CARBON CATALYSTS DERIVED FROM COMPOST FOR WET PEROXIDE OXIDATION OF LANDFILL LEACHATES

Gabriel de Freitas Batista[a,*], **Fernanda Fontana Roman**[a,b,c], **Jose Luis Diaz de Tuesta**[a,d], **Adrián M.T. Silva**[b,c], **Helder Teixeira Gomes**[a]

[a] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-252 Bragança, Portugal*

[b] *Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[c] *ALiCE—Associate Laboratory in Chemical Engineering, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[d] *Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Spain*
**E-mail: gabriel.batista@ipb.pt*

Resumo

O constante crescimento populacional levou a um grande aumento na produção de resíduos sólidos, principalmente resíduos sólidos urbanos (RSU). Uma estratégia ecologicamente correta para gerenciar os RSU é o tratamento mecânico e biológico (TMB). Nas unidades TMB, a fração orgânica dos RSU é tratada, gerando biogás e subprodutos (lixiviado e composto). O composto é ultilizado principalmente como fertilizante agrícola. No entanto, a quantidade de composto produzida é superior à sua procura como fertilizante, criando um excesso de produto. Este trabalho visa a valorização do composto através de carbonização hidrotérmica (CHT), e pirólise, produzindo os catalisadores HC230 e PC800, respectivamente, e sua aplicação na oxidação catalítica com peróxido de hidrogénio (CWPO) do lixiviado gerado na unidade TMB. Os catalisadores foram caracterizados por análise elementar e teor de cinzas. Os ensaios de CWPO do lixiviado (COT = 27 g L^{-1}, DQO = 60 g L^{-1} e DBO_5 = 23 g L^{-1}) foram conduzidos nas seguintes condições operacionais: $C_{Catalisador}$ = 1,8 g L^{-1}; T = 80 ºC; $C_{H_2O_2}$ = 85,7 g L^{-1} e pH de 3,0 a 7,3. A pH = 6, o catalisador HC230 permitiu alcançar uma redução de DQO de 41%, aumentar a razão DBO_5/DQO para 0,42, moldando o lixiviado como adequado para tratamento biológico posterior.

Palavras chave: resíduos sólidos urbanos, valorização, catalisadores à base de carbono, águas lixiviantes, tratamento de águas residuais.

Abstract

The population growth leads to a large increase in solid waste production, notably municipal solid waste (MSW). In this context, the mechanical and biological treatment (MBT) arouses as an environmentally friendly strategy to manage MSW. In MBT plants, the organic fraction of MSW is treated, generating biogas and, as by-products, leachate and compost. The compost is mainly used as an agriculture fertilizer. However, the amount of compost produced is higher than its demand, resulting in excess and accumulation. This work deals with the valorization of compost through hydrothermal carbonization (HTC) and pyrolysis, producing respectively the catalysts HC230 and PC800, and their application in the catalytic wet peroxide oxidation (CWPO) of the leachate waters generated in the MBT plant. The catalysts were characterized by elemental analysis and ash content. The CWPO runs of the leachate waters (TOC = 27 g L^{-1}, COD = 60 g L^{-1} and BOD_5 = 23 g L^{-1}) were conducted under the following operating conditions: $C_{Catalyst}$ = 1.8 g L^{-1}; T = 80 ºC; $C_{H_2O_2}$ = 85.7 g L^{-1} and pH from 3.0 to 7.3. At pH = 6 the HC230 achieved a COD abatement of 41 %, enhancing the BOD_5/COD ratio to 0.42, shaping the leachate as suitable for further biological treatment.

Keywords: municipal solid waste, valorization, carbon-based catalysts, leachate, wastewater treatment.

1. Introduction

Since humanity started living in communities and towns, the generation of solid waste has largely increased. According to a report published by the Eurostat in 2020, the amount of MSW used for composting in the EU has increased from 467 kg per capita in 1995 to 505 kg per capita in 2020, and its generation is expected to reach around 3.4 billion tonnes by 2050 [1].

Authorities are concerned with this production, since MSW has a complex composition, comprising plastics, metals and complex electronics wastes, among others. If MSW is not properly managed, it can cause irreversible damage to the environment [1,2].

