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Application of Compost-Derivated Carbon Catalysts on Catalytic Wet Peroxide Oxidation of Leachate Waters from Mechanical and Biological Treatment Plant Units for Municipal Solid Waste

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Master thesis report submitted to:
ESTIG – Escola Superior de Tecnologia E Gestão
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Master degree in
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Supervisors:
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Dr. José Luis Díaz de Tuesta (IPB)

Bragança, Portugal
November, 2020

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Abstract

Alternatives to deal with municipal solid waste (MSW), such as mechanical biological treatment (MBT) plants, are a trend. In these plants, the organic matter is digested by anaerobic bacteria, generating biogas and reducing the solid mass, generating simultaneously a solid compost and a liquid leachate as side-streams. The leachate has a complex composition and cannot be treated by conventional wastewater treatment methods, while the compost is mainly used as an agriculture fertilizer, but the amount produced is higher than its demand. This work deals with the valorization of compost to produce hydrochars and biochars, through hydrothermal carbonization (HTC) and pyrolysis, respectively, with suitable properties to serve as catalysts for the catalytic wet peroxide oxidation of the landfill waters generated in MBT (TOC = 27 g L^{-1}, COD = 60 g L^{-1}, 38.8 mS/cm and 5 g L^{-1} of chloride ions). Seven catalysts were produced from compost and characterized by several techniques. The catalysts were subjected to screening tests of H_2O_2 decomposition and the best two were selected to be further studied in the catalytic wet peroxide oxidation (CWPO) of leachate. The experimental conditions of the process, temperature, pH, catalyst load and H_2O_2 addition were studied seeking optimization. The best experimental conditions found were T = 80 ºC, pH = 3.0, 7.2 g L^{-1} of catalyst, 85.71 g L^{-1} of H_2O_2, added in five batches each hour. Under these experimental conditions, the hydrochar prepared at 230 ºC (HTC-230) achieved removal of 43 % of chemical oxygen demand (COD) and total organic carbon (TOC), turbidity, aromaticity, phenols, chlorides and 5-day biological oxygen demand, (BOD_5) removals of 52, 95, 93, 72, 35 and 93 %, respectively. Resins were used to pre-treat the leachate, in order to enhance the CWPO results. Using a cationic adsorption resin (TP-207), considering again operating conditions of T = 80 ºC, pH = 3.0, 7.2 g L^{-1} of catalyst, 85.71 g L^{-1} of H_2O_2, the catalyst HTC-230 achieved 62 %, 55 %, is 97 %, 95 %, 46.5 %, and 97 % for COD, TOC, turbidity, aromaticity, chlorides, and BOD_5.

Keywords: Municipal solid waste; Valorization; Wastewater treatment; CWPO; Leachate waters; Carbon-based catalysts.

Resumo

As unidades de tratamento mecânico e biológico (TMB) são alternativas para lidar com os resíduos sólidos urbanos (RSU). Essas unidades através da digestão anaeróbia da matéria orgânica, geram biogás e reduzem a massa sólida, porém geram um resíduo sólido (convertido em composto) e águas lixiviantes (ou lixiviado) como sub-produtos. O lixiviado tem uma matriz complexa, o que inviabiliza o seu tratamento pelos métodos convencionais, enquanto o composto é usado principalmente como fertilizante agrícola. Este trabalho tem como objetivo a valorização do composto para a produção de materiais carbonáceos, através de carbonização hidrotérmica (CHT) e pirólise, respectivamente. Os materiais obtidos, com propriedades para atuarem como catalisadores no processo de oxidação catalítica com peróxido de hidrogénio (CWPO), são posteriormente usados no tratamento do lixiviado (TOC = 27 g L^{-1}, CQO = 60 g L^{-1}, 38,8 mS / cm e 5 g L^{-1} de iões cloreto). Neste trabalho foram produzidos sete catalisadores a partir de composto e caracterizados por diversas técnicas. Após testes de screening da atividade catalítica na reação de decomposição de H_2O_2, dois deles, o primeiro de pirólise e o segundo de CHT, C-800 e HTC-230, foram selecionados para ensaios de CWPO do lixiviado. Foram estudadas as condições experimentais para otimizar o processo, variando temperatura, pH, carga de catalisador e adição de H_2O_2. A condição experimental ótima encontrada foi T = 80 ºC, pH = 3,0, 7,2 g L^{-1} de catalisador, 85,71 g L^{-1} de H_2O_2, adicionados em cinco doses com 1 h de intervalo. Sob essas condições experimentais, o catalisador HTC-230 permitiu remoções de 43, 52, 95, 93, 72, 35 e 93% de carência química de oxigénio (CQO), carbono orgânico total (TOC), turbidez, aromaticidade, fenóis, cloretos e carência biológica de oxigénio de 5 dias (CBO_5), respectivamente. Afim de potencializar os resultados de CWPO foram utilizadas resinas para pré-tratar o lixiviado. Utilizando a resina de adsorção catiónica TP-207, em condições de T = 80 ºC, pH = 3,0, 7,2 g L^{-1} de catalisador, 85,71 g L^{-1} de H_2O_2, o catalisador HTC-230 permitiu remoções de 62, 55, 97, 95, 46,5 e 97% de COD, TOC, turbidez, aromaticidade, cloretos e CBO_5.

Palavras-chave: Resíduos sólidos urbanos; Tratamento de águas residuais; CWPO; Águas lixiviantes; Catalisadores de base carbono.

Index of Abbreviations

AOP	Advanced Oxidation Processes
BOD_5	Five-day Biological Oxygen Demand
CWPO	Catalytic Wet Peroxide Oxidation
COD	Chemical Oxygen Demand
CN	Colour Number
FTIR	Fourier-transform infrared spectroscopy
HTC	Hydrothermal Carbonization
MC	Mature Compost
MSW	Municipal Solid Waste
MSWM	Municipal Solid Waste Management
MBT	Mechanical and Biological Treatment
SAC	Spectral Absorption Coefficient
TOC	Total Organic Carbon

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INTRODUCTION

1 INTRODUCTION

1.1 Introduction

Since humanity started living in communities and towns, the generation of solid waste has largely increased. According to the Encyclopædia Britannica, technological approaches for the management of municipal solid waste (MSW) started to be applied only by the end of the 19th century [1].

According to a report published by Eurostat in 2018, MSW worldwide corresponds to 10% of the total waste generation. In 2017, each European citizen generated, on average, 480 kg of MSW, and its generation is expected to reach around 3.4 billion tonnes by 2050 [2]. Globally, authorities are concerned with this production, since MSW has a complex composition, comprising plastics, metals, and complex electronic wastes, among others. If the MSW is not properly managed, the environment could suffer from irreversible consequences [2,3].

The main approaches for MSW management are recycling, landfilling, composting, and incineration. Landfilling is the most harmful approach, as no pre-treatment is usually performed, causing health-related risks, and discarding profitable resources. Therefore, several studies have been performed in the recent past in order to develop methods to deal with the MSW in an economically and eco-friendly way. This results in a decrease of 60% on the use of landfills between 1995 and 2017, and in an increase of the recycled and composted fractions, 195% and 196%, respectively, in the same time frame. However, the main approach is still landfilling [2–4].

More sustainable strategies to manage MSW have been developed, such as mechanical and biological treatment (MBT). In MBT plants, the collected waste is directed to an organic matter separation step. This organic fraction goes to a biological treatment stage, generating biogas, which is a sustainable source to supply energy and, as sub-products, wastewater (leachate) and a solid fraction (converted to compost). The compost is mainly used as an agricultural 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 [5,6].

The leachate, the wastewater generated in the MBT (as well as in landfills), is far away from the standards needed for direct disposal on rivers, requiring treatment. The leachates have a complex composition and a high content of total organic carbon (TOC), resulting in high values of chemical oxygen demand (COD) and biological oxygen demand (BOD_5). Table 1 displays the general characteristics of leachates.

Table 1: Usual range of leachate characteristics according to its age

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

Adapted from Renou et al (2008) [7] *and Schiopu & Gavrilescu (2010)* [8].

With such low quality, the traditional water treatment processes are not able to deal appropriately with leachate waters, creating a need for more robust and efficient alternative chemical treatments, such as advanced oxidations processes (AOP). AOPs have displayed interesting results towards the treatment of wastewaters from many sources, bearing different organic pollutant loads [7]. Among them, catalytic wet peroxide oxidation (CWPO) is an AOP based on the selective decomposition of hydrogen peroxide into hydroxyl radicals by the use of a suitable heterogeneous catalyst [9].

On the other side, besides being accumulated on landfills due to high production, other concerns related to compost are the variation of its properties, which depends on the waste that enters the MBT, and also the presence of metals, which can be toxic for agricultural purposes, allied to the high percentage of organic matter of the compost. In this way, compost can be regarded as valuable for its application on alternative processes, such as a catalyst in wastewater chemical treatments, as it is the case of CWPO [5,10].

1.2 OBJECTIVES

1.2.1 General Objective

The main objective of this work is to evaluate the use of carbon-based materials obtained from compost to treat by CWPO the leachate waters produced in MBT units.

1.2.2 Specific Objectives

- Fully characterize the leachate before and after treatment in terms of its COD, BOD_5, TOC and other relevant parameters on wastewater monitoring;
- Evaluate different carbon-based catalysts obtained from compost, using thermal and chemical treatments, on the decomposition of hydrogen peroxide and on the CWPO of the leachate waters obtained in the same MBT unit where the compost is produced;
- Choose the material with the highest activity towards the CWPO of the leachate, for further studies;
- Evaluate the efficiency of CWPO on the treatment of the leachate;

1.3 Document Structure

This master thesis is divided into five chapters. Chapter 1 presents the introduction and objectives of the work, when relevant topics are raised for the understanding of the theme regarding the generation and management of MSW, generation of leachate by the MBT units and its characteristics, and possible treatments of the leachate by AOP process.

Chapter 2 presents the state of the art, the part of the work where the bibliographic survey was carried out about MSW, MBT treatment of the MSW, review of AOP treatments of leachate, CWPO mechanism and optimization and carbon-based materials.

The experimental part of the work is detailed in chapter 3, where the reagents, equipment, and experimental processes are described.

The results obtained for the characterization of carbon-based and raw material, catalysts hydrogen peroxide decomposition screening and CWPO runs are presented in chapter 4.

Finally, chapter 5 presents the conclusions with topics of interest for future research.

STATE OF THE ART

2 STATE OF THE ART

2.1 Municipal solid waste management (MSWM)

The continuous increase of mass consumption patterns has a direct impact on the increase of MSW production. This presents a strong concern to the authorities around the world since wrong disposal and management could result in pollution, mainly related to the emission of carbon dioxide and methane, gases that are responsible for the greenhouse effect [11]. MSW is the waste generated in cities that comes mainly from three sources. The first source is originated in houses, called domestic waste. It has a simple composition, usually plastic, food waste, glass and some metals. The second source arises from commercial facilities, which includes restaurants, shopping malls, stores, supermarkets, among others. The commerce-related MSW, since it comes from different kinds of establishments, has a more heterogeneous composition, making it harder to deal with than the domestic-related MSW. The third source is industry, which generates MSW much more complex to treat than the other sources [12].

In order to prevent the generation of excess waste and to better promote waste management, Europe released the Directive 2008/98/EC, which sets the concepts and definitions about waste management, explains when waste ceases to be waste and becomes a secondary raw material, and how to distinguish between waste and by-products. This directive focuses on waste prevention programs, which are the more sustainable strategy to deal with waste [13].

There are big gaps in the MSWM, such as the lack of segregation of the waste at its origin, lack of recycling systems, poor reutilization and, sometimes, in the carelessness of the disposal method [11]. Figure 1 shows a strategy for a MSWM suggested by the European Commission, through the EU directive 2008/98/EC [13].

Figure 1: MSWM preferable strategies
Adapted from European Commission (2019) [13]

As observed in Figure 1, landfill disposal is the last and worse option in the waste management hierarchy. However, there is a trend to use this method for industrial and municipal waste, due to its cheapness [8,14].

One of the major drawbacks of landfilling is the generation of leachate waters. A leachate water is a liquid generated by the degradation of the waste disposed on the landfill combined with rainfall. The oldest landfills usually do not have a proper way to capture the leachate and to treat it, so it easily enters the soil, causing serious problems for the environment [8,14,15]. Figure 2 illustrates the mechanism of leachate generation and infiltration into the environment.

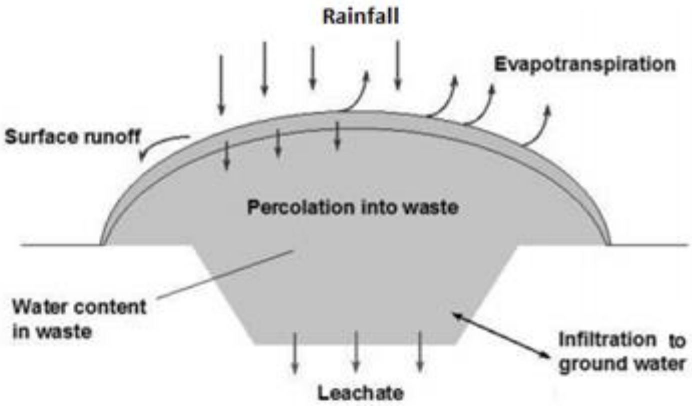

Figure 2: Leachate generation and infiltration mechanism
Adapted from Morling, 2007 [16]

A leachate is characterized by the high content of heavy metals, TOC and ammonium, which results in high conductivity, COD and BOD_5. Its composition depends on the leachate age, the kind of landfill, the types of waste deposited, temperature and moisture. Due to its characteristics, the generation of leachate must be reduced, to be collected and treated.

