de compostos fenólicos e DQO. Após tratamento por adsorção com CA, foi obtido redução de 32.2% de compostos fenólicos e 28.4% de DQO. Para os testes de peroxi-EC foi utilizado como parâmetros a concentração de peróxido de hidrogênio (H_2O_2), a densidade de corrente (DC) e o pH de inicio. Ao analisar as tabelas ANOVA e RSM percebe-se que para os experimentos de peroxi-EC o parâmetro com mais significância é a concentração de H_2O_2 adicionada ao sistema. Ao final do processo de peroxi-EC foi alcançado diminuição de 90.4% de compostos fenólicos e 19.6% de DQO. Assim que tratamento por adsorção com CA apresentou remoção insuficiente de compostos fenólicos e carga orgânica, considerado os limites propostos para os fatores estudados. Enquanto que o processo por peroxi-EC com eletrodos de alumínio demostrou diminuição satisfatória na concentração de compostos fenólicos. No entanto, para ambos os processos, há espaço para melhoria na eficiência dos processos. Portanto, futuros trabalhos serão importantes na busca de tratamento adequado para esse tipo de efluente.

Palavras-chave: Adsorção; Bagaço de azeitona; Compostos fenólicos; Demanda química de oxigênio; Peroxi-eletrocoagulação.

INDEX OF ABBREVIATIONS

AC - Activated Carbon

ANOVA - Analysis of Variance

BBD - Box Behnken Design

BOD_5 - Biochemical Oxygen Demand

CCD - Central Composite Design

CD - Current Density

COD - Chemical Oxygen Demand

EC - Electrocoagulation

FO - First Order

IC - Inorganic Carbon

OMWW - Olive Mill WasteWater

OOEIW - Olive Oil Extraction Industry Wastewater

PhC - Phenolic Compounds

PQ - Pure Quadratic

RSM - Response Surface Methodology

TC - Total Carbon

TDS - Total Dissolved Solids

TFS - Total Fixed Solids

TOC - Total Organic Carbon

TS - Total Solids

TSS - Total Suspended Solids

TVS - Total Volatile Solids

TWI - Two-Way Interaction

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1. INTRODUCTION

The Mediterranean is one of the main olive producers, responsible for 95% of the world's olive oil production. The production of olive oil provides around 96% of total olive production, with table olives representing the remaining 4%. Olive oil extraction has been explored in the Mediterranean region since ancient times due to the favorable climate for the growth of olive trees. The European Commission estimates that around 2 million tons of olive oil are produced annually in the European Union (Brito, 2016; Mazur, 2021).

Olive pomace is one of the main by-products generated in the olive oil industry. According to Clodoveo et al. (2015), after the olive oil extraction process, the olive pomace produced has a substantial amount of oil, as well as, compounds of economic value.

According to Ergü et al. (2000), Gotsi et al. (2005), Kiril Mert et al. (2010) and Reis (2016), the effluent from this industry has some specificities, such as high organic load, seasonal operation, high territorial dispersion and the presence of organic compounds that are difficult to biodegrade, such as long chain fatty acids and phenolic compounds. When discarded without prior treatment, the effluent causes severe environmental impacts, such as the coloring of natural waters, significant threat to aquatic life, surface and underground water pollution, changes in soil quality, phytotoxicity and bad odor.

Therefore, this effluent is one of the major concerns of countries like: Greece, Italy, Spain, Portugal, Syria, Tunisia and Turkey, as it is a potential source of environmental problems, with a negative impact on soil and water quality (Ergü et al., 2000; Dhouib et al., 2006). As Azbar et al. (2004) presents in their work, with the increase in the world demand for olive oil, countries in the Mediterranean region face the challenge of finding an environmentally and economically viable solution for the handling and disposal of the residue.

Within this context, the present work aims to evaluate two different treatment techniques for the effluent produced in the olive pomace oil extraction industry, adsorption with activated carbon and peroxy-electrocoagulation with aluminum electrodes.

2. OBJECTIVE

2.1. Main Objective

To assess the removal of phenolic compounds and the decrease of organic load (COD) in an effluent generated from an olive pomace oil extraction unit using activated carbon adsorption and peroxy-electrocoagulation (aluminum electrodes), located in Frechas-Mirandela (Portugal).

2.2. Specific Objectives

- Physicochemical characterization of the natural effluent and after treatment by adsorption with an activated carbon and by peroxy-electrocoagulation;
- Evaluate the treatment process by adsorption with activated carbon and peroxy-electrocoagulation with aluminum electrodes to remove phenolic compounds and organic load (COD) as the primary contaminants;
- Using the Response Surface Methodology (RSM) and Analysis of Variance (ANOVA), statistically assess the significance of the proposed processes;
- Propose initial treatments for the effluent generated in the extraction of oil from olive pomace.

3. STATE OF ART

3.1. Olive oil production

According to Tsagaraki et al. (2006) and Reis (2016), there are three main methods for extracting olive oil: the pressing process (traditional system), two-phase centrifugation and three-phase centrifugation.

The pressing process is the oldest system used for the production of olive oil. Due to the pressure exerted, the olive paste releases an oily must (water and oil) that will later be separated by centrifugation, into virgin olive oil and raw water. For this extraction process, a small amount of water is added, resulting in less effluent, but concentrated wastewater (Tsagaraki et al., 2006; Reis, 2016).

In the three-phase centrifuge process, the olive paste is centrifuged at high speed, promoting the separation of solid and liquid phases. The liquid phase is again submitted to centrifugation to separate the oil and the red water (Reis, 2016). According to Petrakis (2006), for this process is used 1.25 to 1.75 times more water than traditional system, increasing wastewater produced in the extraction.

In the two-phase centrifuge process, a decanter is used, which rotates at different speeds, allowing the bagasse to be directed to the ends of the equipment and the liquid phase to its interior. This type of process produces a large amount of wet pomace (da Cunha, 2014; Reis, 2016). Petrakis (2006) reports that wet bagasse can pass by another three-phase centrifugation process to decrease its humidity and recover a small percentage of oil.

According to Petrakis (2006) and Gebreyohannes et al. (2016), the extraction process produces an effluent with dark color, acid, and a bad odor, mainly called olive mill wastewater (OMWW).

3.2. Olive pomace oil production

Olive pomace is a solid by-product of olive oil production, consisting of pieces of skin, pulp and olive stone (Sánchez Moral & Ruiz Méndez, 2006). It has considerable amount of oil and it can be a source of valuable compounds, such as triterpenic acids and triterpene alcohol.

The olive bagasse is mainly used for the extraction of residual oil present through solvent extraction, such as n-hexane. After extraction, the oil is refined to be considered suitable for human consumption (Clodoveo et al., 2015; Skaltsounis et al., 2015).

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

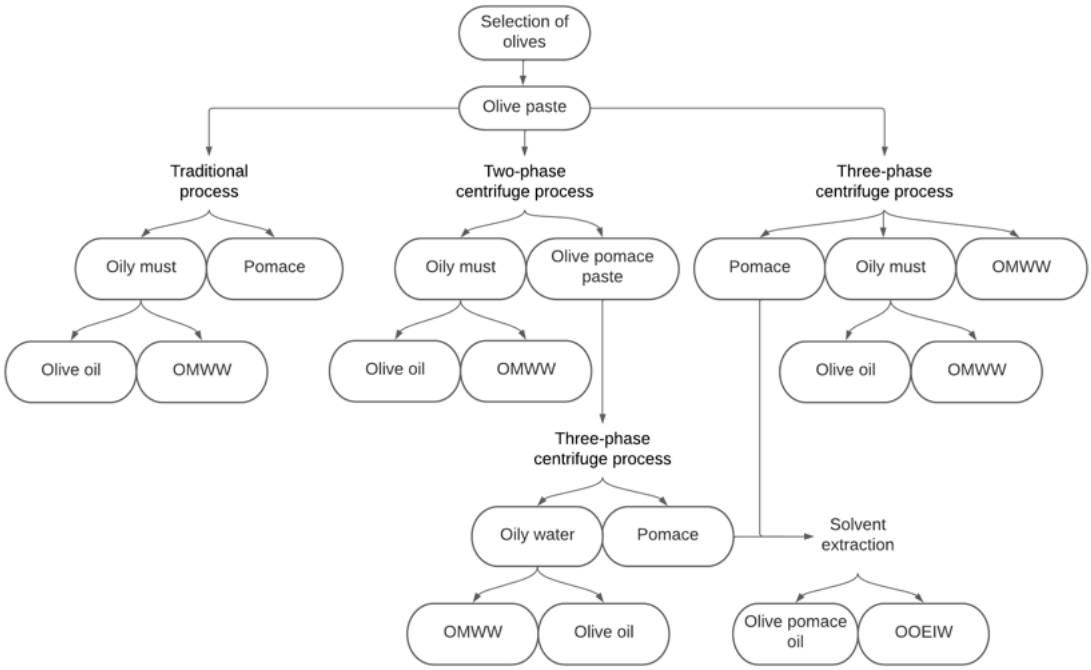

Figure 1: Olive pomace oil extraction process.
Adapted from Petrakis (2006) and Domingues et al. (2021).

According to Domingues et al. (2021) and Mazur (2021), is a little or almost unstudied effluent, presenting physicochemical characteristics similar to OMWW. Table 1 presents the physicochemical characteristics of OOEIW and OMWW collected by Gebreyohannes et al. (2016), Domingues et al. (2021) and Mazur (2021).

Table 1: Physicochemical characteristics of OMWW and OOEIW.