The main approaches for MSW management are recycling, landfilling, composting, incineration and mechanical and biological treatment (MBT). Among those strategies, landfilling is the most harmful approach, as no pre-treatment is usually performed and the waste is accumulated, causing health-related risks, occupying a lot of areas, and discarding profitable resources [2]. Therefore, different actions have been taken in order to develop methods to deal with MSW. This reflects in a decrease of 60% in the use of landfills, between 1995 and 2017, and in an increase in the recycled and composted fractions, 195% and 196%, respectively, in the same time frame [1,3]. Among those sustainable strategies to manage MSW, MBT is being used in several countries. In MBT plants, MSW is collected, transported and mechanically or manually sorted into discarded, recyclable and organic waste streams. The organic fraction goes to the biological treatment stage, generating biogas, which is a sustainable source to supply energy. The sub-products are a wastewater (leachate) and a solid fraction (compost) [4,5]. Compost is mainly used as an agriculture fertilizer, but the amount produced is higher than its demand, resulting in an excess that is currently accumulated in landfills. Thus, researchers are trying to find new technical solutions for its valorization or application [2].

Waste management companies also face the generation of leachate, a wastewater generated from landfills or from the MBT plants. The leachate has a complex inorganic and organic composition, which results in a high content of total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD_5) [6]. The general characteristics of leachate waters are given in Table 1.

Table 1: General characteristics of leachate waters as a function of age [6].

Leachate age	COD (mg/L)	BOD_5 (mg/L)	BOD_5/ COD
0 to 5 years	10000 - 50000	2000 - 10000	> 0.3
5 to 10 years	1000 - 10000	100 - 2000	0.1 – 0.3
> 10 years	100 - 5000	2 - 150	< 0.1

Landfill leachates have a very complex matrix, influenced by a lot of geographical and socioeconomic parameters. They contain several ions, such as chlorides, carbonates and sulphates. With such low quality, the traditional water treatment processes are not able to deal appropriately with leachates, creating a need for a more robust and efficient alternative chemical treatment. In this sense, advanced oxidation processes (AOP) have shown interesting results towards the treatment of wastewaters from many sources, bearing different organic pollutant loads [7].

AOPs are demonstrating promising results for the degradation of resistant compounds or their transformation into biodegradable forms for further biodegradable treatments [8]. However, treating leachates with AOPs also present some challenges, since some substances can react with the catalyst, creating undesirable complexes that are not able to generate the hydroxyl radicals and lowering the efficiency of the process [10].

Among the heterogeneous-catalyst-promoted AOPs, a very promising option is catalytic wet peroxide oxidation (CWPO), due to its low cost, easy experimental apparatus and easy catalyst recovery. CWPO consists in the use of a catalyst present in the system that reacts with hydrogen peroxide to generate hydroxyl ($HO^\bullet$) and hydroperoxyl ($HOO^\bullet$) radicals, which are highly oxidizing species able to degrade a variety of organic pollutants present in wastewaters [8,11].

According to Márquez et al. (2018), since CWPO can operate with no lamps, and in some cases at atmospheric pressure and room temperature, it is considered a low-cost technology to deal with leachate and industrial wastewaters [8].

One of the main benefits of CWPO reactions is the low damage to the environment. In this perspective, the use of complex metallic catalysts, which have expensive reagents, complex synthesis methods and possible leaching to nature, is falling, and the use of cheap and renewable catalysts is desired. In this regard, carbon-based materials (such as biochars and hydrochars) are valuable alternatives that can be produced from renewable sources, like biomass or C-containing wastes (e.g. the organic fraction of MSW), and usually have a simple and cheap synthesis process, fulfilling the desired requirements of green chemistry [2,12].

According to Qambrani et al. (2017), pyrochar is a carbon-rich solid product of biomass pyrolysis that contains numerous pores. Pyrochars can be produced by slow pyrolysis from different sources of organic matter and/or as by-product of fast pyrolysis, gasification or combustion processes [13]. Hydrochars are carbon-based materials produced by hydrothermal carbonization (HTC) of a carbon-containing precursor, in presence of water at temperatures higher than 100 ºC and at autogenous pressure [14,15].

In this context, the application of compost as feedstock to produce biochars and hydrochars is assessed as a viable way to valorize the compost through its transformation into catalysts that fulfill the economical and environmental standards of CWPO to treat leachate waters.