To deal with the MSW and to reduce the generation of leachate, the solution must fulfill a few criteria, such as being environmentally sustainable, being as cheap and efficient as possible, socially acceptable and politically practicable. Fortunately, the direct deposition of MSW in landfills is decreasing in Europe year by year, as illustrated in Figure 3.

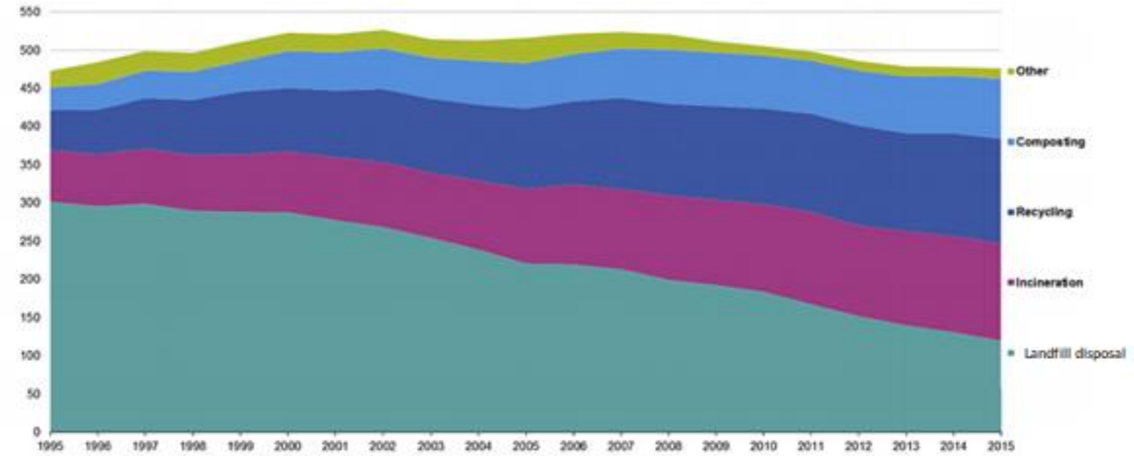

Figure 3: Municipal waste treatment in Europe by type of treatment, (kg per capita) Adapted from Malinauskaite et al(2017) [17].

More environmentally friendly strategies, such as recycling and composting, have been increasingly adopted, stressing the European concern with MSWM, as displayed in Figure 3 [17].

The recycling, that can be carried out for different kinds of wastes, mostly for plastics, glasses, papers and aluminium, has a huge positive impact on MSWM. In the recycling, waste that has no value, and would be disposed directly in a landfill, after the recycling process, generate cheaper raw materials. The main goal of recycling is to save landfill space and to improve the local economy, creating more jobs and new products that can be sold [18–20].

According to Wei e*t al* (2017), biodegradable material represents between 40 to 70% of MSW [21]. In this context, the composting process is essential, since it biodegrades the organic matter, under aerobic or anaerobic conditions. There are several composting methods, but they operate in the same way. First, the organic matter of MSW is separated, then it is biodegraded and, after some maturing and stabilization processes, it leads to the final product, the compost. All composting methods have the same goal, which is to reduce the mass of waste and to generate the compost, which can be used mainly on soil fertilizing. Even when the compost is not used somewhere, it has more calorific value when incinerated.

Some composting methods also produce biogas, that has good economic value for industries [21–23].

2.2 Mechanical Biological Treatment

In 1999, Europe, through the Directive 1999/31/EC, established regulations for reducing landfill usage, the less preferable way on the waste management hierarchy [24]. One of the big problems is the direct disposal of biodegradable organic matter in a landfill since this matter can be treated in several alternative ways, such as by Mechanical Biological Treatment (MBT) [25]. MBT is a process that degrades the organic matter present in MSW, using biological treatments and generating compost and biogas.

In order to avoid and reduce the presence of biodegradable waste in landfills, the use of MBT plants is growing over the last two decades, as reported by Bernat, *et al.* (2020) [26].

In Portugal, many companies are working with waste management and more environmentally friendly sources to generate energy. As an example, Resíduos do Nordeste S.A. built an energy valorization center to produce energy from biogas. This center produces annually 4.500 MWh of energy, which is capable to supply one year of energy to around 1500 houses [27].

Figure 4 shows a scheme of the working process of a general anaerobic MBT plant.

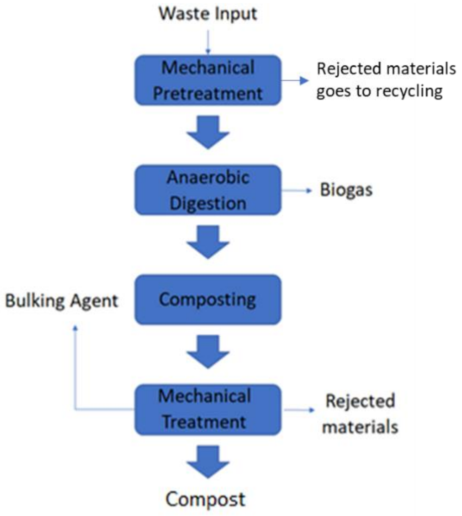

Figure 4: Scheme of the steps of MBT plants
Adapted from Ponsá et al (2008) [28].

In the first part, the mechanical pre-treatment, the MSW is separated into two main fractions, the organic matter and the inorganic matter, the latter comprising plastics, metals and glass, among others, which are directed to proper recycling. [25,28,29].

Once the MSW is separated, it goes to the anaerobic digestion step, where the organic matter is broken by the anaerobic bacteria. In this step, there is a significant reduction of the organic matter mass and the production of biogas, mostly composed of methane and carbon dioxide, that is kept for later usage in production of electricity or for selling. The retention time in this step usually goes from 2 to 4 weeks, for more efficient digestion [25,28,30].

A lot of variables influence the digestion step. First, there is the composition and granulometry of organic matter particles. In addition, if the inorganic matter is not properly separated, the potential for biogas drops off. Other parameters, such as temperature, pH and dissolved oxygen also have a huge influence in the anaerobic digestion [25,28,31].

One of the issues of the anaerobic digestion step is the leachate that comes out of the reactor. This leachate sometimes can be recycled to the system again, but when it has high COD, TOC and some metals, the bacteria used on the digestion step may not work properly, so usually the leachate becomes wastewater, and the usual physical and biological treatments are not adequate to deal with it [28,31]

After the anaerobic digestion step, the remaining organic matter goes to composting, where it is combined with a bulk agent and transferred into composting tunnels for at least two weeks. This step is important to stabilize and sanitize the compost. According to Ponsá (2008), longer composting times should lead to compost with more stability [28].

A final step of mechanical treatment of the compost may be applied. The objective is to remove the inorganic matter that came all the way through the process, further stabilizing the compost. Compost has been largely used in agriculture as a fertilizer [22].

According to Di Lonardo *et al.* (2012), the quantity and quality of the outputs of an MBT is a function of the input characteristics, which depends on the location where it has been generated, either rural or urban, the type and percentage of materials that are separated in the pre-mechanical treatment and, lastly, on the types of mechanical and biological processing units employed in the plant [32].

As reported by Montejo *et al.* (2013) and Velis *et al.* (2010), the main issues that limit further growth of the MTB plants and their ideal work are the many variables that interfere in the microbiological digestion (and that need to be controlled), the fact that most part of the compost is still discarded on landfills, even knowing that the compost has many applications and economical value, and the need to improve the technology of the plants, since some of them are more than 15 years old and have not gotten the necessary upgrades [29,33].

2.3 AOPs in the treatment of leachate wastewater

According to Renou *at al* (2008), leachate has a huge potential for contamination of surface water and groundwater, due to its high concentration of pollutants, requiring more robust treatments [7].

AOPs are demonstrating promising results for the degradation of resistant compounds or for their transformation into biodegradable compounds for further biodegradation treatments [34]. AOPs were first defined by Glaze *et al* (1987) as an alternative to conventional water treatment processes, performed at ambient temperature and pressure, based on the *in situ* generation of a powerful oxidizing agent (hydroxyl radicals), to promote the unselective decomposition of pollutants in wastewater [35]. The main AOPs are catalytic wet peroxide oxidation (CWPO), Fenton ($Fe^{2+} + H_2O_2$), photolysis and photocatalysis, electrochemical oxidation, and ozonisation. Additionally, these processes can be intensified by combining them with other technologies, such as in the case of Fenton, which can be enhanced by the use of light sources (Photo-Fenton), ultrasounds (Sono-Fenton), electricity (electro-Fenton), or microwaves (microwave-assisted Fenton).

The first reported AOP is the Fenton process, based on the use of a soluble iron(II) salt mixed with hydrogen peroxide, also called the Fenton reagent, that was applied to degrade organic pollutants from water [36]. The Fenton process is well known to reach high conversions of pollutants at short times of reaction. However, some pollutants are refractory to the process or their conversions are slow, reason why efforts were done to use intensified Fenton to reach higher conversions in lower time, such as Photo-Fenton, Sono-Fenton, electro-Fenton or microwave-assisted Fenton. However, intensified processes require an extra supply of energy and lead to an increase in the operative cost of the process. Additionally, Fenton or intensified Fenton show a significant drawback, since soluble iron stays on the effluents at the end of the treatment process, being hard to recover or to eliminate [36–38].

The treatment of leachates with AOPs also presents some challenges, as leachates have a very complex matrix, influenced by a lot of geographical and socioeconomic parameters. There are several ions, such as chlorides, carbonates and sulphates, that can react with the catalyst surface, creating undesirable complexes that limit the generation of the hydroxyl radicals, deactivation the catalyst and lowering the efficiency [34,39].

Also, some of the ions present in the medium, such as bicarbonates and chlorides, may act as radicals scavengers, consuming hydroxyl radicals and hindering the oxidation of the organic content of the leachate [6].

The concentration of the organic pollutants changes heavily according to the age of the leachate (in landfills), as previously shown in Table 1. In fresh leachates, with a high organic pollutant concentration, studies have shown that the catalyst loses its activity faster. The organic molecules present in the leachate can enter into the catalyst pores, hindering the generation of hydroxyl radicals, this being the main responsible for the catalyst poisoning [34,40].

There are a few reports on the literature regarding the treatment of leachate waters and other sources of real wastewater using AOPs. Table 2 summarizes the studies performed on different sources of leachates treated by AOPs, the experimental conditions applied, the catalysts used and the main results obtained.

Table 2: Review of AOP treatments applied to leachates from various sources

Source	AOP	Catalyst	Experimental conditions	Main results (Removal)	Ref.
Landfill Leachate	Photo-Fenton	$FeSO_4 \cdot 7H_2O$	V: 750 mL t: 1 h pH: 3 to 3.5 $[H_2O_2]$: 10,000 mg/L [Cat]: 2000 mg/L wavelengths: 200 to 600 nm, H_2O_2 in four feedings	[COD]: 86% [TOC]: 74% Color: 92%	[41]
Leachate from a Central MSW	Fenton	Fe^{2+}	T: 25 ºC t: 30 min V: 100 mL pH: 2.5 $[H_2O_2]/[Fe^{2+}]$: 1.5 [Cat]: 0.1 mol/L	[COD]: 61.3%	[42]
Landfill leachate	Electro-Fenton	Iron electrodes	T: 25 ºC Stirring: 200 rpm $[H_2O_2]$: 5000 ppm V: 900 mL 6 electrodes t: 30 min pH:3,4 Current density: 20 mA/cm^2	[COD]: 74.2%	[43]
Landfill leachate	Heterogeneous catalytic ozonation	Activated carbon	Gas flow: 200 mL/min $[O_3]$: 80 g/m^3 T: 20 ºC pH: 8 t: 40 min [Cat]: 6.7 g/L	[COD]: 45% Color: 70%	[44]
Municipal Landfill leachate	Fenton with a microfiltration and nanofiltration system	$FeSO_4 \cdot 7H_2O$	H_2O_2/g $COD_{raw\ leachate}$: 1.7 g $[FeSO_4 \cdot 7H_2O/H_2O_2]$: 1:5.3 pH: 3.8 t: 28 min Stirring: 118 rpm pH: 8	[COD]: 63% True color: 76% Humic substances: 50% [TOC]: 71.0%	[45]
Stabilized landfill leachate	CWPO	Al/Fe-pillared clay catalyst	t: 4h T: 18 ºC pH: 3.7 [Cat]: 20 g/L $[H_2O_2]$ = 4.68 mol/L	[COD]: 50% Enhanced of BOD_5/COD 0.135 to 0.321	[46]
Mid-aged MBT leachate	CWPO	Hybrid magnetic graphitic nanocomposites	t: 24h T: 80 ºC pH: 6.0 [Cat]: 0.5 g/L $[H_2O_2]$ = 27.7g/L	Aromaticity: 95% [COD]: 55 % [TOC]: 55% BOD_5/COD 0.21 to 0.42	[6]

Source	AOP	Catalyst	Experimental conditions	Main results (Removal)	Ref.
Stabilized landfill leachate	Fenton followed by ozonation	Fe^{2+} (Fenton process)	T: 22 ºC pH: 3.7 (Fenton) pH: basic (ozonation) Ozone with hydrogen peroxide: 400 mg/L t: 40 min Fenton and 30 min ozonation [H_2O_2/Fe^{2+}]: 3 [Cat]: 4 mmol/L	Removal of: [COD]: 72% BOD_5/COD increased from 0.01 to 0.24	[47]
Stabilized landfill leachate	CWPO	Flyash augmented Fe_3O_4	V: 150 mL T: 20 ºC [Cat]: 1.0 g/L pH: 3 [H_2O_2]: 0.05 mol/L t: 90 min	Removal of [COD]: 84.7% [TOC]: 68% BOD_5/COD increased from 0.034 to 0.41	[48]

Abbreviations: t = Time; T = Temperature; V = Leachate volume; [Cat] = Catalyst concentration

Primo *et al.* (2008) achieved removals of 86, 74 and 92% for COD, TOC, and color, respectively, under optimized conditions, with a photo-Fenton process for landfill leachate [41]. Even though high conversions were achieved, the leachate needed initial acidification to pH 3 and, in the end, a basification step to pH 8, in order to precipitate iron particles. The recyclability of the catalyst was not evaluated.