	OMWW							OOEIW		
Parameter	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**7**	**8**	**Average**
pH	5.2	5.1	5.7	5.3	5	4.8	5.2	4.8	4.97	4.9
Conductivity (mS cm^{-1})	5	-	11	24	81	17.5	27.7	-	8.8	8.8
COD (g L^{-1})	16.5	95	48	156	53	150	86	50.4	28.5	40
BOD (g L^{-1})	-	-	-	-	13.4	37.5	26	8	15.01	12
Dry residue (g L^{-1})	11.5	84.2	-	90	39.4	53.16	56	-	-	-
Lipids (g L^{-1})	-	-	-	7	-	-	7	-	2.63	2.63
PhC (g L^{-1})	0.8	4.82	8.8	4.1	8.6	8.9	6.0	4.3	1.42	2.9
Sugar (g L^{-1})	1.3	-	-	4.3	-	-	2.8	-	-	-
TN (g L^{-1})	0.06 -0.3	-	0.9	-	0.5	-	0.4	-	-	-

1. Paraskeva et al. (2007), 2. Asses et al. (2009), 3. Karpouzas et al. (2010), 4. El-Abbassi et al. (2013b), 5. Mekki et al. (2013), 6. Khoufi et al. (2015), 7. Domingues et al. (2021) and 8. Mazur (2021).

3.3. Olive oil industry wastewater treatment

When the concept of circular economy is applied in industrial processes it aims to use and/or transform waste into materials to be reinstated in the production chain, increasing the efficiency of the process in order to reduce the costs and environmental impacts associated with the dumping of toxic waste (Korhonen et al., 2018; Mazur, 2021; Donner et al., 2022).

As mentioned by Tsagaraki et al. (2006), the residue from the olive oil industry presents a dual nature, it's a strong pollutant and source of valuable resources, such as polyphenols, flavonoids, anthocyanins and inorganic elements that can be isolated and exploited economically. And it presents high content in organic matter, suspended solids and lipids.

The effluent produced has high cytotoxic potential and antimicrobial properties, mainly due to the high concentration of phenolic compounds, making the residue highly polluting (Galiatsatou et al., 2002; Layachi et al., 2022). Phenolic compounds and their derivatives are a family of common environmental contaminants, even at low concentrations present an obstacle to the use/reuse of water, their presence causes bad

taste and odor to drinking water and cause negative effects to biological processes (Dąbrowski et al., 2005).

Due to the increasing environmental concern regarding the handling of this type of effluent, numerous types of treatments and recovery of compounds methodologies were tested, such as mechanical, physical, biological, thermal, physical-chemical and application methods in the soil (Azbar et al., 2004; Ferraz, 2012). Thus, in more recent studies, flexible and efficient treatments have been evaluated in order to reduce capital costs for their treatment with the recovery and recycling of economically interesting components (Tsagaraki et al., 2006).

According to Reis (2016), the most used method for the treatment of this residue is the evaporation ponds (Figure 2). In this method, the residue is stored in ponds and evaporated during the heat months. Although it is a simple process, it presents some concerns due to the risk of infiltration if it doesn't present appropriate isolation. In addition to this risk, this procedure has low efficiency, difficulty in eliminating sludges and generates bad odor.

Figure 2: Evaporation ponds of the olive pomace oil extraction wastewater.

Until present moment, a large number of autonomous and integrated processes have been recommended for the treatment of OMWW, as direct irrigation of fields, natural evaporation and thermal concentration, clay treatment, lime treatment, co-composting, physicochemical processes (coagulation and flocculation), electrocoagulation, electrolysis, biological treatment by aerobic treatment (activated sludges) and anaerobic treatment, advanced oxidation process (ozonation, Fenton reaction and photocatalysis) and membrane technologies (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) (Arvanitoyannis et al., 2007; Kiril Mert et al., 2010; Gholamzadeh et al., 2016).

3.4. Adsorption with Activated Carbon

Adsorption is a non-destructive process, environment-friendly, easy operation, low health risk and it is cost-effective. The addition of activated carbon to the adsorption process allows the removal of contaminant and carcinogenic components, such as pharmaceuticals products, metallic and non-metallic pollutants, dyes, and can remove the taste and odor of aqueous solutions (Reza et al., 2020).

Activated carbon (AC) is a solid amorphous carbon-based material filled with well-developed pore structures with zero electronic density and wide surface area (Marsh & Rodríguez-Reinoso, 2006; Çeçen & Aktas, 2012; Bhatnagar et al., 2013; Amola et al., 2020). It is an adsorbent with peculiar characteristics, such as: high surface area, satisfactory distribution of pore size, stability at high temperatures, low affinity for acids and bases and fast adsorption (Din et al., 2017).

According to Marsh & Rodríguez-Reinoso (2006), AC has intense forces of Van der Walls, due to the proximity of carbon atoms, responsible for the adsorption process. Like Reza et al. (2020) said in their work, there are three main types of pores on the surface of AC: micropores, mesopores and macropores. In Galiatsatou et al. (2002) research, the adsorption of molecules with AC occurs due to the attractive interaction between the molecules and the walls of micropores and mesopores with compatible dimensions.

The adsorption properties of the material depend on the functional group on the surface, the material activation process, carbon matrix and thermal purification. The carbonic materials present, on their surface, functional groups responsible for contaminants adsorption, such as carboxyl, carbonyl, phenol, lactone and quinone (Heidarinejad et al., 2020).

According to Reza et al. (2020), AC is produced by activating carbonic materials by physical, chemical, physical-chemical or microwave-assisted procedure. It is produced from carbon-rich materials such as wood, coal, lignite, coconut shell, as well as agro-industrial waste, sewage and forest waste (Bhatnagar et al., 2013; Reza et al., 2020).

Currently, AC is the most widely used adsorbent in the treatment of water and sewage and its application in other areas is expanding, like in water treatment and desalination, wastewater treatment and air purification (Galiatsatou et al., 2002; Bhatnagar et al., 2013; Heidarinejad et al., 2020). Its particular properties make it an

interesting adsorbent for the treatment of domestic water and industrial wastewater (Din et al., 2017).

Bhatnagar et al. (2013) and Reza et al. (2020) report in their studies that in more recent research the use of AC for adsorption is promising in the removal of organic compounds such as dyes, phenolic compounds and inorganic compounds. According to Dąbrowski et al. (2005), AC presents excellent adsorption of low molecular weight organic compounds, such as phenolic compounds, and adsorption with AC is the most widely used technique for the removal of such compounds.

3.5. Peroxy-electrocoagulation

Coagulation and flocculation are physical-chemical processes in which phase separation occurs. In coagulation happens the destabilization of the suspended matter and in flocculation takes place the junction of destabilized matter, by attraction and contact, in clusters (Bratby, 2006; Cañizares et al., 2007; Teh et al., 2016; Garcia-Segura et al., 2017).

Unlike the traditional coagulation process in which it is necessary to add metal salts, in electrocoagulation (EC) is used of the electric current to dissolve the coagulant agents, in situ, from the electrolytic oxidation of sacrificial electrodes immersed in the effluent. Electrodissolution increases the concentration of coagulating agents or their complexes in the media (Cañizares et al., 2007; Garcia-Segura et al., 2017).

According to Cañizares et al. (2007) and Khandegar & Saroha (2013), the electrodes of iron, aluminum, stainless steel, soft steel and graphite are the most commonly used, because they are cheap, easy availability, non-toxic and efficient. But, the aluminum electrodes have, as advantage, to be easily oxidized and have no corrosion problems. Yazdanbakhsh et al. (2015) reports in their work that the process of EC produces a strong oxidant, hydroxyl radicals, which degrade the organic substances present in the effluent.

In the electrodes, different mechanisms occurs due to the direction of the electric current, where the reactions to aluminum electrodes can be observed in Equations (1), (2) and (3), as well as a scheme of physical-chemical interaction during EC (Figure 3).

- In the anode occurs the electro dissolution of the metal.

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \quad (1)$$

- In the cathode occurs the production of hydrogen gas and hydroxyl radicals.

$$2H_2O_{(aq)} + 2e^- \rightarrow H_{2\,(g)} + OH^- \quad (2)$$

- In bulk occurs the formation reaction of the aluminum hydroxide.

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3\,(s)} \quad (3)$$

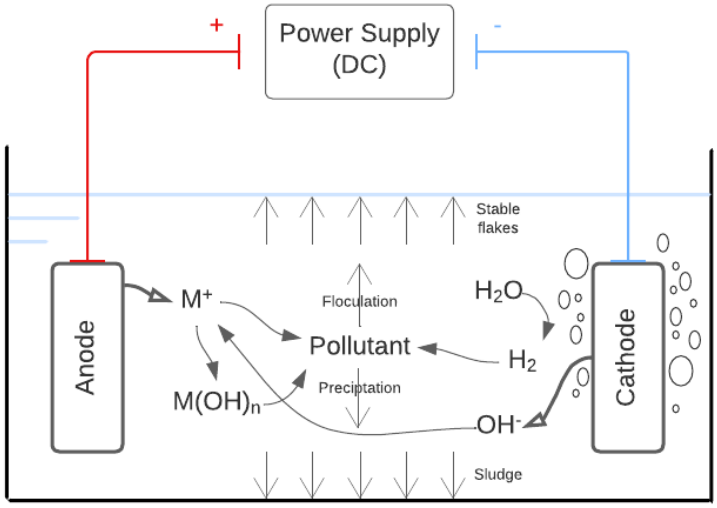

Figure 3: Scheme demonstrating interactions that occur during EC.
Adapted from Almukdad et al. (2021).

Depending on the pH of the solution, Al^{3+} ions can generate hydroxides and/or polyhydroxy (Equation (4). Studies suggest that these compounds formed have great affinity in the capture of pollutants (Esfandyari et al., 2015; Khandegar & Saroha, 2013).

$$Al^{3+} \rightarrow Al(OH)_n^{3-n} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_3(OH)_4^{5+} \rightarrow Al_{13}conplex \rightarrow Al(OH)_3 \quad (4)$$

Merma (2008), Khandegar & Saroha (2013), Garcia-Segura et al (2017) and Almukdad et al. (2021), report in their research that the EC presents some advantages and disadvantages when compared to the traditional method of coagulation (Table 2).