2. Experimental

2.1 Reagents

The compost and leachate used in this work were collected from a MTB plant for MSW located in Northern Portugal. 98% Sulfuric acid (H_2SO_4) was supplied from Labkem. 30% w/v Hydrogen peroxide (H_2O_2) and 98.73% Sodium hydroxide (NaOH) were supplied from Fisher Chemical. 99.99% Titanium (IV) oxysulfate ($TiOSO_4$) was supplied from Aldrich. Silver Nitrate for analysis, ACS, ISO ($AgNO_3$); 99% Mercury (II) Sulphate PA-ACS ($HgSO_4$), and 99.5% Potassium Dichromate PA-ACS-ISO ($K_2Cr_2O_7$) were supplied from Panreac. Folin-Ciocalteu´s phenol reagent was supplied from Merck. Distilled water was used throughout the research.

2.2 Catalysts preparation

The compost was first washed with water (100 g L^{-1}) under strong stirring to homogenize the precursor and to remove suspended solids. The suspension was later filtered and the homogenized solid dried overnight at 60 ºC. Afterward, the matured compost was sieved to obtain particle sizes from 53 to 106 µm.

The pyrolyzed catalyst, PC800, was obtained following the procedure described elsewhere [16]. Briefly, PC800 was produced by thermal treatment using 5 g of homogenized compost, under a N_2 flow (100 Ncm^3 min^{-1}) with 1 h holding time at 120, 400 and 600 ºC for 1 h and at 800 ºC for 4 h (heating ramp of 120 ºC min^{-1}).

The other catalyst (HC230) was prepared by hydrothermal treatment of the matured compost, as described elsewhere [17]. The preparation was carried out in a 125 mL removable Teflon vessel inserted in a stainless steel body (Model 249M 4744-49, Parr Instrument co., USA).

Briefly, 3 g of matured compost was measured and mixed with 30 mL of distilled water. Then the reaction vessel was inserted into an oven set at 230 ºC. After 2 h, the reaction vessel was removed and left to cool down overnight at room temperature. The solid was vacuum filtrated with a membrane filter (pore size: 0.45 µm), washed with abundant distilled water, and dried in an oven overnight at 100 ºC, leading to catalyst HC230.

2.2 Characterization techniques

Ash content was determined by calcination and mass weighting. Firstly, an empty crucible was weighed, then 0.2 g of carbon-based material was added to the crucibles, and the crucible with the sample was placed in the muffle furnace at 450 ºC for 4 h. After this period, it was cooled down until room temperature inside a desiccator, and the mass was measured. The crucible was placed again in the muffle furnace at 450 ºC for 1 h, then cooled down until room temperature, and the mass was measured. This process was repeated until constant mass.

Elemental composition (C, H, N, and S) of the catalysts were quantified through a Carlo Erba EA 1108 Elemental Analyzer.

2.3 Analytical methods

H_2O_2 concentration was determined by a UV-VIS colorimetric method using $TiOSO_4$, at a wavelength of 405 nm, adapted from [11]. TOC was measured using a Shimadzu TOC-L CSN analyzer. COD was determined by a UV-VIS colorimetric method using $K_2Cr_2O_7$, at a wavelength of 440 nm, adapted from [11]. BOD_5 was determined by the standardized respirometric OxiTop method (WTW, Weilheim, Germany). Conductivity (WTW InoLab Cond Level 1), pH (Bante Instruments – PHS-3BW Bench TOP pH/mV/ºC Meter) and turbidity (WTW Turb 550) were measured at room temperature. Phenolic compounds were determined by the Folin-Ciocalteu method using a UV-VIS spectrophotometer at a wavelength of 765 nm, adapted from [18]. Aromaticity was determined by a UV-VIS spectrophotometric methodology at 254 nm, adapted from [11]. The leachate and CWPO samples were characterized using those techniques.

2.4 CWPO of the leachate

The CWPO runs were carried out during 24 h in a 500 mL glass round-bottom flask continuously stirred and equipped with a condenser. First, the leachate with the adjusted pH (3.0, 6.0 or natural leachate pH = 7.3) was added to the flask. Then it was submerged in a heat oil bath with temperature control. Upon reaching the desired temperature of 80 ºC, all hydrogen peroxide was added to reach the concentration of 85.71 g L^{-1}. After the complete mixing of the reactants, the first sample was taken, and the catalyst was added ($C_{Catalyst}$ = 1.8 or 3.6 g L^{-1}), considering this time t = 0. The samples for analysis were collected at 0, 15, 30, 60, 120, 240, 360, 480 and 1440 minutes of reaction. Blank tests with no catalyst were also performed.

3. Results and Discussion

3.1 Characterization of catalysts

Table 2 summarizes the values of carbon, hydrogen, sulfur and ashes for the prepared carbon-based materials (nitrogen content was found to be less than 1.7% for all samples and with no significant changes among the samples).