Zhang *et al.* (2005) performed optimization of a Fenton process for the treatment of a landfill leachate and obtained a COD removal of almost 62% after 30 min of reaction and with a low residual concentration of iron oxides (only 0.005 mol/L) [42]. The main issue is that the leachate was diluted with distilled water, the pH needed to be adjusted from 7 to 2.5 and only COD removal was assessed. These experimental conditions make it hard to implement in real leachate conditions.

Orkun and Kuleyin (2010) treated landfill leachate with an Eletrochemical-Fenton process in order to degrade COD. A removal of 74% was obtained in optimum conditions[43]. The authors also performed an economical study of the process and concluded that the Eletrochemical-Fenton process is more efficient from an economical and chemical point of view than the usual Fenton. However, the leachate evaluated has a low COD concentration (11 g/L) when compared with other leachates and the removal of any other parameters, like color, TOC or BOD_5 was not evaluated.

Tizaoui *et al.* (2007) tested the effect of various catalysts for the heterogeneous catalytic ozonation of landfill leachate. The best result was obtained with activated carbon, combined with an ozone concentration of 80 g/m^3 [44]. A COD reduction of approximately 45% was obtained. The main issue with this methodology is the big setup needed, with a constant flow rate of O_3 and N_2, separator and gas recovery equipment, making this process costly. Furthermore, the applied process was not able to increase properly the BOD_5/COD ratio (an increase was observed from 0.1 to about 0.2), making the leachate still not proper for further biological treatment.

Moravia *et al.* (2013) treated a landfill leachate with Fenton reagent followed by two membrane separation processes, the first considering a micro membrane and a nanomembrane in the second, obtaining satisfactory COD, color and TOC removals in 30 minutes [45]. However, the proposed process is expensive, due to the maintenance of membrane systems, and the leachate treated in this work had characteristics of a stabilized leachate, with low concentrations of COD and TOC.

Galeano *et al*. (2011) used a clay-based catalyst to treat a stabilized landfill leachate, through a CWPO process. In their work, a removal of 50% of initial COD and an enhancement of the BOD_5/COD ratio from 0.135 to 0.321 was obtained [46]. The catalyst reuse was evaluated, being found to be only stable within 3 cycles, due to damage on its surface probably because of metal complexing by light carboxylic acids or pore obstruction by suspended particles. The experimental methodology is simple and scalable, however, the study was performed for a stabilized leachate, which has the characteristic of having lower COD, BOD_5 and TOC concentrations than non-stable leachates and, therefore, the experimental set up may not be efficient for leachates with higher concentrations profile.

Ribeiro *et al.* (2017) evaluated the usage of a complex hybrid magnetic graphitic nanocomposite catalyst, with copper and iron in the composition, which would be hard to produce on a large scale. The main advantage of the magnetic catalyst is the easy recovery at the end of the process, only requiring a magnet.

The CWPO at optimized experimental conditions achieved a good TOC and COD removal, 55% each, and 95% removal of aromatics compounds [6].

Cortez *et al.* (2011) studied leachate with a low BOD_5/COD ratio (0.01), meaning that the leachate is not easily biodegradable, creating a need for a chemical pre-treatment. After the Fenton process, the BOD_5 concentration increased (from 5 to 28 mg/L), consequently leading to an increase in the BOD_5/COD ratio (to 0.24), as some organic compounds were chemically oxidized to simpler compounds that can be degraded by biological treatments. However, the desired ratio of 0.4 was not reached [47]. COD removal reached 72%.

Niveditha and Gandhimathi (2020) reported the use of a magnetic Flyash augmented Fe_3O_4 to treat a stabilized landfill leachate in a heterogeneous Fenton-like process [48]. The catalyst revealed good results for 3 reuses, proving its stability and, since the catalyst has magnetic properties, it was easy to separate from the leachate. The BOD_5/COD ratio achieved a value of 0.41, making the leachate suitable for a further biological treatment. The adjustment of pH was necessary.

2.4 Catalytic Wet Peroxide Oxidation

Due to the disadvantages of the homogeneous Fenton reaction, heterogeneous catalysts, that allow easier recovery of the catalyst started being developed for catalytic wet peroxide oxidation (CWPO). CWPO is a process in which the heterogeneous catalyst present in the system reacts with hydrogen peroxide to generate hydroxyl ($HO^•$) and hydroperoxyl ($HOO^•$) radicals, highly oxidizing species able to degrade a variety of organic pollutants present in wastewaters [9,39,40].

According to Márquez *et al.* (2018), since CWPO can operate without 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 [34].

Figure 5 illustrates a scheme of the CWPO mechanism to degrade organic pollutants.

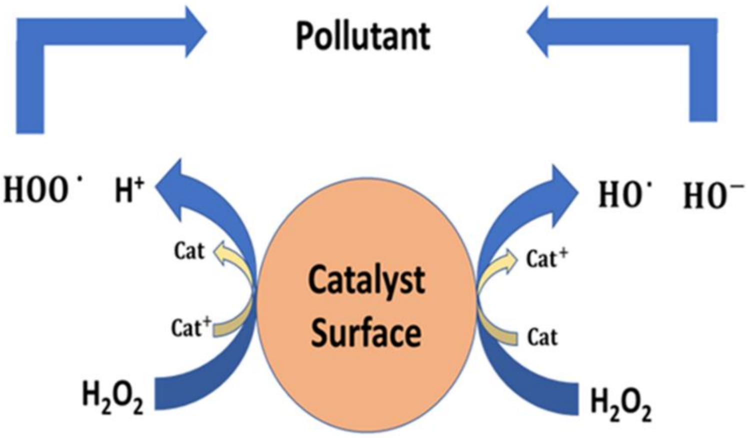

Figure 5: Scheme of hydroxyl radical generation by CWPO
Adapted from Márquez et al (2018) [34]

Equations (1) and (2) represents the mechanism of CWPO for hydroxyl radical generation, from the selective decomposition of hydrogen peroxide [34].

$$H_2O_2 + Cat \rightarrow HO^{\bullet} + HO^{-} + Cat^{+} \quad (1)$$

$$H_2O_2 + Cat^{+} \rightarrow Cat + HOO^{\bullet} + H^{+} \quad (2)$$

In CWPO, iron-based materials (known as heterogeneous Fenton) are the most used as catalyst. The main issue with iron-based materials is the stability of the catalyst since the iron can leach during the CWPO process, and release iron to the solution, generating additional pollution and leading to catalyst deactivation. In recent reports, researchers are trying to develop new catalysts, with different metals, with increased stability and sustainability for this process [40,49]. The main factors that may interfere with CWPO efficiency are temperature, pH and the concentration of organic pollutants. Reports have shown that an increase in temperature enhances CWPO efficiency, but most studies concluded that increasing the temperature after around 80 ºC, does not seem to improve organic content removal [34].

The pH has a great impact on the oxidation efficiency. Even though CWPO can be operated on a wider range of pH when compared to other processes, such as Fenton, its efficiency may be greatly impacted by the operating pH. Some studies demonstrated that the consumption of hydrogen peroxide is not heavily impacted by the pH when operating on a range from neutral to acidic pH. However, the removal of organic pollutants, measured as COD, enhances in an acidic pH (around 3), as the mechanism may change at acidic versus alkaline pH, mainly when using iron-loaded catalysts. Despite that, some studies also evaluated the operation under basic pH, due to easier adjustment and operation. The adjustment of pH is also an important factor when considering the scalability of the process, as the need to adjust pH before and after treatment may greatly impact the cost of the operation. Operating at the natural pH of the wastewater would be advantageous [34,39].

One of the main benefits of CWPO reactions is the low-cost of this technology and its benign nature to the environment. In this perspective, the usage of complex metallic catalysts, which have expensive reagents, complex synthesis methods and possible leaching issues are falling, and the usage of cheap and renewable catalysts is desired. Carbon-based materials (such as biochars and hydrochars) are valuable alternatives that can be produced from renewable sources, like biomass or wastes, and usually have a simple and cheap synthesis process, fulfilling the desired requirements of the green chemistry [50,51].

2.4.1 Carbon-Based Materials

As MSW generation and CO_2 emission become a worldwide concern, scientists and politicians search for methods to reduce or recycle the discard of carbon sources. One interesting alternative for recycling and reducing the emission of greenhouse effect gas is the production of carbon-based materials, such as biochars and hydrochars. According to Qambrani *et al.* (2017), biochar is a carbon-rich (65–90%) solid product of biomass pyrolysis that contains numerous pores and oxygen functional groups, and aromatic surfaces. Biochars can be produced by slow pyrolysis and/or as a by-product of the fast pyrolysis, gasification or combustion processes, from different sources of organic matter feed. Temperature and time of pyrolysis are key factors to control the physical and chemical characteristics of biochars [52,53]. Table 3 displays different pyrolysis methodologies applied to synthesize biochars.

Table 3: General conditions used in methodologies for synthesis of biochars

Process	Temperature range (°C)	Average residence time	Biochar production* (%)
Slow pyrolysis	300 – 700	Day or days	35
Intermediate pyrolysis	Around 500	10 to 20 seconds	20
Fast pyrolysis	500 – 1000	Less than 2 seconds	12
Gasification	750 – 900	10 to 20 seconds	10
Hydrothermal carbonization (HTC)	180 – 300	1 to16 h	50 to 80

**in mass yield. Adapted from Qambrani et al (2017)* [53] *and Bridgwater (2012)* [54].

Biochars can be produced in different scales, from large industrial facilities down to domestic level, making them applicable to a variety of socioeconomic situations. They have a positive environmental impact, such as by enhancement of soil fertility and improvement of nutrient availability for the growth of plants, removal of metals from soil leachates and by raising the microbial communities in soils, when used in soil remediation. They can also be used as catalysts in some chemical reactions and, as an important aspect, leading to the immobilization of the organic carbon, mitigating the gases of the greenhouse effect, such as methane (CH_4) [53,55,56].

Hydrochars are carbon-based materials similar to biochars. The difference between both types of materials is the synthesis process. Hydrochars are produced by hydrothermal carbonization (HTC) of biomass, submerging the biomass in water (or its original moisture) and supplying heat, with enough pressure to maintain the water in the liquid phase. Operating temperatures are higher than 100 ºC [57,58]. Table 4 summarizes the main advantages, disadvantages and goals of the thermal treatments applied to biomass to produce biochars and hydrochars, according to Wang *et al* (2018) [59].

Table 4: Biomass conversion techniques and its advantages/disadvantages

Biomass conversion	Product	Advantages	Disadvantages	Approach and objective
Pyrolysis	Biochar	High efficiency and flexibility	Not suitable for biomass waste with high moisture	Slow or fast pyrolysis producing biochar, bio-oil, and gases like CO, CO_2, CH_4 and H_2
HTC	Hydrochar	Directly appliable to biomass with high moisture	Difficult to collect the products and high requirements for equipment	Carbonization, liquefaction and gasification producing hydrochar, bio-oil, and gas

Adapted from Wang et al (2018) [59].

Biochars and hydrochars can be applied, as already mentioned, as catalysts in chemical processes, such as AOPs. They can be used as support materials for active centers or even as catalysts themselves, due to their surface chemical characteristics. There are a few reports on the literature regarding the application of carbon-based materials from waste sources as environmentally friendly catalysts for CWPO reactions to remove different organic pollutants from water matrices, as shown in Table 5 [60].

Table 5: Review of carbon-based materials produced from residue sources for application in CWPO reactions

Residue source	Catalyst	Wastewater	Experimental conditions	Main results	Ref.
Dewatered sewage sludge	Porous carbon derived from sewage sludge	Naphthalene dye intermediate 1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid)	[1,2,4-Acid]: (150 mg/L) [H_2O_2]: 15 mmol/L [Cat]: 0.5 g/L T: 25 ºC V: 50 mL pH: 5	Removal of: [1,2,4-Acid]: 94% [TOC]: 48%	[61]
Biomass based wood	Granulated composite of biomass-based carbon and metakaolin	Bisphenol aqueous solution (60 mg/L)	[bisphenol]: 60 mg/L [H_2O_2]: 1.5 g/L [Cat]: 1 g/L T: 50 ºC V: 160 mL pH: 9 to 11	Removal of: [bisphenol]: 51% [TOC]: 34%	[62]
Olive stones	Iron catalyst supported on activated carbon	Orange II dye solution (0.1 mmol/L)	V: 200 mL T: 30 ºC pH: 3 [H_2O_2]: 0.6 mmol/L t: 4 h [Cat]: 91.5 g/L	Removal of [TOC]: 23% [Orange II]: 55%	[63]
Grape seeds	Iron catalysts supported on activated carbon	Bisphenol aqueous solution (100 mg/L)	[bisphenol]: 100 mg/L [H_2O_2]: 530 mg/L [Cat]: 0.5 g/L T: 80 ºC t: 3 h V: 160 mL pH: 3	Removal of: [bisphenol]: Total [TOC]: 60%	[64]
Biological sludge from dyeing industry	Iron magnetic biochar composite	Real dyeing industry wastewater	[COD]: 450 mg/L [TOC]: 250 mg/L BOD_5/COD: 0.25 [H_2O_2]: 1 ml/L [Cat]: 1.0 g/L T: 25 ºC V: 500 mL	Removal of: [COD]: 47% [TOC]: 49% BOD_5/COD increased to 0.68	[65]
Residue source	**Catalyst**	**Wastewater**	**Experimental conditions**	**Main results**	**Ref.**

Aerobic granular sludge from cosmetics factory	Iron supported on activated carbon	phenol, bromophenol blue or dimethoate aqueous solution (100 mg/L)	[Pollutant]: 100 mg/L [H_2O_2]: 500 mg/L [Cat]: 500 mg/L T: 80 ºC t: 4 h V: 50 mL pH: 3	Removal of: [Pollutant*]: Total [TOC]: 64%	[66]
Sludge from wastewater of reactor treatment in cosmetic industry	Iron supported on activated carbon	Antipyrine aqueous solution (20 mg/L)	[Pollutant]: 20 mg/L [H_2O_2]: 100 mg/L [Cat]: 500 mg/L pH: 3 V: 1 L T: 50 ºC t: 4 h	Removal of: [Pollutant]: Total [TOC]: 70%	[67]

Abbreviations: t = Time; T = Temperature; V = Pollutant volume; [Cat] = Catalyst concentration
*Tree different pollutant were tested, using one pollutant per batch, all were totally removed after 240 min of CWPO reaction

Most of the works that use some environmentally friendly source of carbon usually combine the carbon source with a metallic compound, mainly iron, to produce a mixed catalyst. The main concern in those works is the leaching of iron in the solution and the stability of the catalyst. The stability can be measured in a long continuous reactor run (more than 12 h reaction) or reusing the catalyst in several consecutive batches [60].