Table 2: Advantages and disadvantages of EC compared to the traditional coagulation method.

Advantages	Disadvantages
• Does not require additional chemicals. • Small volume of sludge generated and it is more easily filtered. • Better removal ability for the same compounds. • Secondary pollution does not occur, as it is not necessarily additional coagulating agents • Lower operating costs. • More effective and faster separation of organic matter.	• Periodic replacement of the sacrificial electrode. • Possibility of formation of chlorinated toxic organic compounds, due to the existence of chlorides in the effluent. • Formation of waterproof oxide film formed in the cathode, it can provide resistance to the flow of electric current.

According to Garcia-Segura et al. (2017), currently advanced EC processes are emerging, those are technologies that promote the production of hydroxyl radicals and other oxidizing compounds by different mechanisms, such as sono-EC (ultrasound irradiation), photo-EC (ultraviolet irradiation) and peroxy-EC (hydrogen peroxide).

In Esfandyari et al. (2015) studies, the use of hydrogen peroxide can promote the pollutants oxidation due to the formation of hydroxyl radicals (Equation (5). Where these radicals cause the chemical degradation of the organic compounds in a short time.

$$H_2O_2 + e^- + H^+ \leftrightarrow H_2O + OH^{\cdot} \quad (5)$$

So, in the peroxy-EC process there is an external addition of hydrogen peroxide into the system, increasing the concentration of hydroxyl radicals in the medium (Farhadi et al., 2012; Esfandyari et al., 2015).

4. METHODOLOGY

The study was carried out at the Laboratory of Chemical Processes, Escola de Tecnologia e Gestão, at Instituto Politécnico de Bragança, from September 2021 to October 2022. The effluent was collected on March 15th and June 14th of 2022, from an extracting unit of olive pomace oil located in Frechas, Mirandela, Portugal.

For the study, two distinct experiments were elaborated: adsorption with activated carbon and peroxy-electrocoagulation with aluminum electrodes. Ultimately, the removal of phenolic compounds (PhC) and the reduction of organic load (COD), as main pollutants, were evaluated. The Response Surface Methodology (RSM) and Analysis of Variance (ANOVA) were used to analyze the experimental data responses for the effluent treatment. The RSM and ANOVA were performed using the RStudio 2022.07.1 statistical software. For the analysis, the level of confidence was set to be at least 95% (alfa value lower than 5%). Then, the results were adjusted for a second-order model Equation (6).

$$Y_i = \beta_0 + \sum_{i=1}^{3}(\beta_i X_i) + \sum_{i=1}^{3}(\beta_{ii} X_{ii}^2) + \sum_{i=1}^{3}\sum_{j=1}^{3}\left(\beta_{ij} X_i X_j\right) \quad (6)$$

where β_0, β_i, β_{ii} and β_{ij} are the regression coefficients for the terms of interception, linear, square and interaction, respectively. And X_i e X_j are the independent variables.

Therefore, from the analysis of the results it was possible to determine the statistical significance of the variable and the interaction between them and the studied response. Also, to check the quality and capacity of independent variables to estimate the results, through the value of Adjusted R^2.

Finally, based on the analyses performed, the physicochemical characterization of the natural effluent was performed and after treatment with both proposed techniques.

4.1. Adsorption with activated carbon

The adsorption tests with AC were performed in two stages. For the first stage was followed the experimental Box Behnken Design (BBD) consisting of 15 experimental runs with three replicas of the central point. While in the second stage, the Central Composite Design (CCD) was used with two variables, three levels and three central points, totalizing 14 experimental tests.

In BBD was analyzed the concentration of AC (10, 35 and 60 g L^{-1}), agitation time (5, 25 and 45 minutes) and agitation speed (100, 300 and 500 rpm). And for CCD was studied the concentration of AC (20, 50 and 80 g L^{-1}) and agitation time (2, 25 and 45 minutes).

In Table 3 was presented the BBD sequences, as well the coded variables (x_1, x_2 and x_3) and uncoded variables ([AC], Agitation Time and Agitation Speed). Meanwhile, the CCD essays were shown at Table 4 with the coded variables (x_1 and x_2) and uncoded ones ([AC] and Agitation Time).

Table 3: BBD - Adsorption with AC (first stage).

	Coded variable			**Uncoded variable**		
Run	**x_1**	**x_2**	**x_3**	**[AC] (g L^{-1})**	**Agitation Time (min)**	**Agitation Speed (rpm)**
1	0	-1	+1	35	5	500
2	-1	+1	0	10	45	300
3	-1	0	-1	10	25	100
4	0	0	0	35	25	300
5	0	+1	+1	35	45	500
6	0	-1	-1	35	5	100
7	+1	0	+1	60	25	500
8	0	0	0	35	25	300
9	-1	-1	0	10	5	300
10	-1	0	+1	10	25	500
11	0	+1	-1	35	45	100
12	+1	0	-1	60	25	100
13	+1	+1	0	60	45	300
14	+1	-1	0	60	5	300
15	0	0	0	35	25	300

Table 4: CCD - Adsorption with AC (second stage).

	Coded variable		Uncoded variable	
Run	**x_1**	**x_2**	**[AC] (g L^{-1})**	**Agitation Time (min)**
1	0	0	50	25
2	0	0	50	25
3	+1	-1	80	5
4	+1	+1	80	45
5	0	0	50	25
6	0	0	50	25
7	-1	-1	20	5
8	0	0	50	25
9	+1	0	80	25
10	0	-1	50	5
11	-1	+1	20	45
12	0	0	50	25
13	0	+1	50	45
14	-1	0	20	25

The AC chosen was the granular type (Figure 4), it had diameter between 1 and 2 mm and it was previously dried at 105 °C in a drying oven for at least 4 hours and waited to cool inside a desiccator.

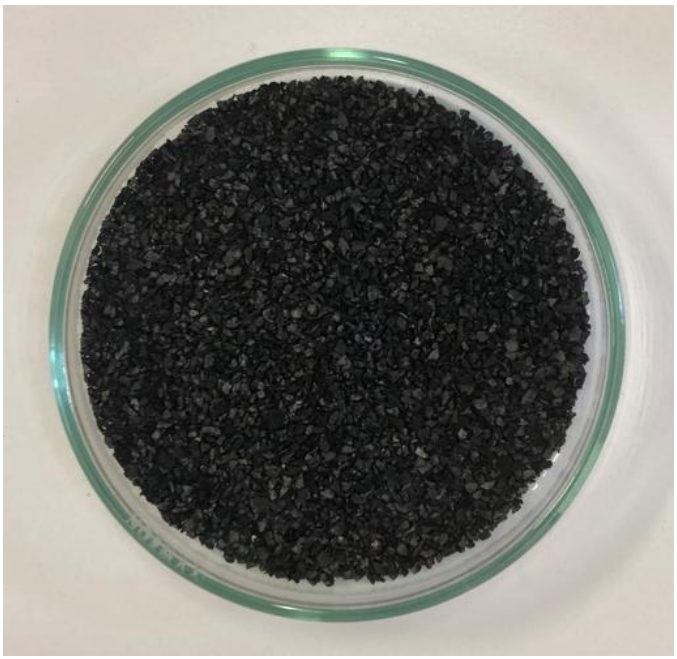

Figure 4: Activated carbon.

The effluent used in the second stage was previously treated with the follow parameters: AC concentration of 35 g L^{-1}, agitation time of 25 minutes and agitation speed of 300 rpm. After both stages of the experiments, a supernatant aliquot was removed and waited to decant for 24 hours.

For both experimental systems were used a 250 mL becker with 100 mL sample and a magnetic stirrer.

4.2. Peroxy-electrocoagulation with aluminum electrodes

For the peroxy-EC experiments were used the BBD (three variables, three level and three central points). In total were 15 experiments runs. The parameters studied were concentration of H_2O_2 (10, 20 and 30 g L^{-1}), pH (2.5, 3.5 and 4.5) and Current Density (CD) (5, 20 and 35 mA cm^{-2}).

In Table 5 was shown the BBD sequence of the peroxy-EC tests, also the coded variables (x_1, x_2 and x_3) and uncoded ones ([H_2O_2], pH and CD).

Table 5: BBD - Peroxy-EC with aluminum electrodes.

	Coded variable			**Uncoded variable**		
Run	**x_1**	**x_2**	**x_3**	**[H_2O_2] (g L^{-1})**	**pH**	**CD (mA cm^{-2})**
1	-1	0	+1	10	3.5	35
2	0	0	0	20	3.5	20
3	-1	0	-1	10	3.5	5
4	+1	0	+1	30	3.5	35
5	+1	-1	0	30	2.5	20
6	-1	-1	0	10	2.5	20
7	0	+1	-1	20	4.5	5
8	0	+1	+1	20	4.5	35
9	0	0	0	20	3.5	20
10	0	-1	-1	20	2.5	5
11	+1	0	-1	30	3.5	5
12	0	-1	+1	20	2.5	35
13	-1	+1	0	10	4.5	20
14	0	0	0	20	3.5	20
15	+1	+1	0	30	4.5	20

The aluminum electrodes picked were 4.1 cm wide and a total height of 14.8 cm. Only 4 cm of height was used for the tests, resulting in a contact area of 16.4 cm^2. After preliminary analysis were selected the distance between the plates of 0.5 cm and agitation time of 30 minutes.

The experimental system (Figure 5) was settled up using a DC power supply (Model 6302D, Topward), an agitation plate (Model RETbasic, IKA Labortechnik) with a magnetic stirrer, two aluminum electrodes in parallel and 1 L beaker with 300 mL of effluent.