Table 2: Elemental composition and ash content of the materials

Sample	C/H	C (%)	H (%)	S (%)	Ash (%)	N.I.* (%)
Compost	9.3	21.3	2.3	0.6	55.5	18.6
PC800	44.0	17.6	0.4	0.5	81.5	0.0
HC230	11.0	19.3	1.8	1.2	32.6	45.0

*N.I. = Non identified, obtained by the difference: 100%-C(%)-H(%)-N(%)-S(%)-Ash(%)

The pyrolyzed material, PC800, showed the highest value of C/H ratio, 44 %, as expected since the thermal treatment leads to the release of many volatile compounds and water. This fact is also supported by the non-identified content of 0.0 %. As observed, the C/H ratio values for all catalysts are higher than that of the compost (C/H > 9.3), so carbonization was successfully accomplished.

Regarding the ashes content, it can be observed that HTC leads to a decrease up to 20%, likely because the HTC treatment can cause the leaching of some inorganic compounds from the raw material to the aqueous solution.

Non-identified (N.I.) species (different from C, H, N, S and ashes) are typically associated with the element oxygen. As observed, in pyrolyzed samples N.I. decreased from the raw material (18.6) to zero, whereas N.I. reach values of 45.0% for HC230, likely due to hydroxylation and formation of surface oxygen groups on the materials.

3.2. CWPO of landfill leachate

The characterization of the leachate is shown in Table 3. By comparison with Table 1, the leachate used in this work is characterized as young leachate, with the higher values of COD, TOC and BOD_5 among the leachate types. Besides those parameters, the leachate also has high concentrations of chloride ions.

Table 3: Physico-chemical characteristics of the raw leachate used in this work

PARAMETER	Units	Value	S.D.*
COD	mg L^{-1}	59,959	3903
BOD_5	mg L^{-1}	23,250	1061
TOC	mg L^{-1}	26,665	435
pH at 25 ºC	-	7.3	-
Conductivity	mS/cm	38.8	-
Turbidity	NTU	410	8
Chloride	mg L^{-1}	5,014.8	12.6
Phenol	mg L^{-1}	704.2	48.8
Aromaticity	mg L^{-1}	10,210	60

S.D. = Standart Deviation

The catalysts PC800 and HC230 were tested for the CWPO experiments of leachate,. Non-catalytic (N.C.) tests were also performed. The kinetic evolution of hydrogen peroxide and COD upon reaction time is presented in Figure 1 nad Figure 2 respectvly.

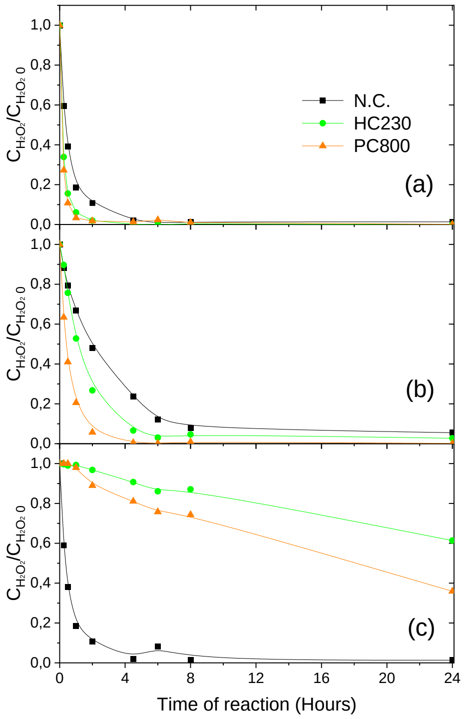

Figure 1: Normalized concentration of H_2O_2 upon time of CWPO run under the experimental conditions: pH = (a) natural leachate pH (7.3), (b) 6.0 and (c) 3.0 , $C_{Catalyst}$ = 1.8 g L^{-1}, T = 80 ºC, $C_{H_2O_2}$ = 85.71 g L^{-1}.