The majority of the works evaluated the CWPO of simulated matrices at low concentrations of organic pollutants (approximately 100 mg/L), which are not comparable with real wastewaters, which have more complex matrices. Very few works studied the use of carbon-based catalysts to treat real wastewaters and typically the results are not satisfactory for a one-step treatment, requiring a posterior biological treatment.

MATERIALS AND METHODS

3 MATERIALS AND METHODS

3.1 Reactants

The reactants used in this work, are given in the list below.

- Sulfuric acid (98%). Labkem. Formula: H_2SO_4
- Hydrogen peroxide (30% w/v). Fisher Chemical. Formula: H_2O_2
- Titanium (IV) oxysulfate (99.99% metal basis, *c.a.* 15 wt.% solution in sulfuric acid) Sigma-Aldrich. Formula: $TiOSO_4$
- Potassium phthalate monobasic (99.5%). Honeywell. Formula: $C_8H_5KO_4$
- Silver Nitrate for analysis, ACS, ISO. Panreac. Formula: $AgNO_3$
- Potassium Dichromate PA-ACS-ISO (99.5%). Panreac. Formula: $K_2Cr_2O_7$
- Nitric Acid (65%). Honeywell. Formula: HNO_3
- Mercury (II) Sulphate PA-ACS (99%). Panreac. Formula: $HgSO_4$
- Phenol crystallized (99.5%). Panreac. Formula: C_6H_6O.
- Sodium hydroxide (98.73%). Fischer. Formula: NaOH
- Sodium Carbonate. José M. Vaz Pereira S.A. Formula: Na_2CO_3
- Folin-Ciocalteu´s phenol reagent. Merck
- Lewatit TP 207 sodium form, ion exchange resin. Sigma-Aldrich
- Amberlite ITA-402(Cl), ion exchange resin. Alfa Aesar
- Potassium chromate (99.6%). Fischer. Formula: K_2CrO_4

As precursor for the catalyst mature compost (MC) was used. This compost was provided by the local waste management company (Resíduos do Nordeste, EIM, S.A.). More characteristics of the compost can be found elsewhere [68].

3.2 Preparation of the catalysts

Before the production of the materials, the MC was washed with water (100 g L^{-1}) under strong stirring in order 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 pretreated compost was sieved to obtain particle sizes of 53-106 µm.

The catalysts were obtained following the procedure described elsewhere [69]. Briefly, C-400 was produced by thermal treatment using 5 g of the homogenized compost, under an N_2 flow (100 $Ncm^3 min^{-1}$) at 120 ºC for 1 h and 400 ºC for 4 h (heating ramp 120 ºC min^{-1}). C-800 was produced in the same manner as C-400, but with a 1 h holding time at 120, 400 and 600 ºC, and at 800 ºC for 4 h (heating ramp 120 ºC min^{-1}). Two more materials were produced: (i) treating the compost precursor with H_2SO_4 before the described thermal treatment at 800ºC (C-S-800) and (ii) treating sample C-800 with H_2SO_4 (C-800-S). To obtain these two samples, 2.5 g of the precursor was immersed in 50 mL of an 18 mol L^{-1} H_2SO_4 solution for 3 h at 150 ºC. Posteriorly, all samples were thoroughly washed with distilled water until the neutrality of the rinsing waters and further dried overnight in an oven at 110 ºC.

Finally, a fifth sample was prepared by the thermal treatment described at 800 ºC, using as a precursor the sample C-800-S, resulting in the catalyst C-800-S-800.

Two additional catalysts were prepared by hydrothermal treatment of the MC. For this purpose, the hydrocarbonization was conducted in a 125 mL removable teflon vessel inserted in a stainless steel body (Model 249M 4744-49, Parr Instrument co., USA).

For the first catalyst, 2 g of compost was measured and mixed with 30 mL of distilled water. Then, the reaction vessel was inserted in an oven set at 150 ºC. After 2 h of HTC, the reaction vessel was removed and left to cool down overnight at room temperature. The solids were vacuum filtrated with a membrane filter (pore size: 0.45 µm), washed with abundant distilled water and dried in drying chamber overnight at 100 ºC, resulting in the catalyst HTC-150. The second catalyst was produced in the same way, except that 3 g of compost was used and the temperature of the oven was set at 230 ºC, leading to catalyst HTC-230.

3.3 Characterization of the materials

3.3.1 Chemistry surface

To determine the acidic and basic sites on the surface of the catalyst samples, 0.2 g of the catalyst was measured for each determination. For the acidic sites, the catalyst sample was added on an Erlenmeyer containing 25 mL of a 0.02 mol L^{-1} NaOH solution and stirred for 48 h at 320 rpm in an orbital shaker (IKA KS 130). The suspension was vacuum filtrated with a membrane filter (pore size: 0.45 µm), in order to remove the solid. Then, 20 mL of the resultant solution was titrated against a 0.02 mol L^{-1} HCl solution, using phenolphthalein as indicator.

For the basic sites, the same procedure was followed, but instead of using 25 mL of NaOH solution, the catalyst was added to 25 mL of a 0.02 mol L^{-1} HCl solution and the filtrated solution was titrated against a 0.02 mol L^{-1} NaOH solution. All the samples were analyzed in duplicate.

The pH_{PZC} of the samples was obtained using a methodology described elsewhere [70]. Briefly, six samples with 25 mL of a 0.01 mol L^{-1} NaCl solution were prepared, and the pH was adjusted to six different initial values (2, 4, 6, 8, 10, and 12) using a 0.02 mol L^{-1} solution of HCl and NaOH. In each of the solutions, 0.2 g of the carbon material was added, and the suspension stirred for 24 h with 360 rpm, then the suspensions were filtered and the equilibrium pH was measured. The pH_{PZC} value of the carbon material was determined by the intercept between the obtained curve of final pH vs initial pH with the straight-line final pH = initial pH.

This characterization is one of the most important parameters used to describe surfaces with variable charges and is usually made combined with the acidity and basicity sites, one being complementary to another [71].

The FTIR spectra of the samples were performed on a Perkin Elmer FT-IR spectrophotometer UATR Two infrared spectrophotometer. The range of wavenumbers used was from 450 to 4000 cm^{-1}. All the measurements were done at room temperature using the solid samples.

3.3.2 Composition

For determination of the ash content, a crucible was washed with a 10% HNO_3 solution and placed in a muffle furnace at 450 ºC for 4 h. Then, around 0.2 g of samples were measured. 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 inside a desiccator and the mass was measured. This process was repeated until the mass of the crucible with the sample reaches a constant mass between the measures. All the samples were analyzed in duplicate.

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

3.4 Catalytic runs

3.4.1 H_2O_2 decomposition

The decomposition of H_2O_2 was performed in a 100 mL Erlenmeyer, with continuous stirring, 50 ºC, a catalyst load of 1.8 g L^{-1}, a H_2O_2 concentration of 85.71 g L^{-1} (determined based on the necessary amount to mineralize the COD content of the leachate), and 25 mL of distilled water, and the test was carried out during 24 h. All catalysts were assessed under different pH conditions (3, 6 and 9).

Samples were taken at 0, 30, 60, 120, 240, 360, 480, and 1440 minutes of reaction. Blank tests, without any catalyst load, were also performed.

3.4.2 CWPO treatment of the leachate

The CWPO runs were carried out in a 500 mL continuously stirred reaction vessel, equipped with a condenser, for 24 h. First, the leachate with the adjusted pH (by means of H_2SO_4 1 M and NaOH 1 M) was added to the reactor, which was submerged in an oil bath with temperature control. Upon reaching the desired temperature, the quantity of hydrogen peroxide needs to reach a concentration of 85.71 g L^{-1} was added. This concentration was established according to the leachate COD concentration of 53 g L^{-1}, using the theoretical relation that the COD and the O_2 concentration needed to oxidize the total organic matter is equal. After the complete mixing of the reactants, the first sample was taken, and the catalyst was added, 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. Before the analysis of any sample, they were centrifugated in order to remove the catalyst. Figure 6 shows the system used for the CWPO runs.

Figure 6: System used for the CWPO runs

At the end of CWPO runs, pH (Bante Instruments – PHS-3BW Bench TOP pH/mV/ºC Meter), conductivity (WTW InoLab Cond Level 1), and turbidity (WTW Turb 550) were measured at room temperature.

When the CWPO test was concluded, the catalyst was removed from the solution by centrifugation and the supernatant was collected to further analyze the concentration of chlorides, aromaticity, phenolic compounds, BOD_5, turbidity, and iron.

In order to optimize the CWPO of the leachate, several experiments were conducted changing temperature (50 and 80 ºC), the pH (pH = 3; pH = 6, and the natural pH of the leachate (7.3)). Also, the catalyst load was studied, testing three different concentrations: 1.8; 3.6; 7.2 g L^{-1}.

To evaluate the effect of the hydrogen peroxide introduction in the system, some tests were performed adding the hydrogen peroxide in batches of 2 mL each hour, on the times 0; 1; 2; 3 and 4 h. For these tests, the samples were taken after the addition of the hydrogen peroxide, and an additional sample at 3 h was analyzed as well.

3.5 Resin pretreatment of the leachate

Some runs of CWPO were conducted with leachate treated by cationic and anionic resins. The first ion exchange was done using TP207 resin, a cationic resin that allows removing cations. 150 mL of the leachate with a pH previously adjusted to 9.5 was added to an Erlenmeyer along with 3.0 g the resin and stirred for 48 h. After the adsorption time, the leachate was vacuum filtrated with a paper filter. The leachate was characterized after the resin treatment. The second treatment followed the same procedure abovementioned, using IRA-402(Cl) ion exchange resin, under the same operating conditions, except for the pH which was adjusted to 3. The objective of this step was to eliminate chloride interference.

Both treatments were conducted separately and sequentially by treating the leachate with resin TP 207 and subsequent treatment with the resin IRA-402(Cl). The objective of this double treatment with resins was to eliminate the interference of both cations and chlorides. CWPO tests were performed using the leachate after the treatment with these resins.

3.6 Analysis of the effluent samples

The analytical methods described below were used to characterize the leachate, the samples during the CWPO runs and the CWPO effluents.

3.6.1 Hydrogen peroxide determination

For monitoring hydrogen peroxide during the CWPO runs, a UV-VIS colorimetric methodology was employed, using a T70 UV/VIS Spectrophotometer – PG Instruments equipment, previously described elsewhere [72]. Briefly, in a 10 mL volumetric balloon, 1 mL of the sample was added (previously diluted 100 times), along with 1 mL of a 0.5 mol L^{-1} H_2SO_4 solution, 0.1 mL of $TiOSO_4$ 15 % reactant, and completing the volume with distilled water. The samples were analyzed at a wavelength of 405 nm.

A calibration curve to correlate the concentration of H_2O_2 with absorbance was constructed, in the range of H_2O_2 concentrations from 0 to 1200 mg L^{-1}. The calibration curve obtained is represented in Figure 7. The R^2 value is 0.9994, indicating a good linear fit.

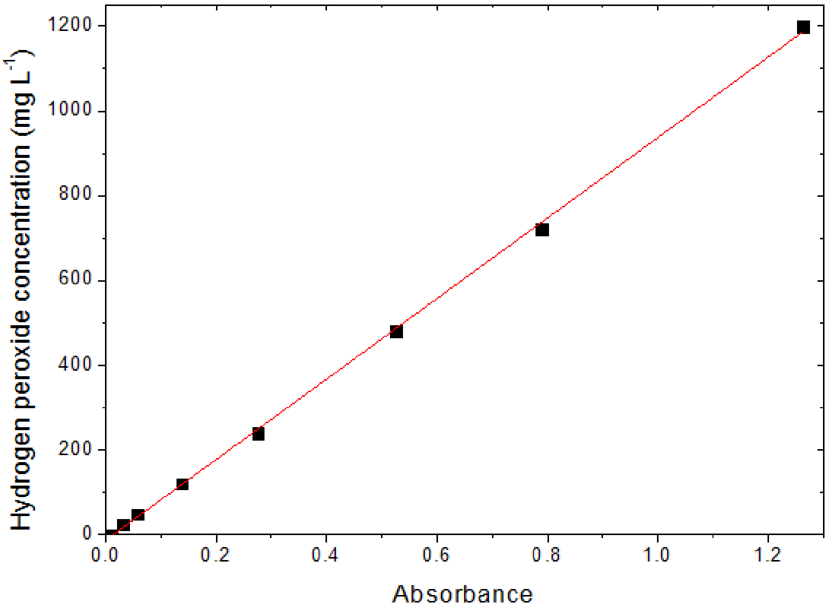

Figure 7: Calibration curve for the determination of hydrogen peroxide concentration

3.6.2 Determination of COD

COD was measured using a colorimetric methodology, as described elsewhere [6]. For the determination of COD, two solutions were initially prepared. First, the digesting solution was prepared by diluting potassium dichromate (0.0167 mol L^{-1}) and mercury sulphate (0.0169 mol L^{-1}) in concentrated sulphuric acid. The mercury sulphate is used to eliminate the interference of the chlorides in the determination of COD, which is the most common interference in this method [73]. The second solution (acid solution) was prepared by diluting silver nitrate (0.0213 mol L^{-1}) in concentrated sulphuric acid.