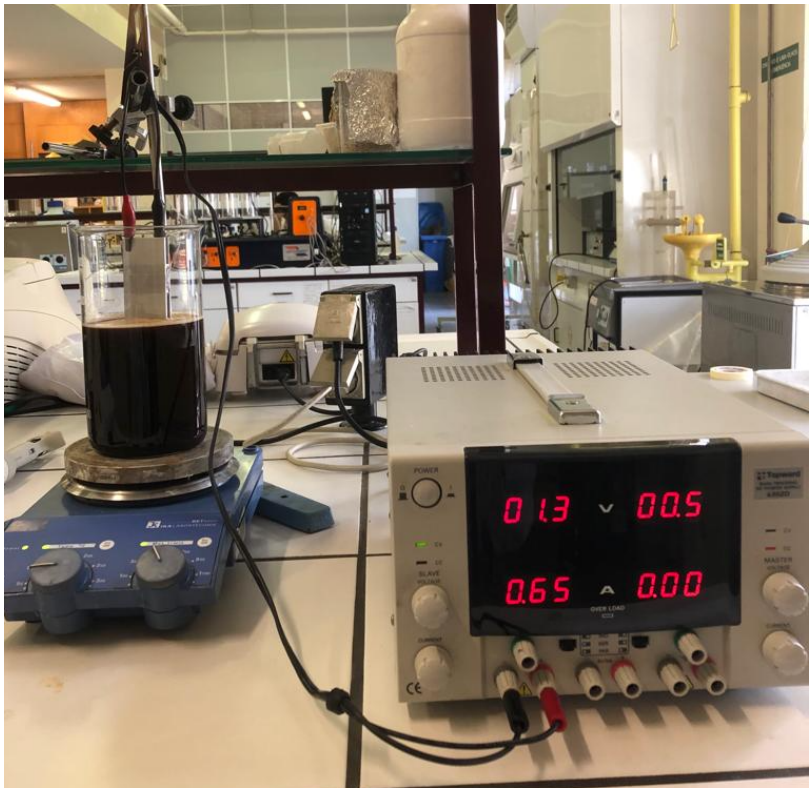

Figure 5: Peroxy-EC system.

After experiments were conducted an aliquot was collected, adjusted to pH greater than 10 to promote the complete reaction stop and it was expected to decant for 24 hours.

4.3. Physicochemical characterization

The characterization of the natural effluent and post-treatments consisted of the following parameters: pH, Turbidity, Conductivity, Total Nitrogen, Total Phosphorus, Phenolic Compounds (PhC), Total Solids (TS), Total Volatile Solids (TVS), Total Fixed Solids (TFS), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), Total Carbon (TC),

Total Organic Carbon (TOC) and Inorganic Carbon (IC). All analyzes were performed in triplicate following proper procedure.

The pH, conductivity and turbidity values were obtained by direct reading using the pHmeter (Model Edge, HANNA), conductivity meter (Model inoLab Level 3, WTW) and turbidimeter (Model TIR 210, VWR), respectively.

The TOC, IC, TC and Total Nitrogen determination were conduct using a TOC analyzer (Model TOC-L, Shimadzu), applying the 680 °C combustion catalytic oxidation method develop by the same company.

For the PhC determination was followed the procedure presented by Mrkva (1979), and the response reading made at the spectrophotometer (Model UV/VIS V-530, JASCO) at the wavelength of 765 nm. The calibration curve was done according to the same methodology, using phenol as standard, in the concentration of 0 to 100 mg/L.

The determination of Total Phosphorus was followed the procedure presented by Valderrama (1981) for the sample preparation and then proceed the analysis based on the section 4500-P E Ascorbic Acid Method (APHA et al., 2017) and the results reading was done at the spectrophotometer (Model UV/VIS V-530, JASCO) at the wavelength of 882 nm. A calibration curve was made according to the same methodology, using monobasic potassium phosphate as standard, at a concentration of 0.1 to 1.8 mg P/L.

For the COD analysis were performed based in section 5220 – D Closed Reflux Calorimeter Method (APHA et al., 2017) and the reading done at the spectrophotometer (Model UV/VIS V-530, JASCO) at the wavelength of 600 nm. The calibration curve was made according to the same methodology, using potassium hydrogenophthatopate as standard, at a concentration of 100 to 900 mgO_2/L.

The BOD_5 determination was made based at the standardized respirometry method using the OxiTop (WTW) equipment. The procedure was carried out in accordance with section 5210 - B BOD for 5 days (APHA et al., 2017) and with the help of the equipment manual.

And for the analysis of TS, TVS, TFS, TSS, TDS were followed the methodology presented in the section 2540 – SOLIDS (APHA et al., 2017).

5. RESULTS AND DISCUSSION

In Table 6, Table 7 and Table 8 were shown the responses for the removal of PhC (%) and COD (%) obtained after AC adsorption (Stage 1 and 2) and peroxy-EC with aluminum electrodes, respectively.

The great removal of PhC and COD obtained by adsorption with AC – Stage 1 were 42.3% and 19.2% (Table 6), respectively, in run 13 ([AC] = 60 g L^{-1}, Agitation Time = 45 minutes and Agitation Speed = 300 rpm).

Table 6: Removal of PhC and COD by adsorption with AC - Stage 1.

Run	[AC] (g L^{-1})	Agitation Time (min)	Agitation Speed (rpm)	PhC (%)	COD (%)
1	35	5	500	18.2	6.9
2	10	45	300	16.8	6.3
3	10	25	100	13.7	5.7
4	35	25	300	25.1	10.5
5	35	45	500	36.7	12.4
6	35	5	100	5.5	5.9
7	60	25	500	39.7	17.2
8	35	25	300	16.0	8.4
9	10	5	300	3.3	1.3
10	10	25	500	8.2	3.5
11	35	45	100	3.0	10.8
12	60	25	100	27.0	16.3
13	60	45	300	42.3	19.2
14	60	5	300	16.6	9.8
15	35	25	300	13.1	9.4

As for Table 7, the run 4 achieved the highest PhC and COD removal with 58.5% and 22.0% for the second stage of adsorption, working under the conditions of [AC] of 80 g L^{-1} and agitation time of 45 minutes.

Table 7: Removal of PhC and COD by adsorption with AC - Stage 2.

Run	[AC] (g L^{-1})	Agitation Time (min)	PhC (%)	COD (%)
1	50	25	38.7	11.2
2	50	25	33.2	9.7
3	80	5	18.8	5.2
4	80	45	58.5	22.0
5	50	25	32.3	13.9
6	50	25	31.1	12.9
7	20	5	10.8	3.8
8	50	25	27.5	13.8
9	80	25	39.4	21.4
10	50	5	18.0	8.0
11	20	45	21.3	8.1
12	50	25	31.9	14.7
13	50	45	36.2	17.8
14	20	25	17.5	8.0

By the peroxy-EC process (Table 8), the run 15 removed the most PhC (87.6%) and the run 5 for COD (29.3%). Run 15 was practiced under pH of 4.5, [H_2O_2] of 30 g L^{-1} and CD of 20 mA cm^{-2}. The only difference between run 5 and run 15 was the initial pH of 2.5 in run 5.

Table 8: Removal of PhC and COD by peroxy-EC with aluminum electrodes.

Run	pH	[H_2O_2] (g L^{-1})	CD (mA cm^{-2})	PhC (%)	COD (%)
1	3.5	10	35	74.4	20.8
2	3.5	20	20	86.5	21.2
3	3.5	10	5	73.9	13.8
4	3.5	30	35	85.0	22.6
5	2.5	30	20	86.3	29.3
6	2.5	10	20	71.1	22.7
7	4.5	20	5	85.2	18.0
8	4.5	20	35	84.6	20.7
9	3.5	20	20	82.5	20.7
10	2.5	20	5	81.4	20.1

Table 8: Removal of PhC and COD by peroxy-EC with aluminum electrodes (continue).

Run	pH	$[H_2O_2]$ (g L^{-1})	CD (mA cm^{-2})	PhC (%)	COD (%)
11	3.5	30	5	86.9	23.0
12	2.5	20	35	78.1	23.1
13	4.5	10	20	76.0	15.4
14	3.5	20	20	82.1	19.9
15	4.5	30	20	87.6	26.1
16	3.5	20	20	83.6	28.3

5.1. Removal of PhC

The RSM (Table 9) determined the AC concentration was the most significant factor (p-value of 4.5e-03), statically, for the adsorption process with AC (Stage 1). It showed that the AC concentration, agitation time and agitation speed presented statistical significance in relation to the response surface, as it exhibited low p-value (less than 5%). But the interaction between the variables and the quadratic term did not presented significance.

Table 9: RSM table for PhC removal by adsorption with AC - Stage 1.

	Estimate	t-value	p-value Pr(>|t|)
Intercept	16.7986	6.1791	4.544e-04
x_1: [AC]	10.4462	4.1078	4.528e-03
x_2: Agitation Time	6.9037	2.7148	0.030
x_3: Agitation Speed	6.6975	2.6337	0.034
x_1:x_2	3.0600	0.8509	0.423
x_1:x_3	4.5825	1.2742	0.243
x_2:x_3	5.2575	1.4619	0.187
x_1^2	4.1502	1.1149	0.302
R^2	**Adjusted R^2**		**p-value**
0.8406	0.6812		0.022

Analyzing the Adjusted R^2 (0.6812) in Table 9, the second order model was reasonably represented by independent variables, and it had statistical significance since

p-value resulted in 0.022. The Equation (7) with the coded variables represented the prediction of the response surface for the adsorption of PhC by AC (Stage 1).

$$PhC_{AC1}(\%) = 16.8 + 10.4x_1 + 6.9x_2 + 6.7x_3 + 3.1x_1x_2 + 4.6x_1x_3 + 5.3x_2x_3 + 4.2x_1^2 \quad (7)$$

The ANOVA table for PhC removal by adsorption with AC (Stage 1) showed that the first order (FO) terms were statistically significant. However, the two-way interaction (TWI) and the pure quadratic (PQ) terms had p-value higher then 5%, therefore insignificant for the PhC removal. As observed the Lack of fit was greater than 0.05, which means the model proposed showed to be statically significant represented by the variables and its interactions.

