Treatment of Pomace Olive Oil Wastewater by Peroxy-Electrocoagulation with Aluminium Sheets

Ramiro José Espinheira Martins[1,2,3*)], Leticia Harumi Tesuka[4,5)], Thais Theomaris Grabowski[6)]

[1*)] Technology and Management School, Polytechnic Institute of Bragança, 5300-253, Bragança, Portugal; email: rmartins@ipb.pt; https://orcid.org/0000-0003-4327-7782

[2*)] LSRE-LCM Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal; email: rmartins@ipb.pt; https://orcid.org/0000-0003-4327-7782

[3*)] ALICE - Associate Laboratory in Chemical Engineering, FEUP, Porto, Portugal; email: rmartins@ipb.pt; https://orcid.org/0000-0003-4327-7782

[4)] Technology and Management School, Polytechnic Institute of Bragança, 5300-253, Bragança, Portugal; email: leticia.tesuka@gmail.com

[5)] Federal Technological University of Paraná, Campus Medianeira, 85884-000, Paraná, Brazil; email: leticia.tesuka@gmail.com

[6)] Technology and Management School, Polytechnic Institute of Bragança, 5300-253, Bragança, Portugal; email: thaistheomaris@gmail.com; https://orcid.org/0000-0001-6872-4441

http://doi.org/10.29227/IM-2024-01-86

Submission date: *16.3.2023* | Review date: *12.4.2023*

Abstract

The extraction of olive pomace oil is a significant aspect of the edible oil industry in Mediterranean regions where olives are widely cultivated. The resulting wastewater generated from this industry is known to harbor pollutants, including residual solvents, oils, and chemicals from the refining process, that can have adverse effects on the environment and public health. Peroxy-electrocoagulation (PEC) is a method that can be used to treat wastewater from the olive pomace oil extraction industry. The purpose of the work was to reduce the concentration of pollutants in the effluent through the use of PEC with aluminum electrodes as a method of treatment. The Box-Behnken Design was used to study the relationship between hydrogen peroxide dosage (10, 20, and 30 g L^{-1}), electric current density (5, 20 and 35 mA cm^{-2}), and the initial pH (2.5, 3.5, and 4.5), in the PEC process, and the removal of chemical oxygen demand (COD) and total phenolic compounds (TPh). The highest removal was obtained with hydrogen peroxide dosage of 30 g L^{-1}, and 20 mA cm^{-2}, and with 29% of TPh removal at pH 2.5, and with 84% COD removal at pH 4.5. The procedure removed an average of 22% COD and 82% TPh. The concentration of hydrogen peroxide was one of the most significant factors in the process. Pre-treatment with other techniques is necessary to reduce harmful elements in the effluent before undergoing biological treatment.

Keywords: treatment, pomace olive oil, wastewater, peroxy-electrocoagulation, aluminium sheets

Introduction

Olive pomace oil refers to a type of edible oil extracted from the residual pulp, pits, and skins of olives that remains after the initial extraction of olive oil [1]. Although it is considered a lower-grade oil than extra-virgin olive oil, it is widely used in various applications, including cooking, frying, and salad dressings, owing to its mild flavor and relatively high smoke point [1].

Within the edible oil industry, the olive pomace oil extraction sector holds significant significance, particularly in regions where olives are a staple crop, such as the Mediterranean countries [2]. This industry utilizes solvents such as hexane to extract the remaining oil from the waste generated during the production of extra-virgin olive oil [3]. The extracted oil is subsequently refined, blended, and bottled for distribution.

Wastewater generated during olive pomace oil extraction contains a range of pollutants, including residual solvents, oils, fats, and chemicals used in the refining process [1]. If not properly managed, wastewater can have considerable environmental and human health impacts.

The discharge of wastewater from the olive pomace oil extraction industry can lead to water pollution, posing risks to aquatic life and contaminating drinking water supplies, thereby endangering public health. Additionally, the high organic content of wastewater can result in the formation of harmful by-products, such as volatile organic compounds and toxic sludge, if not adequately treated [4].