The COD procedure was as follows: on a test tube, 0.75 mL of the digesting solution was added, followed by 3.25 mL of the acid solution and 2 mL of the sample (previously diluted 500 times). The reactants were mixed with the aid of a vortex. Then, the tubes were placed in a digester block (Hanna instruments HI 839800 COD Reactor) for digestion at 150 ºC for 2 h. After cooling to room temperature, the samples were analyzed by UV–VIS spectrophotometry, at the wavelength of 440 nm to determine its absorbance. All the samples were analyzed in duplicate.

Equations (3), (4) and (5) represent the reactions involved in this methodology [73]. In equation (3), the general reaction between potassium dichromate and organic matter is shown, with potassium hydrogen phthalate used to represent the organic matter. Equation (4) shows the relation of how many moles of oxygen are needed to oxidize the organic matter, again represented by potassium hydrogen phthalate. Those equations show that one mole of dichromate oxidizes the amount of potassium hydrogen phthalate that is equivalent to 1.5 mol of O_2. Equation (5) represents the reaction where mercury eliminates the interference of chloride.

$$10K_2Cr_2O_7^{2-} + 2KC_8H_5O_4 + 41H_2SO_4 \leftrightarrow 16CO_2 + 46H_2O + 10Cr_2(SO_4)_3 + 11K_2SO_4 \quad (3)$$

$$15O_2 + 2KC_8H_5O_4 + H_2SO_4 \leftrightarrow 16CO_2 + 6H_2O + K_2SO_4 \quad (4)$$

$$Hg^{2+} + 2\,Cl^- \leftrightarrow HgCl_2 \quad (5)$$

In order to determine the concentration of COD in the samples, a calibration curve was built, in the range of 0 to 150 mg L^{-1}, using potassium hydrogen phthalate as standard and following the digestion procedure described above. The calibration curve is represented in Figure 8. The R^2 value is 0.9899, which indicates a good linear fit.

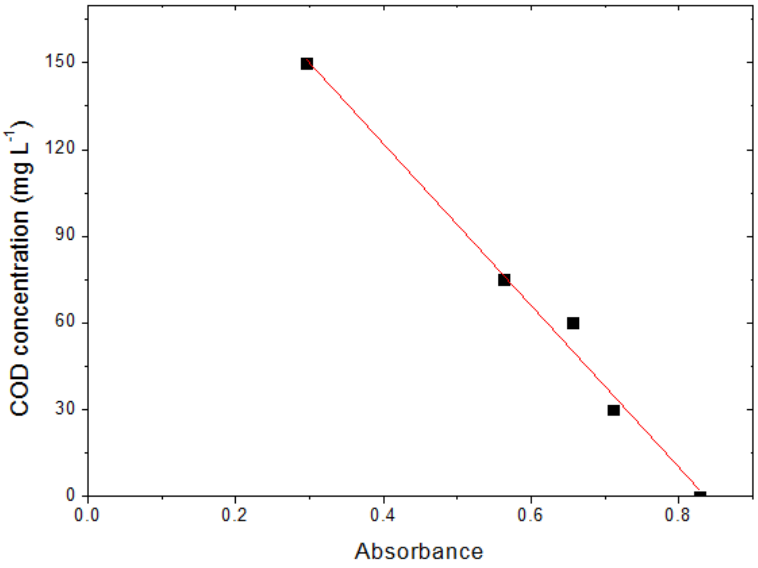

Figure 8: Calibration curve for determination of COD

Another interference in the COD measurement is the presence of H_2O_2. Since hydrogen peroxide is used during CWPO, it was necessary to build a calibration curve of the concentration of H_2O_2 versus the COD value, to make it possible to discount the contribution of H_2O_2 on the determined COD. To build this curve, several solutions of known concentrations of H_2O_2 were digested following the procedure described above and analyzed by UV-VIS at 440 nm. This calibration curve is represented in Figure 9. The R^2 value is 0.9935, indicating a good linear fit.

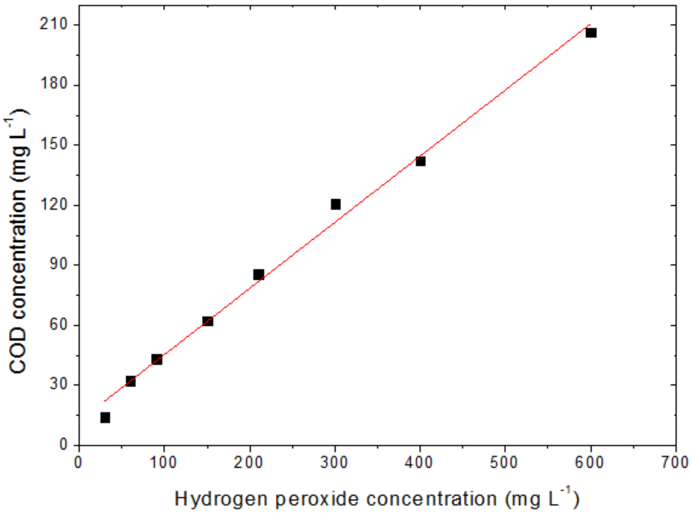

Figure 9: Calibration curve for correction of the interference of the presence of hydrogen peroxide in the COD measurement

To eliminate the interference of H_2O_2 on the COD measured, Equation 6 was obtained from the calibration curve of Figure 9, where $COD_{app.}$ is the apparent COD value and the COD_{real} is the COD without the interference of H_2O_2.

$$COD_{real} = COD_{app.} - 0.3305 * [H_2O_2]\ mg\ L^{-1} + 12.39\ mg\ L^{-1} \qquad (6)$$

3.6.3 Determination of TOC

The TOC was determined using a Shimadzu TOC-L CSN analyzer, with the samples being previously diluted 100 times.

3.6.4 Determination of BOD_5

The BOD_5 was determined by the standardized respirometric OxiTop method (WTW, Weilheim, Germany), adapting a methodology reported elsewhere [6]. 43.5 mL of sample (previously diluted 100 times) was placed into a brown glass bottle equipped with a magnetic stirrer and NaOH pellets in the headspace. Then the bottles were placed in an incubator box with a constant temperature of 20 ºC, during the five days, for incubation purposes. After the incubation period, the OxiTop equipment delivers the result of BOD_5.

To compensate for the interference of residual H_2O_2 on the samples, an equation considering the theoretical interference was used, as previously described elsewhere [6]. Equation 7 shows the relation between H_2O_2 concentration and its compensation on the BOD_5 measurement.

$$BOD_5 = BOD_{5\,app} + 0.4706 * [H_2O_2] \tag{7}$$

3.6.5 Determination of chlorides

Chloride was determined using the Mohr method. A solution of 0.05 mol L^{-1} $AgNO_3$ was used to titrate 5 mL of the sample, with 50 mL of distilled water, using a solution of K_2CrO_4 as an indicator. Before the titration, the pH of the samples was adjusted within the range 6 to 9.

3.6.6 Determination of aromaticity

Aromaticity was determined by measuring the absorbance of the samples, previously diluted 100 times in a pH 7 buffer solution, at a wavelength of 254 nm, in which most aromatic compounds typically present the maximum value of absorbance [74].

In order to truly determine the aromaticity of the samples, it was necessary to make a calibration curve, in the range of 0 to 200 mg L^{-1}. For this purpose, a phenol was used as model compound. The calibration curve is represented in Figure 10. The R^2 value of 0.9987 indicates a good linear fit.

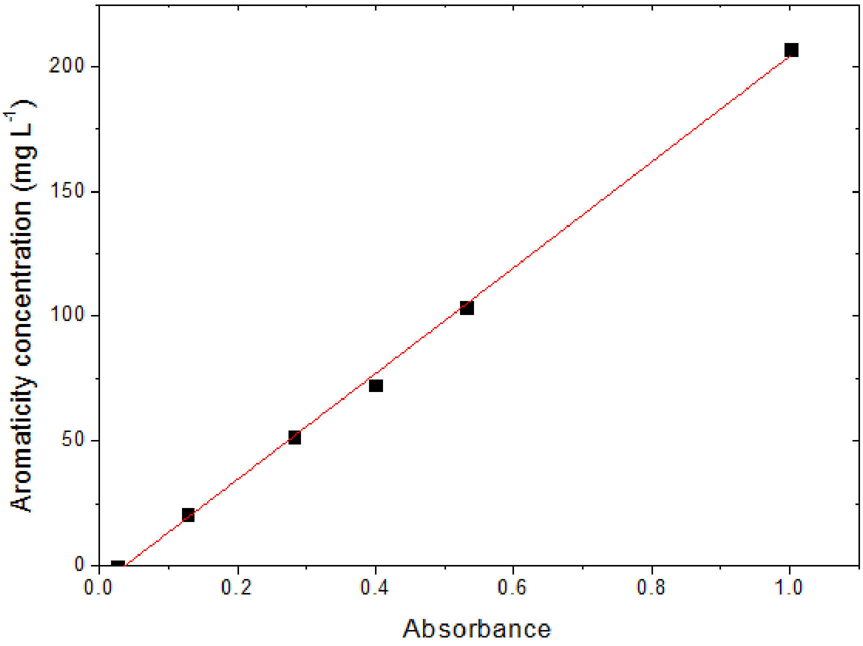

Figure 10: Calibration curve for determination of aromaticity

3.6.7 Determination of phenolic compounds

The determination of phenolic compounds was made using the Folin-Ciocalteu method, adapting a methodology described elsewhere [75,76]. In a 30 mL glass flask, 0.5 mL of the Folin-Ciocalteu reactant was added, along with 0.2 mL of the sample (previously diluted 50 times) and 8.2 mL of distilled water. The solution was left to rest for 10 minutes. After this, 1 mL of a 10% Na_2CO_3 solution was added. The flask was left to rest for 60 minutes, after which the samples were analyzed in a UV-VIS equipment at the wavelength of 765 nm.

A calibration curve was built, in the range of 0 to 100 mg L^{-1}, using phenol as the model compound. The calibration curve is represented in Figure 11.

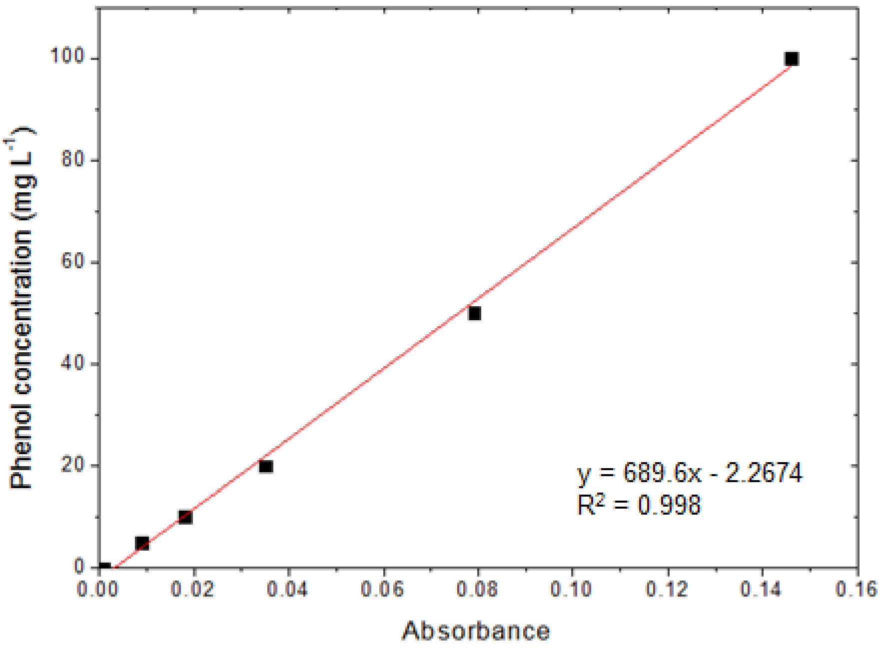

Figure 11: Calibration curve for the determination of phenolic compounds

3.6.8 Determination of iron

For the determination of iron 2.5 mL of the leachate waters was placed in a teflon vessel with 7.5 mL of *aqua regia* (1:3 HNO_3: HCl, molar basis). The Teflon vessel was inserted in a stainless steel body and the vessel was digested for 48 h at 60 ºC. After cooling to room temperature, the liquid was filtrated using a syringe filter (pore size: 0.45 µm) and the volume was made up to 50 mL using a 5% HNO_3 (v/v) solution.

To determine the iron content of the CWPO effluents, 1 mL of the samples were diluted in a 10 mL volumetric ballon, using a 5% HNO_3 (v/v) solution and filtered using a syringe filter (pore size: 0.45 µm). The iron content was measured by an atomic absorption spectroscopy, using a Varian SpectrAA 220.