Table 10: ANOVA table for PhC removal by adsorption with AC - Stage 1.

	Df	**Sum Sq**	**Mean Sq**	**F value**	**p-value Pr(>F)**
FO (x1, x2, x3)	3	1613.14	537.71	10.3935	5.688e-03
TWI (x1, x2, x3)	3	232.02	77.34	1.4949	0.297
PQ (x1)	1	64.30	64.30	1.2429	0.302
Lack of fit	5	282.79	56.56	1.4255	0.461

In Figure 6 were presented the contour and surface graphics for the removal of PhC by adsorption with AC (Stage 1). The response surface plot did not show the optimal point for the PhC removal. And for the PhC adsorption (Figure 6) was necessary great AC concentration, agitation time and agitation speed.

According to Azzam et al. (2004, 2010) research, the higher the amount of AC added into the system, the greater is the contact surface, therefore, more molecules can be adsorbed by the material.

To Priddy & Hanley (2003) and Kuśmierek & Sviatkowski (2015), as the agitation speed increases, the resistance decreases between the bulk liquid and the boundary layer surround the AC particles, due to the turbulence effects and the decrease of the same boundary thickness, allowing the molecules to get into the AC pores.

As mentioned by Kuśmierek & Sviatkowski (2015), the adsorption effect of the material increases with the agitation speed until a certain limit. Which was explained by the fact that at superior agitation speed occurs the release of the loosely attached

pollutants molecules into the AC pores, due to the rapid collision between the pollutants and the adsorbent particles.

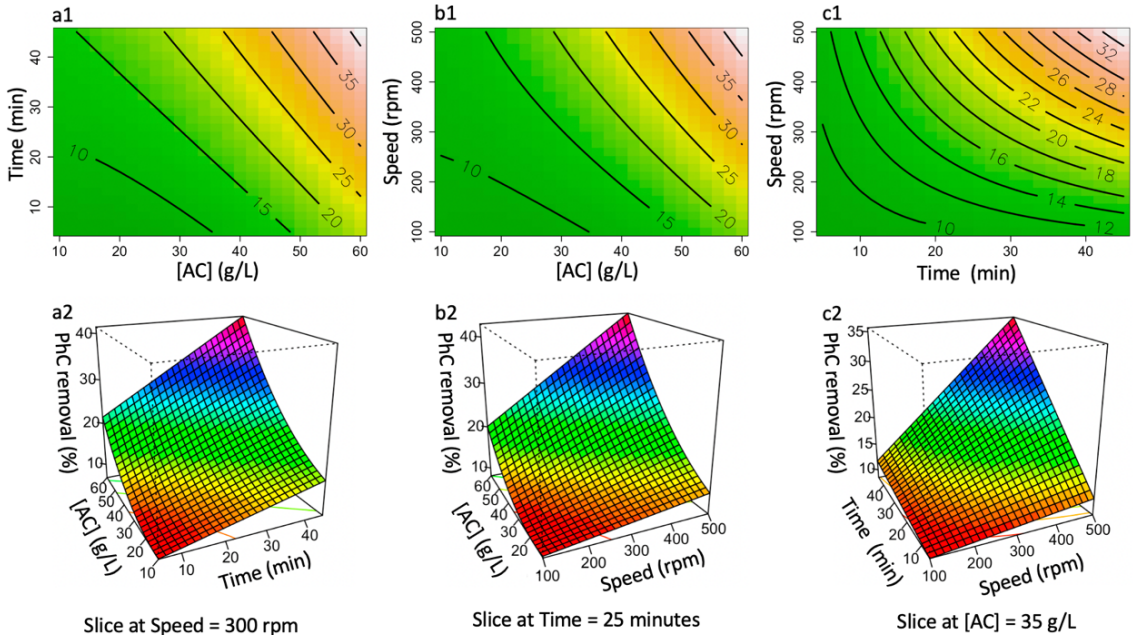

Figure 6: Contour and surface plots for PhC removal by AC adsorption - Stage 1.

The parameter agitation time became a relevant factor when the AC concentrations remains constant (Figure 6 – b), mainly at values higher than 40 g L^{-1}. So, as mentioned by the previously authors, the increase in the contact surface resulted in more empty pores for the molecules to be adsorbed and the increase in the agitation speed allowed these molecules to enter the pores.

In Table 11 was presented the results obtained by the RSM data analysis for the tests of Adsorption with AC - Stage 2, where the AC concentration and agitation time had statistical significance relationship with the response, as it exhibited values lower than 0.05 (4.648e-05 and 4,006e-05, respectively).

Table 11: RSM table for PhC removal by adsorption with AC - Stage 2.

	Estimate	t-value	p-value Pr(>|t|)
Intercept	31.9374	24.1330	9.268e-09
x_1: [AC]	11.1733	7.9308	4.648e-05
x_2: Agitation Time	11.4067	8.0964	4.006e-05
x_1:x_2	7.3200	4.2423	2.829e-03
x_1^2	-1.9844	-0.9679	0.361
x_2^2	-3.3344	-1.6264	0.142
R^2	**Adjusted R^2**		**p-value**
0.9501	0.9189		5.257e-05

The Adjusted R^2 (0.9189) in Table 11 suggested that the proposed quadratic model was well represented by the independent variables and it presented statistical significance (p-value = 5.257e-05 < 0.05). The Equation (8) in terms of coded variables for the surface model for the PhC removal by AC adsorption (Stage 2) was given below:

$$PhC_{AC2}(\%) = \ 31.9 + 11.2x_1 + 11.4x_2 + 7.2x_1x_2 - 2.0x_1^2 - 3.3x_2^2 \qquad (8)$$

As exhibited by the ANOVA results (Table 12), the Lack of fit had a high p-value (0.581), so the parameters studied represented significantly the response achieved for PhC removal by AC adsorption (Stage 2). And the FO and TWI coefficients were statistically significant, with p-values less then 0.05, although the PQ was insignificant.

Table 12: ANOVA table for PhC removal by adsorption with AC - Stage 2.

	Df	Sum Sq	Mean Sq	F value	p-value Pr(>F)
FO (x_1, x_2)	2	1529.73	764.87	64.2246	1.182e-05
TWI (x_1, x_2)	1	214.33	214.33	17.9969	2.829e-03
PQ (x_1, x_2)	2	70.53	35.26	2.9610	0.109
Lack of fit	3	28.80	9.60	0.7221	0.581

Like in the adsorption with AC (Stage 1), the more AC added in the solution and the longer agitation time resulted in greater removal of PhC, as it was also noted for the stage 2 in AC adsorption (Figure 7).

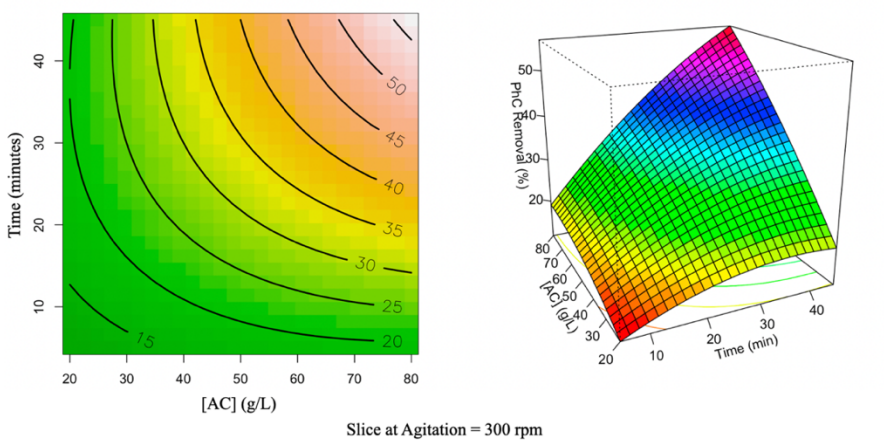

Figure 7: Contour and surface plots for PhC removal by AC adsorption - Stage 2.

In Figure 7 was observed the expected behavior, increasing the AC concentration and the agitation time, correspond a greater removal of PhC, a deeper explanation of the matter was presented previously in this work. And there was a significant difference in removal of PhC with AC concentration greater then 50 g L^{-1} over time, a fact that was also explained beforehand in this research.

The experiments by peroxy-EC (Table 13) showed that only the initial pH and the concentration of H_2O_2, as well the quadratic term of the H_2O_2 concentration, had statistical significance for the results, given the low p-values of 0.011, 3.443e-05 and 0.013, respectively. On the other hand, all the other terms, inclusive the CD factor, showed p-value greater than 5%, so it was not statistically significant.

Table 13: RSM table for PhC removal by peroxy-EC with aluminum electrodes.

	Estimate	**t-value**	**p-value Pr(>|t|)**
Intercept	83.6700	102.7170	5.739e-11
x_1: pH	2.0725	3.5982	0.011
x_2: [H_2O_2]	6.3075	10.9508	3.443e-05
x_3: CD	-0.6700	-1.1632	0.289
x_1:x_2	-0.9200	-1.1294	0.302
x_1:x_3	0.6900	0.8471	0.429
x_2:x_3	-0.5800	-0.7120	0.503
x_1^2	-0.5750	-0.7059	0.507
x_2^2	-2.8250	-3.4681	0.013
x_3^2	-0.7850	-0.9637	0.372
R^2	**Adjusted R^2**		**p-value**
0.9616	0.9040		1.373e-03

Table 13 revealed that the proposed model had 90% of the variability explained by the independent variables and it was considered statistically significant (p-value lower then 5%). By the estimated value of the coded variables showed in Table 13, it was possible to set up the Equation (9) for the second order model.

$$PhC_{PeroxiEC}(\%) = 83.7 + 2.1x_1 + 6.3x_2 - 0.7x_3 - 0.9x_1x_2 + 0.7x_1x_3 - 0.6x_2x_3 - 0.6x_1^2 - 2.8x_2^2 - 0.8x_3^2 \quad (9)$$

The analysis results showed that just the FO term in the peroxy-EC process (Table 14) presented p-value below 5%, being statistically significant. The others terms did not prove to be significant, with p-value higher then 5%. The Lack of fit had p-value around 0.8, proving that the PhC removal was represented significantly by the variables studied.