The treatment of wastewater from the olive pomace oil extraction industry typically involves a combination of physical, chemical, and biological processes to effectively remove pollutants. Physical treatments such as sedimentation and filtration are employed to eliminate suspended solids [4]. Chemical treatments, including oxidation and neutralization, aid in the breakdown of oils and other contaminants [4]. Biological treatments such as aerobic and anaerobic digestion play a vital role in degrading organic matter and removing residual pollutants [4].

A promising method for the treatment of wastewater from the olive pomace oil extraction industry is peroxy-electrocoagulation (PEC) [5]. PEC is an innovative technology that combines electrocoagulation and advanced oxidation processes to efficiently remove pollutants from wastewater [5]. By applying electrical current to wastewater, highly reactive hydroxyl radicals and hydrogen peroxide are generated, effectively oxidizing and breaking down pollutants [5]. Simultaneously, the electrical current promotes the formation of metal hydroxides, which act as coagulants and facilitate the removal of suspended solids and other contaminants [5].

The main aim of this study was to reduce the pollutant concentration in the effluent by employing peroxy-EC with aluminum electrodes as a treatment method.

The objective of this study was to reduce the concentration of pollutants in the effluent by employing peroxy-electrocoagulation with aluminum electrodes as a treatment method.

Methods

In this research, the focus was on utilizing wastewater derived from the olive pomace oil extraction industry, which was obtained from a specific plant situated in Mirandela, Portugal. The industrial facility receives olive pomace sourced from two-stage olive oil extraction units. Subsequently, the wastewater underwent sieving and was stored under ambient conditions within the laboratory setting.

The characterized wastewater exhibited distinct properties, including a pH value of 4.8. Notably, it showed a high concentration of total phenolic compounds (TPh) amounting to 8100 mg L^{-1}, along with significant levels of chemical oxygen demand (COD) at 86400 mg L^{-1}, biochemical oxygen demand (CBO_5) at 11900 mg L^{-1}, and total solids measuring 61.7 g L^{-1}.

Peroxy-Electrocoagulation Process

In this investigation, a comprehensive analysis of the Peroxy-Electrocoagulation (PEC) process was conducted to treat wastewater derived from the olive pomace oil extraction industry. To simulate real-world conditions, a scaled-down 0.6 L reactor was employed for the experiments, utilizing a batch system with magnetic stirring. Within this setup, 0.3 L of the wastewater sample was subjected to treatment.

For the electrochemical reaction, two meticulously prepared rectangular planar aluminum sheets served as the cathode and anode electrodes. Prior to each test, the electrodes underwent a rigorous cleaning process, involving meticulous polishing and washing using a 5% HCl solution followed by thorough rinsing with distilled water. Positioned vertically within the reactor, the electrodes were set at a constant separation distance of 0.5 cm, ensuring consistent exposure of their active surface area of 12 cm^2.

To initiate the process, both electrodes were connected to a power supply (Topward 6302D) to facilitate the application of a direct current. The reaction time was precisely set at 30 minutes, allowing for the optimum interaction between the electrodes and the wastewater constituents.

Throughout the PEC process, a carefully designed series of steps was implemented. This included the adjustment of pH levels, the controlled addition of hydrogen peroxide, the initiation of the reaction time, and the subsequent separation of an aliquot. The separated aliquot was then basified to pH 12 and left undisturbed for a period of 24 hours to facilitate the natural decantation process.

The effectiveness of the PEC process was evaluated by closely monitoring the removal efficiency of key parameters such as Chemical Oxygen Demand (COD) and Total Phenolic compounds (TPh) from the supernatant generated during the oxidative treatment. By scrutinizing these removal rates, the efficacy of the process in reducing pollutant concentrations was accurately assessed.

Data Analysis

The Box-Behnken Design (BBD) is a powerful tool within the realm of Response Surface Methodology (RSM) that allows for the examination of the intricate relationship between a set of independent variables and a dependent variable. By maintaining the independent variables within a predetermined range, the BBD excels in capturing the nonlinear dynamics that exist between these variables and the desired response, ultimately leading to the identification of optimal conditions.