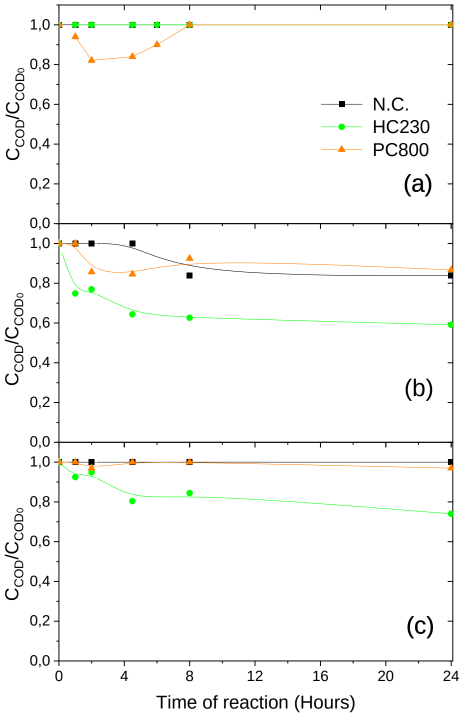

Figure 2: Normalized concentration of COD upon time of CWPO run under the experimental conditions: pH = (a) natural leachate pH (7.3), (b) 6.0 and (c) 3.0 , $C_{Catalyst}$ = 1.8 g L^{-1}, T = 80 ºC, $C_{H_2O_2}$ = 85.71 g L^{-1}.

The non-catalytic tests presented minor removals for COD and TOC under all pH conditions studied. On the other hand, for pH 3 and 6 the catalyst enhanced the COD and TOC removal, proving that those materials are active for the CWPO of leachate.

As observed, at pH = 3.0, the consumption of H_2O_2 reaches 39% with HC230 and 65% with PC800. This low decomposition reflects the low conversions of COD and TOC. The best TOC removal occurred with PC800, being able to remove 28% of TOC, and the best COD removal was obtained with HC230, 26%. It is noteworthy that HC230 has higher efficiency for peroxide consumption, considering that having a lower peroxide consumption the material had a higher COD conversion at this pH. This indicates that by performing some experimental optimization this material could have the potential to perform a higher COD removal.

An asymptotic concentration profile of hydrogen peroxide, COD and TOC was observed in tests performed at pH 6. The consumption of H_2O_2 was not very efficient, since the materials were not able to degrade 50% of the organic matter.

Figure 3 shows the percentage decrease in TOC, BOD_5, conductivity, chloride, phenols, aromaticity and turbidity.

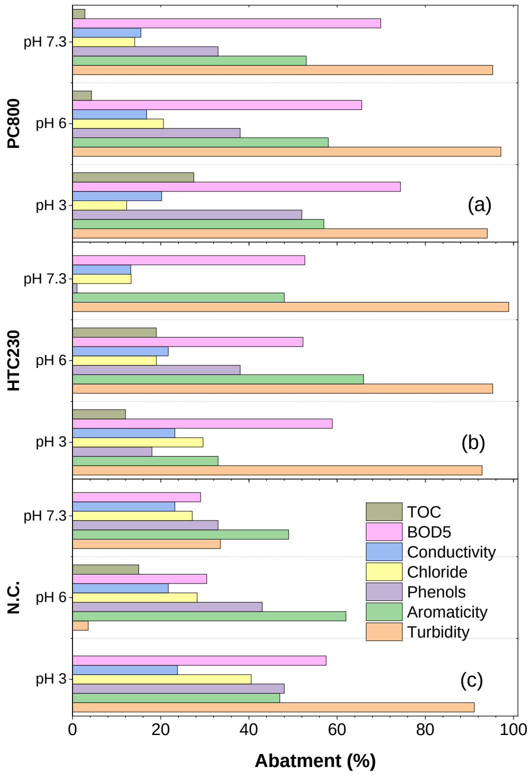

Figure 3: Final conversion of TOC, BOD_5, conductivity, chloride, phenols, aromaticity and turbidity under the experimental conditions:

catalysts = (a) PC800, (b) HC230 and (c) Non-catalytic, pH = 3.0, 6.0 and natural leachate pH (7.3), T = 80 ºC, $C_{Catalyst}$ = 1.8 g L^{-1}, $C_{H_2O_2}$ = 85.71 g L^{-1}.

The maximum removal of aromaticity was achieved with catalyst HC230 at pH = 6.0. Catalyst HC230 allows achieving COD, aromaticity, BOD_5 and turbidity removals of 41, 64, 57, and 95%, respectively. Alongside, HC230 enhanced the BOD_5/COD to 0.42, likely enabling the leachate for a posterior biological treatment [7].

The catalysts tested for the CWPO performed in the natural leachate pH were not able to degrade almost any COD or TOC. Although being the most cost-effective treatment, requiring no pH adjustment, the results were negligible.