Table 14: ANOVA table for PhC removal by peroxy-EC with aluminum electrode.

	Df	**Sum Sq**	**Mean Sq**	**F value**	**p-value Pr(>F)**
FO (x_1, x_2, x_3)	3	356.23	118.743	44.7398	1.686e-04
TWI (x_1, x_2, x_3)	3	6.64	2.212	0.8334	0.523
PQ (x_1, x_2, x_3)	3	35.71	11.903	4.4849	0.056
Lack of fit	6	4.11	1.370	0.3479	0.796

The PhC removal response graphics by peroxy-EC with aluminum electrodes (Figure 8) showed that it was almost possible to find the optimum conditions of treatment, using the proposed limits for the parameters studied.

It was observed a greater removal of PhC when increase the concentration of H_2O_2. However, the range of current density studied does not have a substantial difference in the outcome. There was no significant PhC removal for H_2O_2 concentration under 20 g L^{-1} in the studied interval for pH and current density.

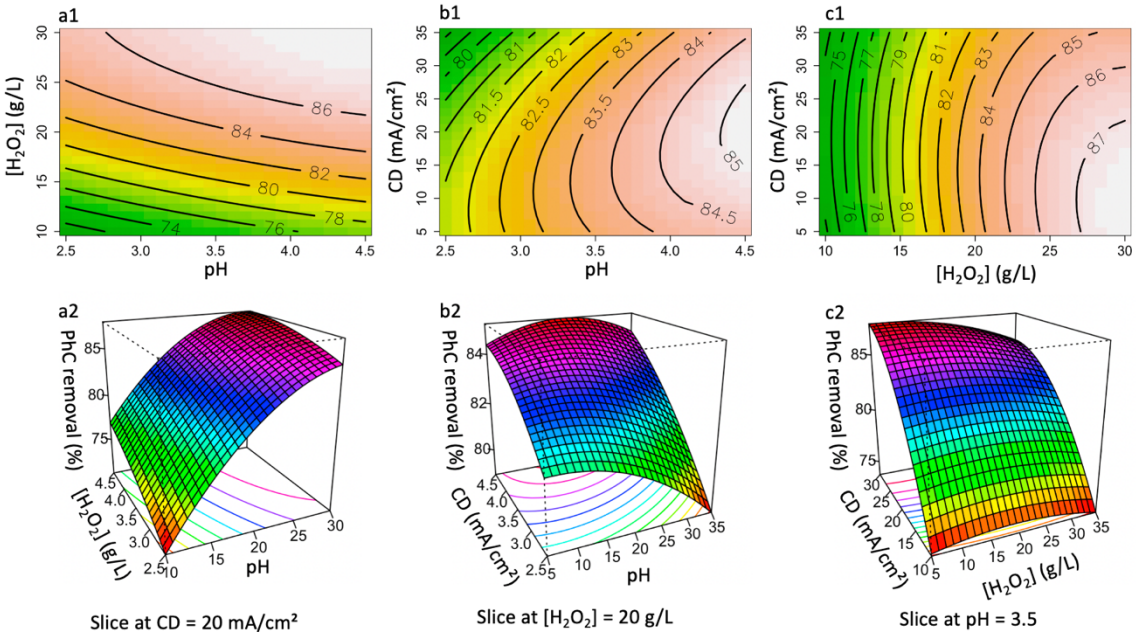

Figure 8: Contour and surface plots for PhC removal by peroxy-EC with aluminum electrodes.

By increasing the CD for values higher than 25 mA cm^{-2}, there was a decrease in the efficiency of PhC removal (Figure 8). For Merma (2008), Vasudevan (2014) and Esfandyari et al. (2015), the low efficiency was due to the difficulty of the passing electric current because of the bubble formation. The excessive bubble production of oxygen and hydrogen cause the union of the small bubbles into bigger ones, avoiding the coagulation effect.

As observed in Figure 8 (graphics "a" and "b"), the initial pH above 3 favor the removal of PhC, however, within the studied limits, it does not present to be a relevant factor in the treatment, as seen by the small variation in the distance between the lines, just 2% and 0.5%, respectively.

5.2. Organic matter removal (COD)

For the first stage of AC adsorption (Table 15), the most significant parameter for COD removal was the AC concentration. As the adsorption surface area increases with the addition of AC to the system, the greater was the COD removed.

The AC concentration and agitation time presented p-value beneath 0.05 (5.916e-06 and 1.945e-04, respectively), meaning it was statically significant for the COD removal. On the other hand, the agitation speed, the interaction between the studied parameters and their quadratic terms resulted in p-value superior to 5%, therefore, it was statistically insignificant.

Table 15: RSM table for COD removal by Adsorption with AC - Stage 1.

	Estimate	t-value	p-value Pr(>|t|)
Intercept	9.4300	15.0061	5.517e-06
x_1: [AC]	5.7062	14.8283	5.916e-06
x_2: Agitation Time	3.1038	8.0654	1.945e-04
x_3: Agitation Speed	0.1600	0.4158	0.692
x_1:x_2	1.1125	2.0442	0.087
x_1:x_3	0.7850	1.4424	0.199
x_1^2	0.7138	1.2601	0.254
x_2^2	-0.9713	-1.7146	0.137
x_3^2	0.5513	0.9732	0.368
R^2	**Adjusted R^2**		**p-value**
0.9802	0.9538		1.481e-04

The adsorption with AC (stage 1) was well represented by the independent variables (Adjusted R^2 value of 0.9538). And it was statistically significant for the COD removal showing p-value (1.481e-04) less than 0.05.

From the estimated values for the coded variables (Table 15) the Equation (10) was formed for COD removal by adsorption with AC (Stage 1).

$$COD_{AC1}(\%) = 9.4 + 5.7x_1 + 3.1x_2 + 0.2x_3 + 1.1x_1x_2 + 0.8x_1x_3 + 0.7x_1^2 - 1.0x_2^2 + 0.6x_3^2 \quad (10)$$

The p-value of the Lack of fit for COD removal by the first stage of AC adsorption (Table 16) was greater than 5%. Hence, the results were well represented by the data used. Also, the FO term shown to be significant for the remove of COD, meanwhile, the TWI and PQ presented insignificant.

Table 16: ANOVA table for COD removal by Adsorption with AC (Stage 1).

	Df	Sum Sq	Mean Sq	F value	p-value Pr(>F)
FO (x_1, x_2, x_3)	3	356.23	118.743	44.7398	1.686e-04
TWI (x_1, x_2, x_3)	3	6.64	2.212	0.8334	0.523
PQ (x_1, x_2, x_3)	3	35.71	11.903	4.4849	0.056
Lack of fit	6	4.11	1.370	0.3479	0.796

By the response surface graphics (Figure 9) was see that the optimal point for the COD adsorption by AC was not found. However, in the same graphics, a similar pattern

to that of the PhC removal analysis by the same technique was observed, the need for a high concentration of AC and longer agitation time (Figure 9 – a). As discussed before, the more adsorbent material, the greater the amount of empty and active pores to adsorb the polluting agents.

The agitation speed did not show significant for the first stage of COD adsorption, with contour lines almost straight and parallels, as observed in Figure 9 - b1 and c1.

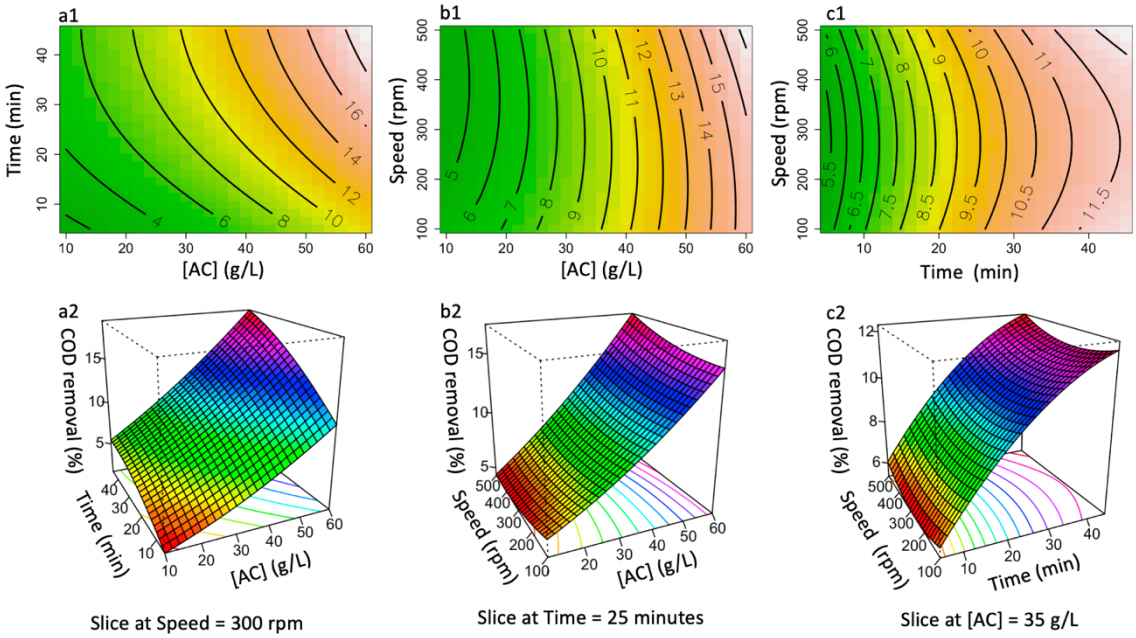

Figure 9: Contour and surface plots for COD removal by AC adsorption - Stage 1.