In this particular study, the BBD was leveraged to investigate the interplay between three crucial factors: hydrogen peroxide dosage ([H2O2]) at three levels (10, 20, and 30 g L-1), electric current density (CD) across three different magnitudes (5, 20, and 35 mA cm-2), and the initial pH set at three distinct values (2.5, 3.5, and 4.5). By scrutinizing the influence of these variables within the Peroxy-Electrocoagulation (PEC) process, the focus was on evaluating their impact on the removal of Chemical Oxygen Demand (COD) and Total Phenolic compounds (TPh).

To assess the response of the model in the realm of RSM, Analysis of Variance (ANOVA) was employed. This statistical technique facilitated the examination of the model's fit to a second-order polynomial equation, as well as determining the significance of each variable. By integrating ANOVA within the broader framework of RSM, it became possible to identify the optimal conditions that would yield the highest degree of contaminant removal.

Through the strategic implementation of BBD, ANOVA, and RSM, this study sought to unlock insights into the intricate relationship between the key parameters in the PEC process and the removal efficiency of COD and TPh. By delving into the significance of each variable and their interactions, a comprehensive understanding of the optimal conditions for effective contaminant removal could be derived.

Results and discussions

The experimental trials conducted in the PEC process, along with the corresponding removal efficiencies for Chemical Oxygen Demand (COD) and Total Phenolic compounds (TPh), have been compiled in Table 1. Analysis of the results reveals that the PEC process exhibits greater efficacy in removing TPh compared to COD. The highest removal was obtained with [H_2O_2] 30 g L^{-1}, and 20 mA cm^{-2}, and with 29% of COD removal at pH 2.5 (point 5), and with 88% TPh removal at pH 4.5 (trial 15).

Tab. 1. Removal of TPh and COD achieved through the use of PEC process.

Trials	pH	$[H_2O_2]$ g L^{-1}	CD (mA cm^{-2})	COD Removal (%)	TPh Removal (%)
1	3.5	10	35	21	74
2	3.5	20	20	21	86
3	3.5	10	5	14	74
4	3.5	30	35	23	85
5	2.5	30	20	29	86
6	2.5	10	20	23	71
7	4.5	20	5	18	85
8	4.5	20	35	21	85
9	3.5	20	20	21	82
10	2.5	20	5	20	81
11	3.5	30	5	23	87
12	2.5	20	35	23	78
13	4.5	10	20	15	76
14	3.5	20	20	20	82
15	4.5	30	20	26	88
16	3.5	20	20	28	84

Tables 2, 3 shows the ANOVA obtained regarding the removal of contaminants. Only the terms where $p < 0.05$ are statically significant, thus for COD removal only $[H_2O_2]$ is statistically significant (Table 2) and for TPh removal the $[H_2O_2]$ and the quadratic term of $[H_2O_2]$ are statistically significant (Table 3).

Tab. 2. ANOVA of the RSM for COD removal by PEC process from olive pomace oil extraction industry wastewater.

COD Removal ANOVA data			
	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

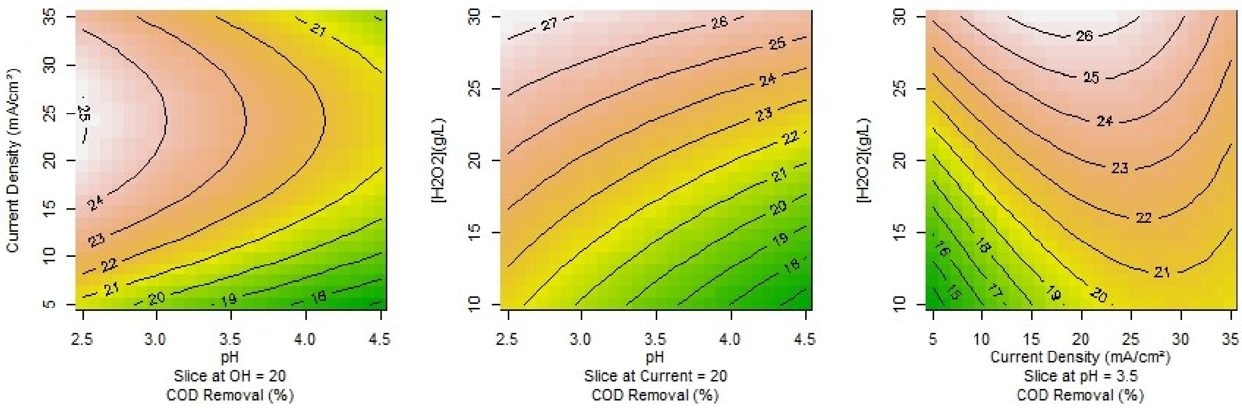
Tab. 3. ANOVA of the RSM for TPh removal by PEC process from olive pomace oil extraction industry wastewater.