3.6.9 Determination of colour number (CN)

The CN determination was determined by a methodology described elsewhere [77,78]. Briefly, 0.2 mL of the sample was mixed with 2.8 mL of distilled water, and the resultant solution was analyzed on a UV-VIS, in the wavelengths of 436, 525 and 620 nm. After this analysis, the spectral absorption coefficient (SAC) was calculated, as described in Equations 8 and 9.

$$SAC = \frac{E}{x} \tag{8}$$

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \tag{9}$$

SAC was calculated as described on Equation 8, dividing the absorption (E) by the cuvette length (x). In this work, the x = 0.01 m. After calculating the SAC for each wavelength, Equation 9 was applied to obtain the CN.

3.7 Calculation methods

The standard derivation, was obtained by applying Equation 10.

$$S.D. = \sqrt{\frac{\sum|x_i - \bar{x}|}{n}} \tag{10}$$

On this equation, x_i represents the value, $\bar{x}$ represents the arithmetic media of the x values, and n the number of samples.

To calculate the efficiency of the hydrogen peroxide consumption, one parameter is selected, such as COD or TOC, and the formula is presented in Equation 11, where the $X_{parameter}$ represents the normalized removal of the parameter after 24 h of reaction and the $X_{H_2O_2}$represents the normalized consumption of H_2O_2 after the same period of time.

$$H_2O_{2_{efficiency}} = \frac{X_{parameter}}{X_{H_2O_2}} \tag{11}$$

The maximum efficiency possible to obtain is 1, and as closer to 1 the efficiency is, the more efficient was the consumption of H_2O_2.

RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSION

4.1 Catalysts characterization

4.1.1 Composition

The results of ash content and the elemental analysis of the catalysts produced from compost are shown in Table 6.

Table 6: Elemental composition and ash content of the compost and of the catalysts

Catalyst	C/H	C (%)	H (%)	S (%)	N (%)	Ashes (%)	Non-identified* (%)
MC	9.3	21.3	2.3	0.6	1.7	55.5	18.6
C-400	17.2	18.9	1.1	0.4	1.1	64.9	13.6
C-800	44.0	17.6	0.4	0.5	0.0	81.5	0.0
C-S-800	41.9	31.0	0.7	0.8	0.9	65.9	0.7
C-800-S	37.6	18.8	0.5	8.2	0.0	69.2	3.3
C-800-S-800	52.9	22.0	0.4	0.6	0.3	76.7	0.0
HTC-150	10.2	20.0	2.0	1.5	0.1	35.9	40.6
HTC-230	11.0	19.3	1.7	1.2	0.1	32.6	45.0

* Non-identified content is the value resulting from the subtraction of 100% by the content on C, H, S, N and ashes.

The pyrolyzed materials (C-400, C-800, C-800-S, C-S-800 and C-800-S-800) showed the highest values of C/H ratio (17.2-52.9), as expected since the thermal treatment leads to the release of many volatile compounds, such as water. This fact is also supported by the increase of the ashes content upon pyrolysis (from 55.5 up to 81.5%), reflecting the loss of volatile compounds, which generates a higher proportion of ashes content in comparison with the total mass of the material. As observed, the values of C/H ratio for all samples are higher than in the pristine material (C/H > 9.3), revealing that carbonization was successfully accomplished.

Regarding the ashes content, it can be observed that HTC leads to a decrease of around 20% when compared to the precursor (MC), 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 [68]. As observed, in pyrolised samples N.I. decreased from the raw material (18.6%) to values close to zero. For the material C-400, since the thermal treatment was performed at lower temperature, it is expected less elimination of volatile compounds, fact reflected in a higher N.I. when compared with C-800, that reached a superior elimination of volatile compounds due the higher temperature used in the thermal treatment. For the hydrochars (HTC-150 and HTC-230), N.I. reaches values of 40.5-45.0%, likely due to hydroxylation and to the formation of surface oxygen groups onto the materials.

4.1.2 Surface chemistry

Following the procedures previously described, the catalyst was characterized for acidity, basicity and pH_{PZC}. Those characterizations were only done for the materials selected for application in the CWPO runs C-800 and HTC-230 (The catalyst selection for the CWPO runs is explained in session 5.3 of this work). The results obtained are presented in Table 7 (Figure 12: pH_{pzc} for the HTC-230 and C-800 samplesFigure 12 shows the interception of pH for the determination of pH_{PZC}).

The charge of a material surface changes as pH is modified. The surface charges of the material are totally equilibrated and equal to zero at pH_{pzc}. For materials with more acidic sites on its surface, the pH of zero charge will be lower than the neutral pH, and the opposite is observed for materials with higher basicity.

Table 7: Results for the acidity, basicity and pH_{pzc} analysis

Samples	Acidity (mmol/g)	Basicity (mmol/g)	pH_{PZC}
C-800	0.9	2.5	11.0
HTC-230	1.1	1.4	7.5

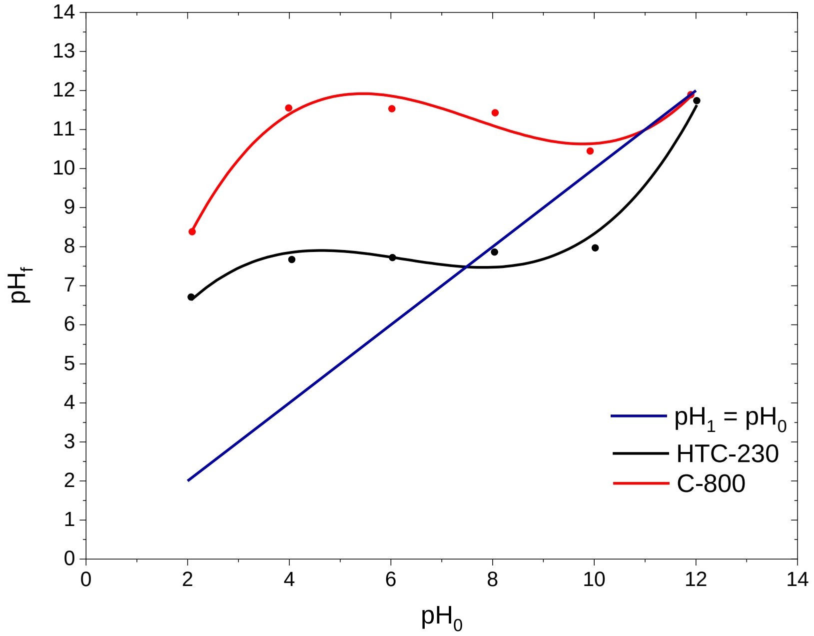

Figure 12: pH_{pzc} for the HTC-230 and C-800 samples

For C-800, the amount of basic sites is almost 3 times the amount of acid sites, resulting in a very basic pH_{pzc} of 11.0. The difference is notable when compared to sample HTC-230, which posses a more balanced acid and basic relation, and a more neutral pH_{pzc}. Both pH_{pzc} are in accordance with their acid/base properties.

The selected materials were also characterized by FTIR. The obtained spectra are shown in Figure 13.

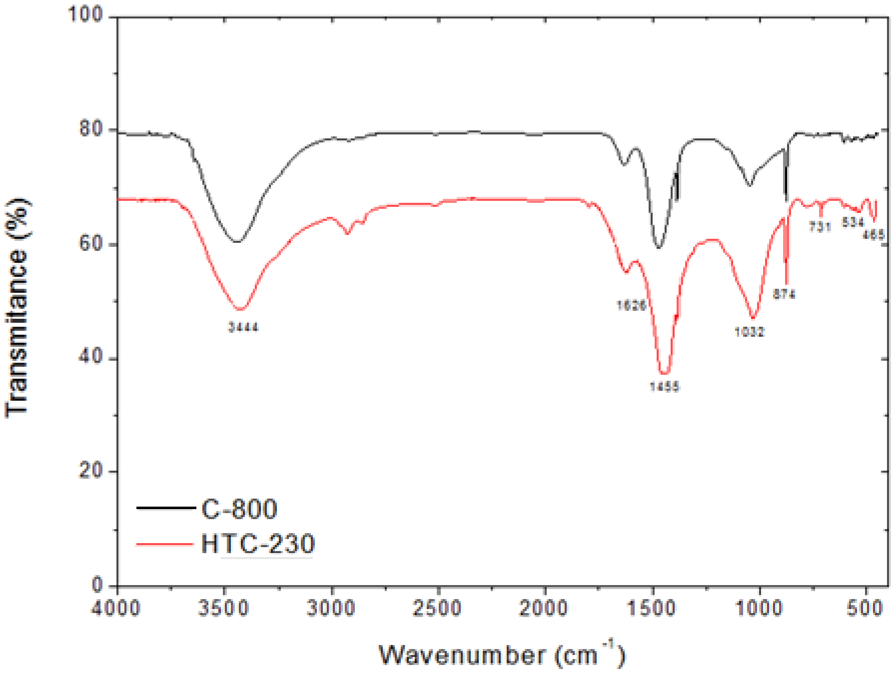

Figure 13: FTIR spectra of C-800 and HTC-230

It is possible to observe that the spectra are similar for both materials in the range of 4000 to 850 cm^{-1}, with minor changes in the transmittance intensity of the bands. The band with a peak at 3444 cm^{-1} is attributed to the –OH stretching of the water molecules adsorbed on the materials [79]. Bands between 1800 and 1000 cm^{-1} were also identified in both samples, the band at 1626 cm^{-1} attributed to C=C stretching vibrations on aromatic groups [80], the band at 1455 cm^{-1} to the C-H deformation on organic compounds [79] and the band at 1032 cm^{-1} represents the stretching vibrations of the Si–O bond group [80], highlighting the presence of inorganic non identified species (such as Si). In addition, in both samples, the band appearing at 874 cm^{-1} corresponds to the C-H out of plane bending vibration [81] and the bands in the range of 600 to 400 cm^{-1} are usually attributed to the presence of metals in the samples [80].

4.2 Characterization of the leachate

The characterization of raw leachate collected at the exist of the MTB plant is shown in Table 8.

Table 8: Physico-chemical characteristics of the raw leachate

Parameter	Unity	Value	Standard derivation
COD	g L^{-1}	59.9	3.9
BOD_5	g L^{-1}	23.3	1.1
pH at 25 ºC	-	7.2	-
Conductivity	mS cm^{-1}	38.8	-
Turbidity	NTU	410	6
Chloride	g L^{-1}	5.01	0.01
Phenolic compouns	g L^{-1}	0.70	0.05
Aromaticity	g L^{-1}	10.21	0.6
TOC	g L^{-1}	26.76	0.43
Iron	mg L^{-1}	38.9	2.8
CN	m^{-1}	40.0	-

Analyzing the characteristics of the leachate used in this work, it is notable the high values of several parameters, such as COD and TOC. The characterization confirms that the leachate matrix has a high concentration of aromatic (10.21 g L^{-1}) and phenolic (0.70 g L^{-1}) compounds and several non-identified organic substances (TOC = 26.76 g L^{-1}), generating a hard environment for the oxidation tests.

The leachate also has high concentrations of chlorides (5.01 g L^{-1}), which could decrease the performance of the CWPO process, by the mechanisms explained in section 3.3. The conductivity (38.8 mS cm^{-1}) also shows that the leachate has other ions that were not identified, such as bromides, sulfates and metallic ions, which can also be a problem in CWPO.

The concentration of iron is not very high, so it is expected that the Fenton process does not have a big contribution in the oxidation of the organic matter with hydrogen peroxide.

4.3 Hydrogen peroxide decomposition

Prior to the assessment of the catalysts in the CWPO of the raw leachate, a catalyst screening in the hydrogen peroxide decomposition was performed, in order to select the best catalysts for CWPO. In Figure 14, the hydrogen peroxide abatement with all catalysts, excluding the precursor MC, at three different pH values is represented.

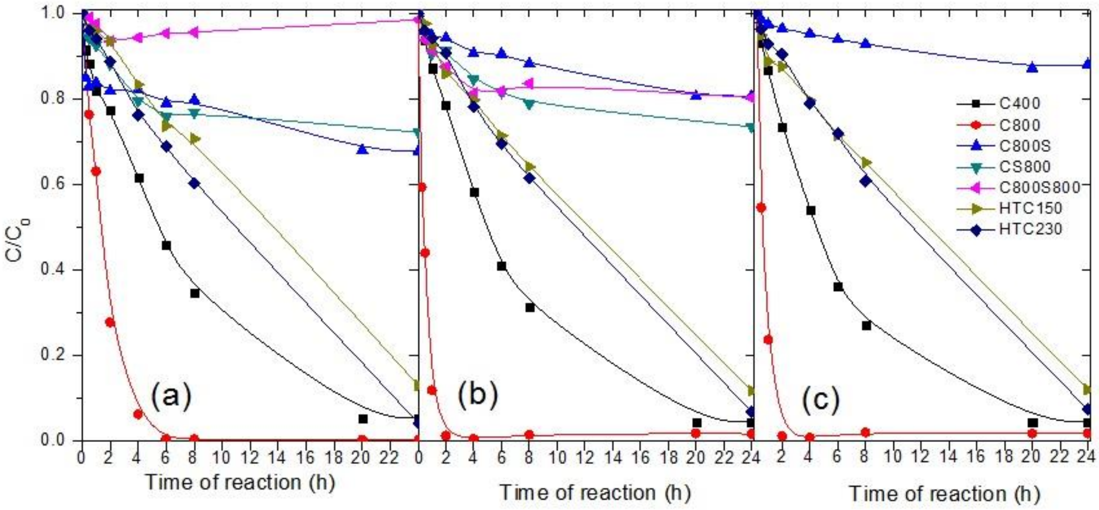

Figure 14: Kinetics of hydrogen peroxide decomposition for the screening of the catalysts with (a) pH = 3.00 ± 0.02, (b) 6.00 ± 0.02 and (c) 9.00 ± 0.02

The majority of the catalysts presented good activity for the degradation of hydrogen peroxide, regardless of the pH considered.