Unlike the first stage for adsorption with AC, in the second stage, the most statically significant factor was the agitation time. Even with the AC concentration having a p-value little higher than the agitation time, it was still statically significant for the response, with a p-value of 6.683e-04 and 4.120e-04, respectively.

Table 17: RSM Table for COD removal by Adsorption with AC - Stage 2.

	Estimate	**t-value**	**p-value Pr(>|t|)**
Intercept	13.1913	16.1573	5.906e-08
x_1: [AC]	4.7833	5.0739	6.683e-04
x_2: Agitation Time	5.1267	5.4381	4.120e-04
x_1:x_2	3.1225	2.7044	0.024
x_2^2	-2.3613	-1.8934	0.091
R^2	**Adjusted R^2**		**p-value**
0.8803	0.8272		3.518e-03

With an Adjusted R^2 value of 0.8272, at least 82% of the COD removal is explained by the independent variables, which is considered a good result. It presented statistical significance since the p-value is less than 5%. Per Table 17, it was possible to set up Equation (11) to the COD removal by AC adsorption (Stage 2) with the coded variables.

$$COD_{AC2}(\%) = 13.2 + 4.8x_1 + 5.1x_2 + 3.1x_1x_2 - 2.4x_2^2 \quad (11)$$

The ANOVA table for the second stage of COD adsorption (Table 18) indicated that the first-order and the two-way interactions showed statically significant for the COD response, with a p-value lower than 5%. Although, the p-value of the pure quadratic term did not prove to be significant statically.

The p-value of Lack of fit was higher than 5%, consequently, the experimental data fitted significantly to the second-order model.

Table 18: ANOVA table for COD removal by Adsorption with AC - Stage 2.

	Df	**Sum Sq**	**Mean Sq**	**F value**	**p-value Pr(>F)**
FO (x_1, x_2)	2	294.98	147.489	27.6588	1.434e-04
TWI (x_1, x_2)	1	39.00	39.00	7.3137	0.024
PQ (x_2)	1	19.12	19.12	3.5849	0.091
Lack of fit	4	30.33	7.582	2.1460	0.212

Like what happened in the first stage of the AC adsorption process, was also observed the same pattern in the second stage (

Figure 10). With an increase in AC concentration and a longer agitation time resulted in higher COD removal.

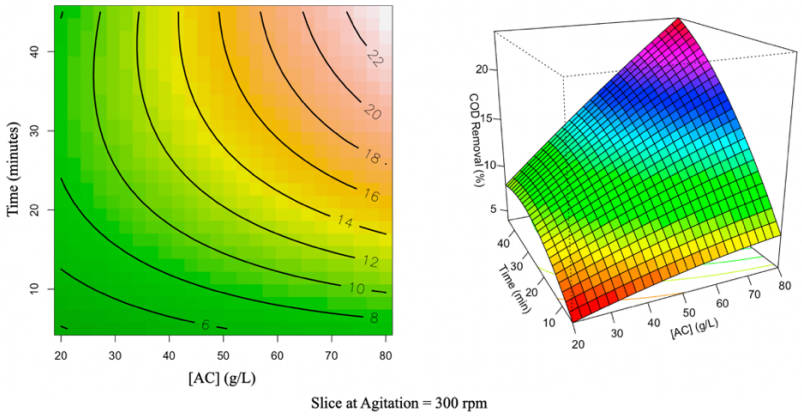

Figure 10: Contour and surface plots for COD removal by AC adsorption - Stage 2.

By the graphics in Figure 10, the highest removal of COD acquired was when performing the test under a concentration of AC greater than 50 g L^{-1} and with an agitation time longer than 30 minutes.

RSM data analysis of the results obtained by Peroxy-EC with aluminum electrodes (Table 19) showed that the hydrogen peroxide concentration was the only factor to be statically significant for COD removal. The H_2O_2 concentration had a p-value less than 0.05. The other factors presented a value above 5%, so statically insignificant.

Table 19: RSM table for COD removal by peroxy-EC with aluminum electrodes.

	Estimate	**t-value**	**p-value Pr(>|t|)**
Intercept	22.9675	25.8998	9.194e-10
x_1: pH	-1.8875	-2.1285	0.062
x_2: [H_2O_2]	3.5413	3.9934	3.142e-03
x_3: CD	1.5238	1.7183	0.120
x_1:x_2	1.0150	0.8093	0.439
x_2:x_3	-1.8425	-1.4092	0.176
x_3^2	-2.6813	-2.1380	0.061
R^2	**Adjusted R^2**		**p-value**
0.7740	0.6233		0.015

More than 60% of the COD removal results (Table 19) were defined by the independent variables studied. Even with a low Adjusted R^2 (0.6233), it was a reasonable outcome. On the other side, the p-value of 0.034 proved that the factors in question were statistically significant for the proposed polynomial equation.

Hence, Equation (11) represents the COD removal (%) within the limits of the parameters investigated in this study. The coded variables' coefficients were shown in Table 19.

$$COD_{PeroxyEC}(\%) = 23.0 - 1.9x_1 + 3.5x_2 + 1.5x_3 + 1.0x_1x_2 - 1.8x_2x_3 - 2.7x_3^2 \quad (11)$$

The result of the ANOVA for the peroxy-EC with aluminum electrodes is in Table 20. The only element statically significant for the COD removal was the FO term. The first-order term showed a p-value of less than 5%. In the meantime, the others, TWI and

PQ, were considered statically insignificant for the response due to the p-value being superior to 0.05.

Nevertheless, the Lack of fit p-value established that the COD response by the peroxy-EC process was well fitted by the variables studied. The Lack of fit had a p-value higher than 5%.

Table 20: ANOVA table for COD removal by peroxy-EC with aluminum electrodes.

	Df	Sum Sq	Mean Sq	F value	p-value Pr(>F)
FO (x_1, x_2, x_3)	3	147.40	49.133	7.8100	7.104e-03
TWI (x_1, x_2)	1	4.12	4.121	0.6550	0.439
TWI (x_2, x_3)	1	13.58	13.579	2.1585	0.176
PQ (x_3)	1	28.76	28.756	4.5710	0.061
Lack of fit	6	11.48	1.913	0.1271	0.983

As seen in the graphics (Figure 11), the optimal point for COD removal by the peroxy-EC process (aluminum electrodes) was almost located. It showed the need to amply the range chosen for the parameters.

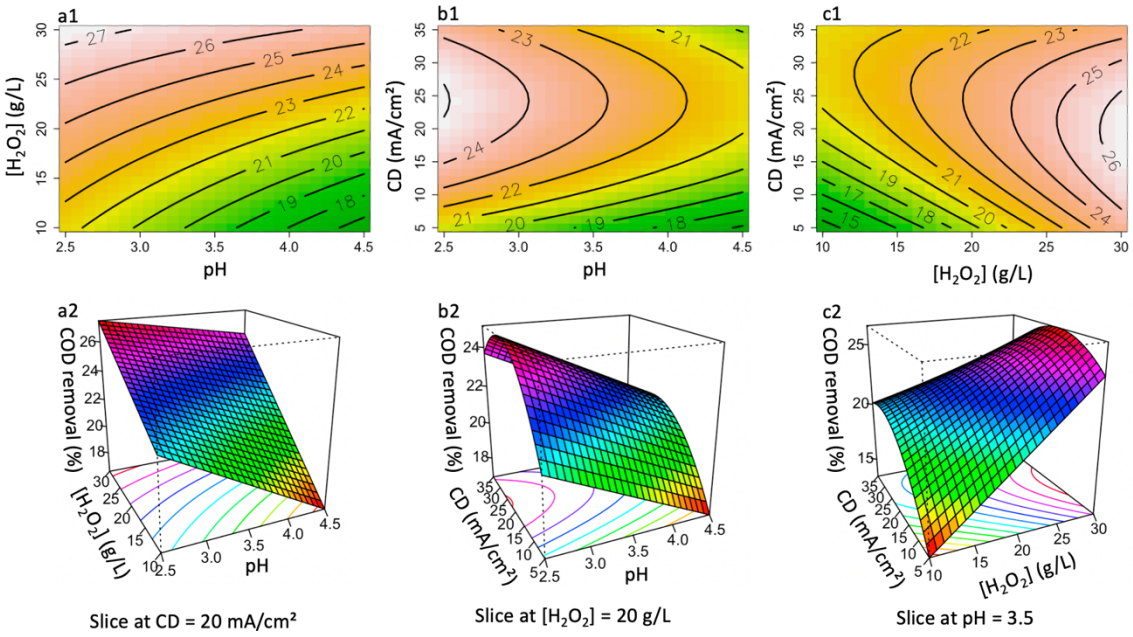

Figure 11: Contour and surface plots for COD removal by peroxy-EC with aluminum electrodes.

At the graphics "b" and "c" in Figure 11, for values above the optimal point, there was a decrease in efficiency when the applied CD was at levels higher than 30 mA cm-².

For Merma (2008), the excessive production of bubbles causes the union of them with each other and not in agglutination with the contaminants, which can lower the efficiency of the process.

As observed in Figure 8, at an H_2O_2 concentration greater than 20 g L^{-1}, there was a higher removal of COD. According to Esfandyari et al. (2015), the increase in H_2O_2 concentrations was related to the production rate of hydroxyl radicals, the main compounds responsible for the nonbiodegradable organic matter reduction present in the effluent.

Values of pH below 3.5 were favorable in the removal of COD by the peroxy-EC process. Esfandyari et al. (2015) mention in their research that the possible justification for the observed fact would be because of the solubility of aluminum hydroxide in the medium, which under acidic conditions is provided by the oxidation reaction of the sacrificial electrode and at the same time occurs the reduction of water with the bubble's formation.