TPh Removal ANOVA data			
	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 2 shows that over 60% of the variability in COD removal can be explained by the studied independent variables, despite a low Adjusted R^2 (0.6233). The p-value of 0.034 confirms the statistical significance of the factors in the polynomial equation. For TPh removal (Table 3), the proposed model explains 90% of the variability, with a p-value indicating statistical significance (p-value lower then 5%).

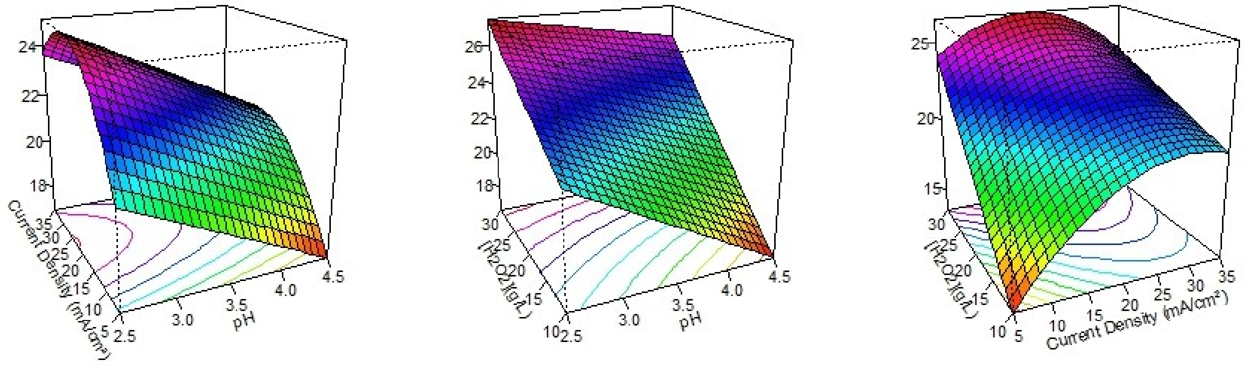
In simpler terms, the Figures 1, 2 demonstrates that the optimal conditions for removing COD using the PEC process with aluminum electrodes were almost found. However, the range of parameters needs to be expanded. When the current density was higher than 30 mA cm^{-2}, there was a decrease in efficiency (Figure 1. a, c, Figure 2. a, c) due to excessive bubble production. This decrease was due to the excessive production of bubbles, which caused them to merge together instead of adhering to the contaminants, reducing the efficiency of the process [6]. Increasing the [H_2O_2] above 20 g L^{-1} led to higher removal of COD. Lower pH values below 3.5 were also beneficial for removing COD. This could be due to the solubility of aluminum hydroxide, which increases under acidic conditions, contributing to the efficiency of the PEC process [7].

The study of TPh removal using PEC with aluminum electrodes showed that the optimal conditions for treatment can be found by adjusting certain parameters, such as the [H_2O_2] (Figure 3, 4). Increasing the [H_2O_2] leads to a higher removal of TPh (Figure 3. b, c, Figure 4. b, c). The range of CD studied did not have a significant effect on the outcome (Figure 3. a, c, Figure 4. a, c). However, using CD values above 25 mA cm^{-2} resulted in a decrease in the efficiency of TPh removal (Figure 3, 4). The low efficiency was due to the difficulty of the passing electric current because of the bubble formation [6, 7]. The excessive bubble production of oxygen and hydrogen cause the union of the small bubbles into bigger ones, avoiding the coagulation effect [6, 7]. The initial pH above 3 was found to slightly favor the removal of TPh (Figure 3. a, b, Figure 4. a, b), but it was not a significant factor in the treatment.