The most promising results were obtained at pH 3, which allows obtaining high COD and TOC removals and, probably, the most efficient consumption of H_2O_2.

4. Conclusions

As demonstrated, compost resulting from the mechanical and biological treatment of MSW can be valorized by HTC and pyrolysis, converting it into hydrochars and pyrochars, respectively, with suitable catalytic properties to be employed in CWPO applications.

The best result in CWPO of the landfill leachate was obtained with the catalyst HC230 at pH 6.0, since it was able to degrade 41% of COD and enhance the BOD_5/COD to a ratio of 0.42, which is suitable for a posterior biological treatment. This means that this treatment could be employed as a primary treatment of leachate, being able to reduce COD and TOC content, making this wastewater more suitable for further biological treatment.

5. Acknowledgment

This work was financially supported by project “VALORCOMP - Valorización de compost y otros desechos procedentes de la fracción orgánica de los residuos municipales”, with reference 0119_VALORCOMP_2_P, through FEDER under Program INTERREG; Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC); CIMO (UIDB/00690/2020) through FEDER under Program PT2020, and national funding by FCT, Foundation for Science and Technology, and European Social Fund, FSE, through the individual research grant SFRH/BD/143224/2019 of Fernanda Fontana Roman.

6. References

[1] Eurostat, Municipal waste statistics, Eur. Comm. (2022). https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Municipal_waste_statistics (accessed February 13, 2022).

[2] G.D.F. Batista, F.F. Roman, J.L.D. De Tuesta, R.V. Mambrini, P. Praça, H.T. Gomes, *Catalysts*, 12 (2022).

[3] J. Malinauskaite, H. Jouhara, D. Czajczyńska, P. Stanchev, E. Katsou, P. Rostkowski, R.J. Thorne, J. Colón, S. Ponsá, F. Al-Mansour, L. Anguilano, R. Krzyżyńska, I.C. López, A.Vlasopoulos, N. Spencer, *Energy*, 141 (2017) 2013–2044.

[4] M.C. Di Lonardo, F. Lombardi, R. Gavasci, *Rev. Environ. Sci. Biotechnol*, 11 (2012) 353–363.

[5] J.L. Diaz de Tuesta, G.F. Pantuzza, A.M.T. Silva, P. Praça, J.L. Faria, H.T. Gomes, *Catalysts*, 10 (2020) 1–14.

[6] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, *J. Hazard. Mater.*, 150 (2008) 468–493.

[7] H. Luo, Y. Zeng, Y. Cheng, D. He, X. Pan, *Sci. Total Environ.*, 703 (2020) 135468.

[8] J.J.R. Márquez, I. Levchuk, M. Sillanpää, , *Catalysts*, 8 (2018).

[9] W.H. Glaze, J.W. Kang, D.H. Chapin, *Ozone Sci. Eng.*, 9 (1987) 335–352.

[10] Q. Zhou, W. Li, T. Hua, *Int. J. Chem. Eng.*, 2010 (2010).

[11] R.S. Ribeiro, R.O. Rodrigues, A.M.T. Silva, P.B. Tavares, A.M.C. Carvalho, J.L. Figueiredo, J.L. Faria, H.T. Gomes, *Appl. Catal. B Environ.*, 219 (2017) 645–657.

[12] J. Baloyi, T. Ntho, J. Moma, *RSC Adv.*, 8 (2018) 5197–5211.

[13] N.A. Qambrani, M.M. Rahman, S. Won, S. Shim, C. Ra, *Renew. Sustain. Energy Rev.*, 79 (2017) 255–273.

[14] M. Sevilla, A.B. Fuertes, *Carbon N. Y.*, 47 (2009) 2281–2289.

[15] D. Kalderis, M.S. Kotti, A. Méndez, G. Gascó, *Solid Earth*. 5 (2014) 477–483.

[16] J.L. Diaz de Tuesta, A.M.T. Silva, J.L. Faria, H.T. Gomes, *Environ. Sci. Pollut. Res.* 27 (2020) 20770–20785.

[17] M. Titirici, C. Fühner, O. Bens, J. Kern, K. Emmerich, *Biofuels*, 2 (2011) 89–124.

[18] M.A.M. Galvão, A.O. De Arruda, I.C.F. Bezerra, M.R.A. Ferreira, L.A.L. Soares, *Brazilian Arch. Biol. Technol*, 61 (2018) 1–20.