5.3. Physicochemical Characterization

The effluent treatment by AC adsorption and peroxy-EC with aluminum electrodes was performed using the central points of the tests. All methodologies were done at room temperature and local pressure. To verify the replicability of the tests concerning the main pollutant agents (PhC and COD) was analyzed if the value of standard variation was less than 5%, it was accepted as appropriate.

With the analysis performed for the adsorption with AC (Stage 1) was observed that the agitation speed was not a relevant factor for the system in the COD removal. However, the agitation speed equal to or greater than 300 rpm showed promising in the PhC adsorption, so the AC adsorption process (Stage 2) was conducted with an agitation speed of 300 rpm.

At the adsorption with AC (Stage 1) was used AC concentration of 35 g L^{-1}, agitation time of 25 minutes and agitation speed of 300 rpm. After treatment, the standard variation was 0.18% and 1.21% for the PhC and COD removal, respectively. For the second stage of adsorption was added 50 g L^{-1} of AC for 25 minutes of agitation, resulting in a standard variation of 2.4% for PhC and 2.2% for COD.

The peroxy-EC test with aluminum electrode was performed using an H_2O_2 concentration of 20 g L^{-1}, current density of 20 mA cm^{-2} and pH of 3.5, achieving the standard variation of 1.38% and 3% for PhC and COD, respectively.

Table 21 shows the physicochemical characterization of the natural effluent and after treatment by adsorption with AC and peroxy-EC with aluminum electrodes. However, only the pH, PhC and COD were discussed, due to the objectives of the research.

Table 21: Physicochemical characterization of the natural effluent and after treatment.

Parameter	Unit	Natural Effluent	Adsorption with AC	Peroxy-EC
pH	-	4.8	5.0	10.9
Turbidity	NTU	59.6	22.3	3.9
Conductivity	mS cm^{-1}	17.5	19.1	38.7
TOC	g L^{-1}	35.6	26.0	33.1
IC	g L^{-1}	0.6	0.22	1.47
TC	g L^{-1}	36.3	26.2	34.5
Total Nitrogen	mg N L^{-1}	478	483	516
Total Phosphorus	mg P L^{-1}	763	820	366
PhC	g L^{-1}	8.1	5.5	0.8
COD	g O_2 L^{-1}	86.4	61.9	69.4
BOD_5	g O_2 L^{-1}	11.9	14.8	14.1
TS	g L^{-1}	61.7	51.7	82.6
TVS	g L^{-1}	37.0	26.0	35.5
TFS	g L^{-1}	24.8	25.7	47.2
TDS	g L^{-1}	59.6	50.8	83.6
TSS	g L^{-1}	0.73	0.45	0.18
BOD_5/COD		0.14	0.24	0.20

As observed in Table 21, there was a subtle increase in pH when was performed the Adsorption with AC process, 4.8 to 5.0, which Al-Malah et al. (2000) explained to be due to the removal of PhC, an acid component. However, the same justification was not valid for the increase in pH in the peroxy-EC process (10.9) because, at the end of the procedure, the sample alkalinization was performed to ensure the complete stop of the reaction by the hydroxyl radicals.

The treatment by Adsorption with AC was applied directly at the OOIEW filtered using the AC total concentration of 85 g L^{-1} resulting in a reduction of 32.2% in PhC levels (30.7 mg PhC/g AC) and 28.4% for COD (288.9 mg COD/g AC).

In other studies, the application of different adsorbent materials was evaluated, Allaoui et al. (2021) used the AC produced from Crude Olive Stones (COS) for the treatment of OMWW without any alteration and reached 78.3% of PhC removal by adding 1 g L^{-1} of COS, representing an adsorption capacity of 235 mg PhC/g COS. Aliakbarian et al. (2015) utilized an commercial AC (Sigma-Aldrich Chemical Co.) by adding 80 g L^{-1} for the treatment of natural OMWW, with an adsorption capacity of 37.8 mg PhC/g AC commercial, resulting in the removal of 95.4% of PhC.

Azzam et al. (2010) performed the AC adsorption process in the OMWW sedimented and filtrated, applying an AC concentration of 24 g L^{-1}, reaching removal of 79% of PhC and 46% of COD. The AC used by the author presented an adsorption capacity of 14.79 mg PhC/g AC and 1137.5 mg COD/g AC. And Al-Malah et al. (2000) used activated clay as an adsorbent material in the treatment of OMWW after its decanting, centrifugation and filtration, obtaining PhC and COD removal of 81% and 71%, respectively. It presented an adsorption capacity of 45.9 mg PhC/g Activated Clay and 8110 mg COD/g Activated Clay.

When analyzing the adsorption capacity of the AC used in this research, the material presented a low capacity for nonbiodegradable organic matter (COD) removal. While for the removal of PhC, the material showed lower capacity compared to other types of adsorbents produced from agro-industrial products and had a superior capacity than the one found in the work of Azzam et al. (2010).

Therefore, the adsorption capacity of the material depends on properties such as the physical nature of pore structures, functional groups, nature of adsorbent material, molecular mass, size, solution conditions (pH and ionic strength) and other factors previously little studied. As a result of this variety of factors, adsorption materials may have a wide range of adsorption capacities (Aliakbarian et al., 2015; Kuśmierek & Sviatkowski, 2015; Allaoui et al., 2021).

The treatment by peroxy-EC with aluminum electrodes achieved the removal of 90.4% of PhC (7.4 g L^{-1}) and 19.6% of COD (16.9 g L^{-1}). The peroxy-EC process was applied in the OOIEW filtered and no other procedure.

The latest works had different results, where Esfandyari et al. (2015) applied a similar peroxy-EC method without altering the OMWW and achieved a reduction of 94.4% of PhC (2.03 g L^{-1}) and 96% of COD (27.36 g L^{-1}), using current density of 40 mA cm^{-2}, H_2O_2 concentration of 1 g L^{-1} and pH of 4.0. Hanafi et al. (2011) used the EC method with aluminum electrodes. The method managed to decrease 3.44 g L^{-1} of PhC (76.44%) and 17.3 g L^{-1} of COD (60.7%), applying the methodology in the untreated OMWW, with current density of 25 mA cm^{-2}, without pH adjustment or addition of hydrogen peroxide.

And Adhoum & Monser (2004) obtained a reduction of 90.3% of PhC and 71% of COD, meaning a removal of 2.2 g L^{-1} and 53.3 g L^{-1} in the original OMWW of PhC and COD concentrations, respectively. The author applied in the treatment a current density of 75 mA cm^{-2}, without change in natural pH (5.1) and without external addition of hydrogen peroxide either.

From the results obtained and those found by other authors, the hydrogen peroxide addition had a significant effect on the PhC removal. Although the current density influenced the removal of COD by the in-situ production of the coagulating agent, favoring the destabilization of the organic matter.

To Adhoum & Monser (2004) and Erraib & el Ass (2019), raising the current density increases the aluminum concentration in the media and the bubbles production, resulting in greater removal of pollutants. And for Esfandyari et al. (2015), the increase in hydroxyl radical concentration was due to the addition of H2O2 in the media. It is a strong oxidative component and is responsible for the removal of pollutant matter.

6. CONCLUSIONS

The adsorption method with activated carbon proved to be insufficient, inside the limits stablished in this study, for the treatment of this effluent with high concentrations of phenolic compounds and nonbiodegradable organic matter (COD). Probably, the results achieved were due to the fast filling of the available pores and the low efficiency of the adsorption capacity of the material.

The analysis of variance (ANOVA) by the AC adsorption proved that the variable with the most significance in the adsorption process was the concentration of the adsorbent material. Thus, the present study pointed out the need to increase the concentration of activated carbon used or to perform a previous treatment of the effluent with other techniques.

In addition to the adsorption process, peroxy-electrocoagulation was studied with aluminum electrodes, in which the main route of reduction of COD in the process is through coagulation and decanting of organic matter, performed by coagulating components from the electro dissolution of the sacrificial electrode.

Thus, the efficiency of the COD removal by the peroxy-EC was expected to be higher than the one found in the development of this research. However, the technique proved to be efficient and promising in the PhC removal, mainly due to the addition of hydrogen peroxide to the medium, the major precursor of hydroxyl radicals. And, based on the ANOVA table, it was concluded that the H_2O_2 concentration was one of the most significant and important factors when using this method, when performing the tests with reaction time within 30 minutes.

Even with the treatment with the proposed procedures, it was not possible to achieve a BOD_5/COD ratio sufficient for the treated effluent to undergo biological treatment. Pre-treatment of effluent by other techniques is necessary to reduce the concentration of elements considered polluting and harmful to the environment.

So, the treatment by adsorption with activated carbon presented unsatisfactory PhC and COD removal, but promising. The peroxy-EC process with aluminum electrodes showed a satisfactory decrease in PhC concentration and unsatisfactory for reduction of COD. However, for both processes, it is necessary to improve the Design of Experiments to find the optimal point for removal efficiency. Therefore, future works will be important in the search for adequate treatment for this type of effluent.

7. FUTURE WORK

For future work, the following suggestions are recommended:

- Perform the optimization of both processes, expanding the limits of the variables proposed by the study;
- Use other types of materials for the electrodes (iron, graphite, stainless steel, copper) and different arrangement of the electrodes (monopolar, bipolar, horizontal);
- Use other types of activated carbon and do the physicochemical characterization of the material, as well as the proportion of existing pores (micro, meso and macro) and the affinity of the surface in relation to compounds considered polluting agents;
- Study the recovery of commercial interest compounds, such as phenolic compounds;
- To research the effluent treatment by different techniques (physical-chemical methods, advanced oxidative processes, membrane system, biological digestion and others.) and apply the procedures in series;

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