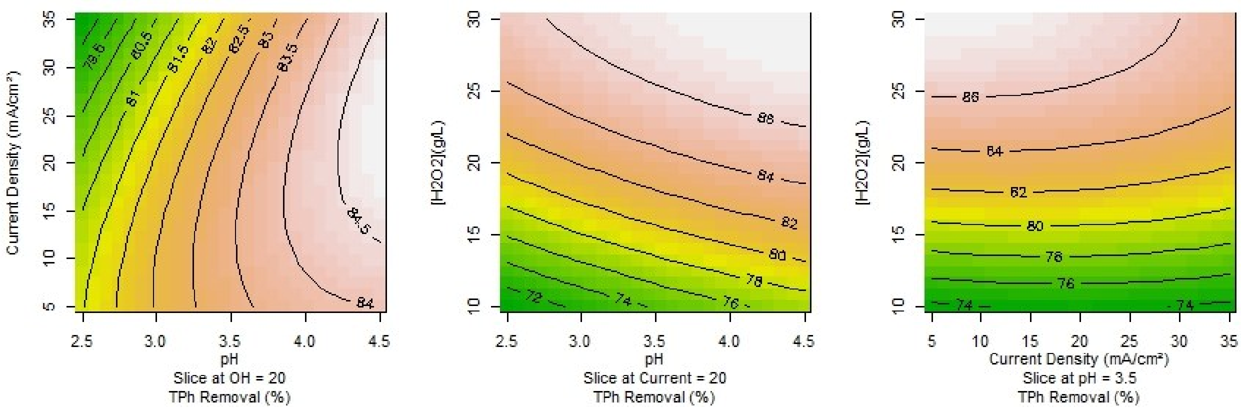
a b c

Fig. 1. Contour plots of COD removal by PEC process from olive pomace oil extraction industry wastewater.



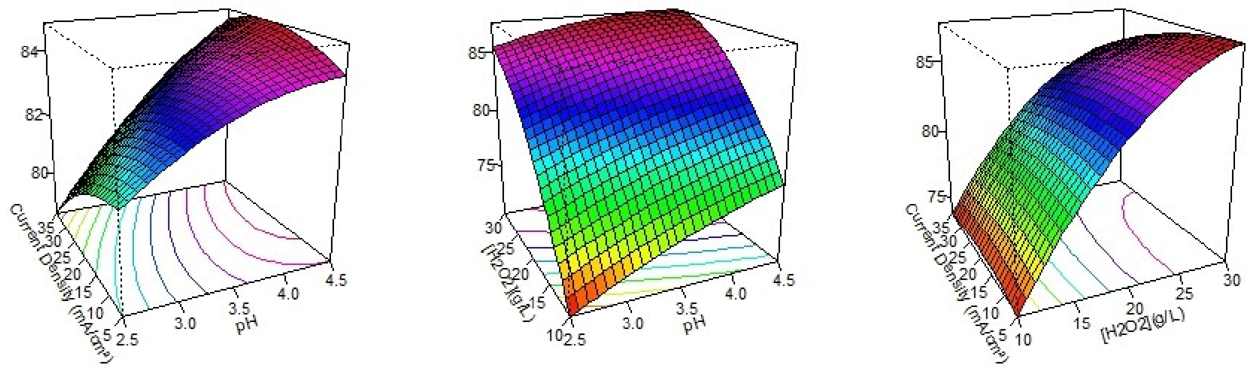
a b c

Fig. 2. Surface plots of COD removal by PEC process from olive pomace oil extraction industry wastewater.



a b c

Fig. 3. Contour plots of TPh removal by PEC process from olive pomace oil extraction industry wastewater.



a b c

Fig. 4. Surface plots of TPh removal by PEC process from olive pomace oil extraction industry wastewater.

The central point configuration emerged as the optimal operating setup for the PEC process. This configuration exhibited notable TPh removal efficiency while maintaining moderate COD removal rates. The effluent treated by the PEC process, along with the supernatant generated under the central point conditions (pH 3.5, [H_2O_2] 20 g L^{-1}, 20 mA cm^{-2}), were subjected to comprehensive characterization (Table 4). To ensure the reliability and reproducibility of the experimental results, the standard deviation was assessed, and values below 5% were considered acceptable. Encouragingly, the central point configuration demonstrated a remarkably low standard deviation of 1.38% and 3% for TPh and COD, respectively, indicating its consistency and robust performance in achieving consistent removal efficacy.