It is observed from Figure 14 that the materials C800-S, C-S800 and C-800S800 were only able to convert 10-30% of the initial hydrogen peroxide.

The highest activities towards H_2O_2 decomposition were found for the catalysts HTC-150, HTC-230, C-400 and C-800. After 24 h, those materials were able to convert more than 90% of hydrogen peroxide. In terms of kinetics C-800 shows the highest catalytic activity in the decomposition of H_2O_2, this material being capable to degrade more than 90% of H_2O_2 within 2-4 h of reaction, regardless of the pH considered. This is explained by the high concentration of basic sites on the surface of the catalyst, enhancing the decomposition of hydrogen peroxide due to the ability of basic functional groups to donate electrons to the H_2O_2 molecules.

The decomposition of H_2O_2 is an important reaction to pre-assess the potential of a catalyst for CWPO. However, it is known that when an hydrogen peroxide molecule is broken, not always lead to the formation of oxidizing radicals, since sometimes side reactions can occur, producing water and oxygen, that do not contribute to the mineralization of organic matter. To circumvent the occurrence of this type of side reactions, slower kinetics may avoid reactions between radicals ($HO^{\bullet}$, $HOO^{\bullet}$ and $O_2^{\bullet-}$) that would lead to the formation of water and oxygen [34]. It is also reported that a faster H_2O_2 decomposition rate does not always result in an increased mineralization [82], so in this sense, the catalyst HTC-230 was also chosen since it is able to consume almost all hydrogen peroxide in the 24 h of reaction time for every pH, but with slower kinetics.

It can be easily observed that pH does not have a big impact on the final consumption of H_2O_2. For catalyst HTC-230, the higher consumption occurred at pH 3, and for catalyst C-800, all pHs tested showed similar results.

The results of H_2O_2 decomposition obtained for both materials reveal their high catalytic activity when comparing with other reported results. In the work performed by Ribeiro *et al.* 2013, six carbon-based materials with different activation processes were tested in the decomposition of H_2O_2, considering a lower H_2O_2 load, 34.6 mmol L^{-1}. Under the reported conditions, only one material was able to decompose more than 50% of the initial load after 150 min, while the other materials presented less than 10% decomposition. In this work, C-800, with the much higher H_2O_2 load of 2.52 mol L^{-1} (almost 75 times higher), after 3 hours was able to decompose more than 90% of H_2O_2 under all pH tested, and even HTC-230, with slower kinetics, was able to degrade around 50% of H_2O_2 [82].

4.4 CWPO runs

4.4.1 The effect of pH

As reported in literature, when real CWPO tests are performed in alkaline conditions, the efficiency is generally worse than in neutral or acidic conditions, leading to a loss of performance of around 50% [34]. Taking this into consideration, in this work the CWPO of leachate was tested in acidic pH and the highest pH value tested was the natural pH of the leachate.

The operation of CWPO in pH values different from the pH_{PZC} of the catalysts has an appreciable influence, since CWPO is a surface phenomenon that can have the efficiency changed by the different charges at the surface, which interact with the molecules in the liquid phase, affecting the conversion of hydrogen peroxide.

In order to experimentally evaluate this influence, three pH values were tested with the catalysts selected upon the H_2O_2 decomposition tests (C-800 and

HTC-230). The obtained H_2O_2, COD and TOC decay curves upon reaction time are shown in Figure 15.

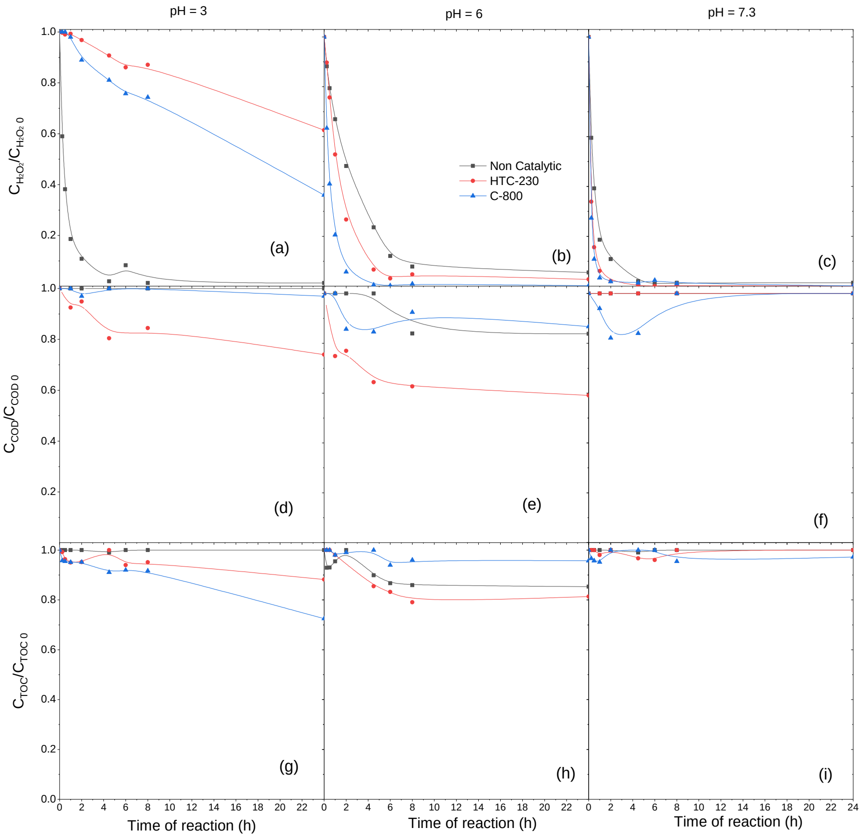

Figure 15: Normalized concentration of H_2O_2, COD and TOC upon time in CWPO runs considering Black: No catalyst, Red: HTC-230 and Blue: C-800, under the experimental conditions: (a) pH = 3.00 ± 0.02, (b) 6.00 ± 0.02 and (c) and natural leachate pH, Catalyst = 1.8 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1}, T = 80 ºC

As observed, the CWPO tests at pH 3 presented slower kinetics of H_2O_2 decomposition, the catalysts not being able to degrade completely the H_2O_2 in 24 h. The consumption of H_2O_2 reaches 39% with HTC-230, whereas 65% was obtained with C-800. This low decomposition and the fact that in acidic pH the interference of the chlorides as hydroxyl radical scavengers is higher [6], reflected the low decomposition results in terms of COD and TOC. C-800 at these conditions was able to degrade 28% of TOC.

For the reaction without catalyst at pH 3, it is observed that the consumption of hydrogen peroxide was almost full after 4 h, although in this case was not observed any decrease in the COD and TOC values. This phenomena may be caused by the consumption of the H_2O_2 generating species that are not powerful oxidants needed for the CWPO.

For the reaction without catalyst, the H_2O_2 degradation efficiency, measured in terms of COD, was 0.06, whilst for the reaction with the HTC-230 the efficiency was 0.67, enhancing the efficiency 10 times, proving that the presence of catalysts enhanced the efficiency of the decomposition of H_2O_2 into the desirables radicals capable of oxidizing the organic matter.

Regarding the tests carried out at pH 6, the conversion of H_2O_2, COD and TOC reached a constant value after 6 h of reaction in all experiments, likely due to the complete consumption of H_2O_2. In these cases H_2O_2 was not consumed efficiently as on the pH 3, for the HTC-230 on pH 3 the efficiency in terms of COD was 0.67 against 0.41 for the same catalyst under pH 6. Besides being less efficient, the best result in terms of COD removal was obtained at this condition, pH 6 with the material HTC-230, achieving a COD removal of 41%.

At the natural pH of the leachate (7.3), which is economically the more desirable option, the results were not promising. In any of the tests performed was not possible to achieve 10% of COD or TOC removal.

The CWPO results at neutral pH were already expected, as discussed in section 3.4, since the mechanism of CWPO may change and other ions begin to act as scavengers, like carbonates [6]. Comparing the results obtained at neutral pH with those at the other pHs, the neutral pH is by far the less promising experimental condition and the less efficient in terms of H_2O_2 consumption.

It has been previously reported that at acidic and neutral pH the consumption of H_2O_2 during the CWPO of industrial wastewater is very similar, while the elimination of organic pollutants is higher in acidic condition [34]. In addition, it was confirmed in those experiments, carried out at pH 6 and 7.3, that the consumption of H_2O_2 is very similar, however, the removals of COD and TOC are remarkably higher at more acidic pH.

In the work of Diaz de Tuesta *et al.* (2019), the effect of pH on CWPO was also studied, considering 4-nitrophenol as model pollutant. It was observed that a more acidic pH enhanced the removal of the organic pollutant, while the consumption of H_2O_2 was not very affected. This observation was related to an increase in the efficiency of H_2O_2 consumption (defined as ratio of TOC to H_2O_2 conversion) as pH decreases [83]. In this work, in opposition to what was reported by Diaz de Tuesta *et al.* (2019), the pH presented a high influence on the consumption of H_2O_2, which may be attributed to the complexity of the leachate matrix. However, it was also observed that the efficiency of consumption of H_2O_2 was enhanced at more acidic pH.

The most promising results were found at pH 6 and 3. At pH 3 there is a big opportunity to enhance the process since hydrogen peroxide consumption was not fully achieved and, when comparing the results of COD and TOC removal at pH 3 and 6, similar values are obtained, showing that the more efficient consumption of H_2O_2 occurs at pH 3 rather than at another pH. Although not being the most efficient pH to consume H_2O_2, the better results of COD and TOC removals were obtained at pH 6, with HTC-230 showing a COD removal of 41%, even with the lowest catalyst concentration.

In Figure 16 are shown the removal results of the other analyzed parameters.

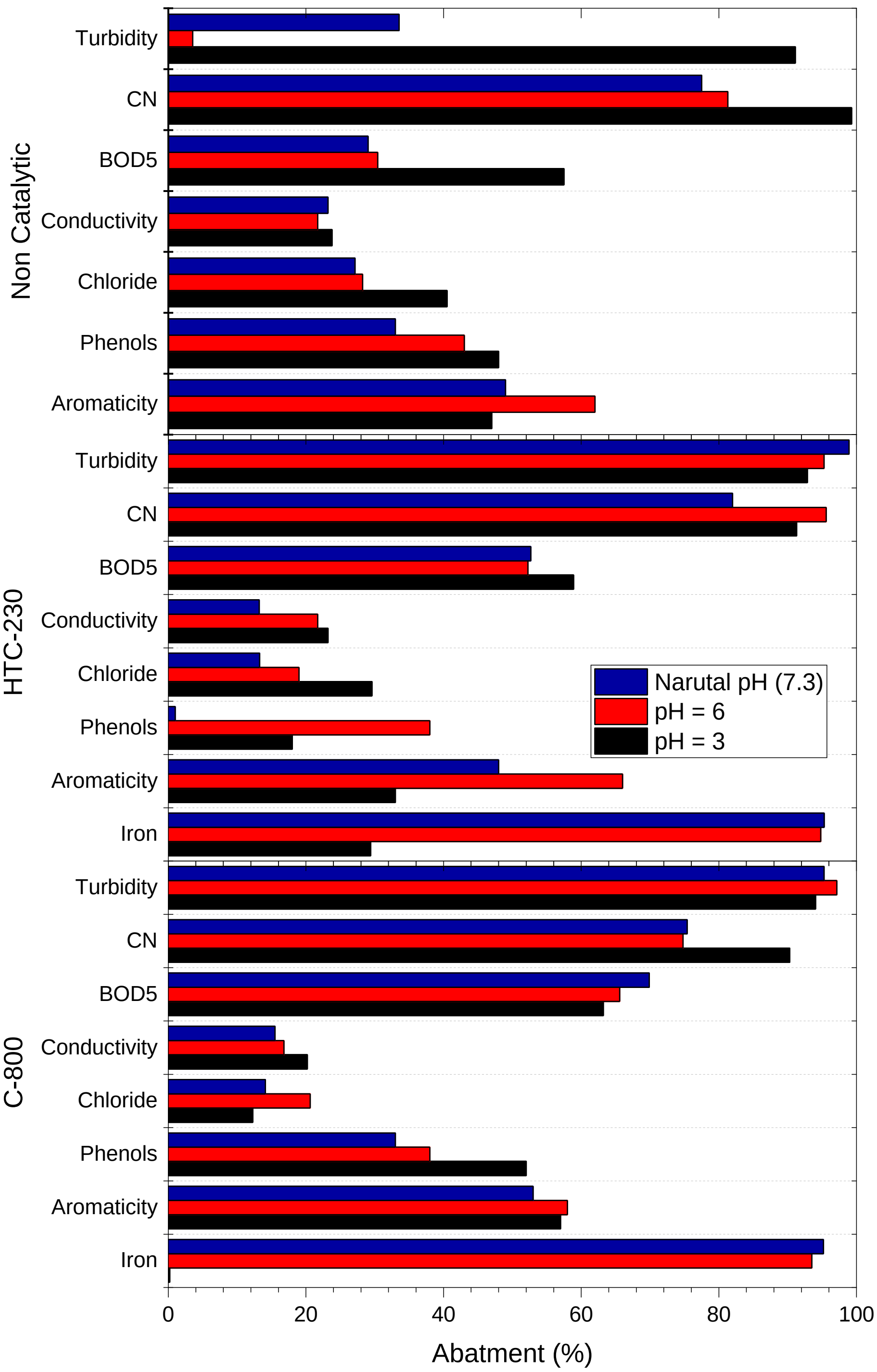

Figure 16: Abatement of CN, turbidity, BOD$_5$, aromaticity, phenols, conductivity, chlorides and iron after 24 h of reaction under the following experimental conditions: pH = 3.00 ± 0.02, 6.00 ± 0.02 and natural leachate pH (7.3), $C_{Catalyst}$ = 1.8 g L^{-1}, $V_{Leachate}$ = 25 mL and C_{H2O2} = 85.71 g L^{-1}

At the natural pH of the leachate (7.3) only the BOD$_5$, CN, aromaticity and, in some cases, the removal of the phenolic compounds were a little satisfactory, and the general results were worse, corroborating with the results of TOC and COD elimination. These results also confirm that the natural leachate pH is not suitable for the CWPO. The removal of BOD_5 is questionable since it was not followed by the reduction of TOC or COD and, theoretically, all the BOD_5 is also COD.