Tab. 4. Characterization of olive pomace oil extraction industry wastewater before and after de PEC process with pH 3.5, [H_2O_2] 20 g L^{-1}, 20 mA cm^{-2}.

Parameter	Unit	Wastewater	PEC
pH	-	4.8	
Conductivity	mS cm^{-1}	17.5	38.7
Total Organic Carbon	mg L^{-1}	35600	33100
Total Carbon	mg L^{-1}	36300	34500
Total Nitrogen	mg N L^{-1}	478	516
Total Phosphorus	mg P L^{-1}	763	366
TPh	mg L^{-1}	8100	800
COD	mg O_2 L^{-1}	86400	69400
BOD_5	mg O_2 L^{-1}	11900	14100
BOD_5/COD		0.14	0.20

From table 4 we can conclude that the PEC process was efficient in removing total phosphorus, TPh and COD. Even removing 20% COD a proportional removal was not observed for total organic carbon. The PEC process minimally improved the biodegradability of the effluent (BOD_5/COD).

Conclusion

The addition of hydrogen peroxide proved to be a crucial factor in the efficient and promising removal of TPh using the PEC technique. The rapid reaction time of 30 minutes further enhanced the effectiveness of the process. However, it should be noted that the achieved BOD5/COD ratio was insufficient for subsequent biological treatment of the effluent. Therefore, pre-treatment using additional techniques is necessary to reduce the presence of harmful components in the effluent prior to subjecting it to biological treatment. This highlights the importance of implementing a comprehensive treatment approach for optimal wastewater remediation.

Acknowledgments

This work was financially supported by: i) Project NORTE-01-0247-FEDER-072124, BagaÇo+Valor - Tecnologia Limpa para a Valorização dos Subprodutos do Bagaço na Indústria Extratora de Azeite, funded by the European Regional Development Fund (ERDF) and ii) LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC).

References

1. P. S. Moral and M. V. R. Méndez, “Production of pomace olive oil,” Grasas y Aceites, vol. 57, no. 1, pp. 47–55, 2006.
2. GPP. (Gabinete de Planejeamento, Políticas e Administração Geral), “SIAZ - Sistema de Informação do Azeite e Azeitona de Mesa,” 2020. gpp.pt.
3. L. Skaltsounis, A. Argyropoulou, N. Aligiannis, and N. Xynos, Recovery of High Added Value Compounds from Olive Tree Products and Olive Processing Byproducts. In Olive and Olive Oil Bioactive Constituents (pp. 333–356) (2015). Elsevier Inc. https://doi.org/10.1016/B978-1-63067-041-2.50017-3.
4. Y. Esfandyari et al., “Degradation and biodegradability improvement of the olive mill wastewater by peroxi-electrocoagulation/electrooxidation-electroflotation process with bipolar aluminum electrodes,” Environ. Sci. Pollut. Res., vol. 22, no. 8, pp. 6288–6297, 2015, doi: 10.1007/s11356-014-3832-5.
5. S. Garcia-Segura, G. Eiband, J. de Melo, and A. Martínez-Huitle, Electrocoagulation and advanced electrocoagulation processes: A general review about the fundamentals, emerging applications and its association with other technologies. In Journal of Electroanalytical Chemistry (Vol. 801, pp. 267–299) (2017). Elsevier B.V. https://doi.org/10.1016/j.jelechem.2017.07.047.
6. G. Merma, Eletrocoagulação aplicada a meios aquosos contendo óleo [Pontifícia Universidade Católica do Rio de Janeiro] (2008). https://doi.org/https://doi.org/10.17771/PUCRio.acad.12209.
7. Y. Esfandyari, et al., Degradation and biodegradability improvement of the olive mill wastewater by peroxi-electrocoagulation/electrooxidation electroflotation process with bipolar aluminum electrodes. Environmental Science and Pollution Research, 22(8), 6288–6297 (2015). https://doi.org/10.1007/s11356-014- 3832-5.