It is notable how the presence of the catalyst enhanced the removal of all parameters, except the chlorides, proving the necessity of catalysts to perform the treatment of the leachate by CWPO. The higher removal of chlorides with no catalyst could be caused by the higher easiness to act as radical scavengers without the presence of the catalyst, considering that the catalyst surface can interact and adsorb those ions, making them unavailable to react with the radicals.

For C-800 and HTC-230, pH had a minor influence, where for most of the parameters, the variation of the abatement on the different pH was lower than 10%. Both catalysts were able to degrade more than 80% of CN and turbidity, regardless of the pH considered.

In the work performed by Bautista *et al.* (2011), the effect of pH on the CWPO of phenol was studied and it was observed that at lower pH values the phenol oxidation was enhanced [83]. Similar results were obtained in this work, where for all CWPO runs, except those with HTC-230, the higher removal of phenolic compounds was achieved with more acidic pH.

4.4.2 The effect of temperature

In order to evaluate the effect of temperature on the CWPO runs, two experimental runs were conducted at 50 and 80 ºC with the catalyst HTC-230, as shown in Figure 17.

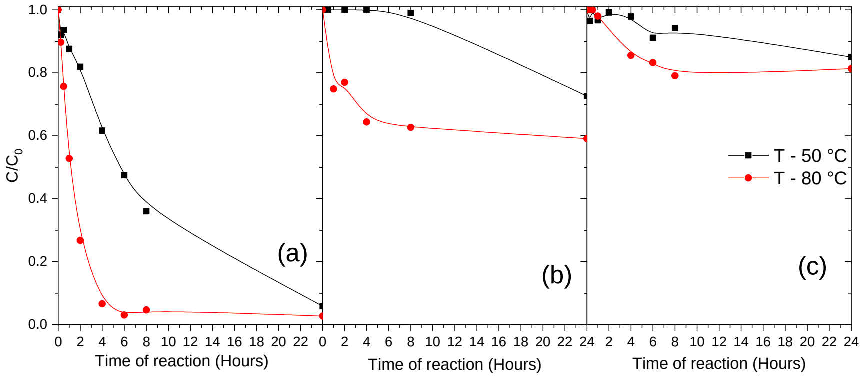

Figure 17: Normalized concentration of (a) H_2O_2, (b) COD, and (c) TOC upon time in CWPO runs performed with catalyst HTC-230 under the following experimental conditions: pH = 6.00 ± 0.02, $C_{Catalyst}$ = 1.8 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1}

Analyzing the curves shown in Figure 17, it is possible to observe that the increase of temperature enhanced the degradation of COD and TOC, were under 80 ºC the degradation was 10 and 5% higher than the reaction under 50 ºC respectively.

It is observed in Figure 17 that at 80ºC the conversion of hydrogen peroxide occurs faster than at 50ºC, as expected. However, the final value of H_2O_2 conversion after 24 h of reaction is almost equal, close to 95 and 98 % for 50 and 80 ºC, respectively. After 8 h of reaction, the conversions are 64 and 96%, respectively, showing the faster kinetics of its consumption, an observation that was also reported in many other works [6,40].

The faster decomposition of H_2O_2 at 80 ºC, when compared with that at 50ºC, enabled a faster mineralization of the organic matter, expressed in terms of COD and TOC, as observed in Figure 17 (b) and (c). It is interesting to observe that at 80 ºC the conversion of COD and TOC starts to be constant at the same time, around 4 h, moment at which hydrogen peroxide was almost fully degraded. This experimental fact is expected, since the degradation of hydrogen peroxide into the powerful oxidative radicals is required for the mineralization of organic matter. Accordingly, when there is no more hydrogen peroxide being degraded in hydroxyl radicals, the decrease of COD and TOC values is no longer observed.

In the work of Diaz de Tuesta, *et al.* (2019), the effect of temperature was also studied, and it was concluded that in the CWPO of 4-nitrophenol with doped carbon catalysts the rise of temperature not only increased the hydrogen peroxide oxidation rate but also reduced the induction period, defined as the initial period of the reaction where the pollutant degradation rate is slow [83]. In this work, the same observation is made for both TOC and COD. At 50 ºC the induction period goes until 8 h for COD, with almost no conversion, while at 80 ºC in less than 8 h more than 30 % of COD was removed. This phenomenon allows for achieving higher degradation with lower reaction times.

In Figure 18 are shown the results of the removal of the other analyzed parameters.

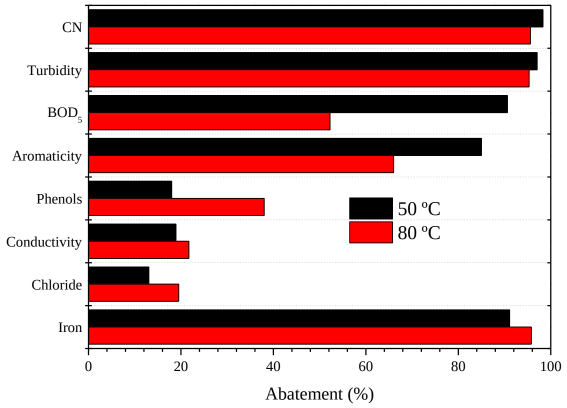

Figure 18: Abatement of turbidity, aromaticity, phenols, chlorides, conductivity, BOD_5, CN and iron after 24 h of reaction with catalyst HTC-230 under the following experimental conditions: pH = 6.00 ± 0.02, $C_{Catalyst}$ = 1.8 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1}

In Figure 18 it is observed that the higher temperature not always resulted in higher abatements of the other parameters measured, such as CN, turbidity, aromaticity and BOD_5. For the run at 50 ºC it is possible that the hydroxylation of the compounds was higher than their mineralization to the final products, leading to oxidized intermediates with low BOD_5 and low absorbance at 254 nm (aromaticity) than the respective final products. It is also observed the almost full abatement of the turbidity, CN and iron concentration, likely occurring due to the precipitation of solids during and after the reaction.

The increase of temperature enhanced the abatement of phenols, from 19 to 40%, more than doubling the capacity of oxidizing these compounds, an observation that is supported in the work of Diaz de Tuesta *et al.* (2017) with phenol and carbon catalysts, where the increase of temperature, from 90 to 130 ºC achieved a complete phenol removal in 4 h, while in the lower temperature, after 6 h, not even half of the initial concentration was mineralized [84].

After the analysis of those results, it was decided that further experiments will be conducted at 80 ºC.

4.4.3 The effect of the catalyst load

To evaluate the effect of catalyst load, two experimental CWPO runs were performed, using the HTC-230 catalyst with loads of 1.8 and 3.6 g L^{-1}.
The decay curves of H_2O_2, COD and TOC are shown in Figure 19 and Figure 20.

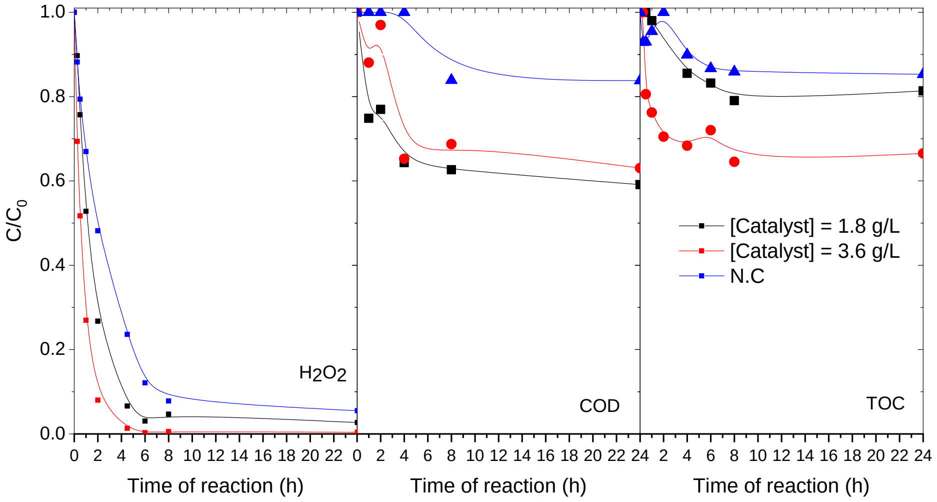

Figure 19: Normalized concentration of H_2O_2, COD and TOC upon time in CWPO runs performed with the catalyst HTC-230 under the following experimental conditions: T = 80 ºC, pH = 6.00 ± 0.02, $C_{Catalyst}$ = 1.8 and 3.6 g L^{-1} , $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1}

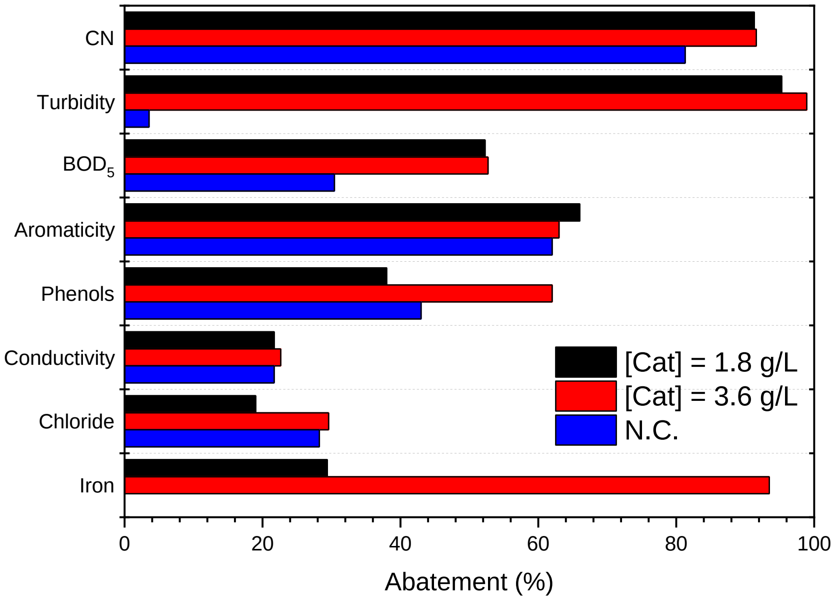

Figure 20: Abatement of CN, turbidity, BOD_5, aromaticity, phenols, conductivity, chlorides and iron after 24 h of reaction under the following experimental conditions: pH = 6.00 ± 0.02, $C_{Catalyst}$ = 1.8 and 3.6 g L^{-1}, $V_{Leachate}$ = 25 mL, T = 80 ºC, C_{H2O2} = 85.71 g L^{-1}

The CWPO run with the catalyst concentration of 3.6 g L^{-1} allows to achieve removals after 24 h of reaction of 37, 34, 98, 64, 62, 29, 22, 52, 90 and 92% for COD, TOC, turbidity, aromaticity, phenols, chloride, conductivity, BOD_5, and CN respectively. A considerable improvement was observed in the removal of TOC, reaching a value of 34%, almost twice as much when compared with the run carried out at 1.8 g L^{-1}. Besides COD, all other removals were superior at higher catalyst load.

In the work of Tizaoui *et al.* (2007), using ozone as oxidizing source, the effect of catalyst load was studied in the oxidation of leachate and it was observed that higher catalyst concentration, until a certain concentration, improved the mineralization. This fact was attributed to the powerful oxidation effect of hydroxyl radicals that would result from ozone decomposition in the presence of catalysts, those radicals mineralizing the organic compounds to CO_2, water and salts [44]. In this work, H_2O_2 was used as oxidant agent instead of ozone, but the same principle can be observed, in which the increase of the catalyst load lead to higher consumption of hydrogen peroxide, and therefore to higher amount of hydroxyl radicals.

In the work of Domínguez *et al.* (2014), the effect of catalyst load was also studied in the oxidation of phenol and it was discovered that higher catalyst loads lead to a linear increase of the degradation rate of H_2O_2 and phenol, resulting in higher conversion at the end of the CWPO runs [85]. The same effect was noted in this work, although phenol was only analyzed at the end of reaction, but higher catalyst concentration results in higher abatement of phenol.

4.4.4 Stepwise additions of H_2O_2

4.4.4.1 At pH 6

Since the initial dose of H_2O_2 requires 85.71 g L^{-1}, measured in 10 mL, and its consumption was not very efficient in the previous runs, a new strategy was adopted to try to overcome those problems. The load of hydrogen peroxide was fractionated in 5 equal portions and added stepwise at time 0 and at each hour until 4 h to guarantee a gradual consumption of hydrogen peroxide.

To represent the consumption of H_2O_2 in the CWPO runs carried out with stepwise addition of H_2O_2, the real concentration of the sample taken was determined and this value divided by the theoretical value (85.71 g L^{-1}). As described previously, the samples were taken after the addition of H_2O_2.

The first two runs were performed using the catalyst and experimental conditions reported so far, under pH = 6.0, using the strategy of stepwise additions of hydrogen peroxide. The CWPO results are shown in Figure 21 and Figure 22.

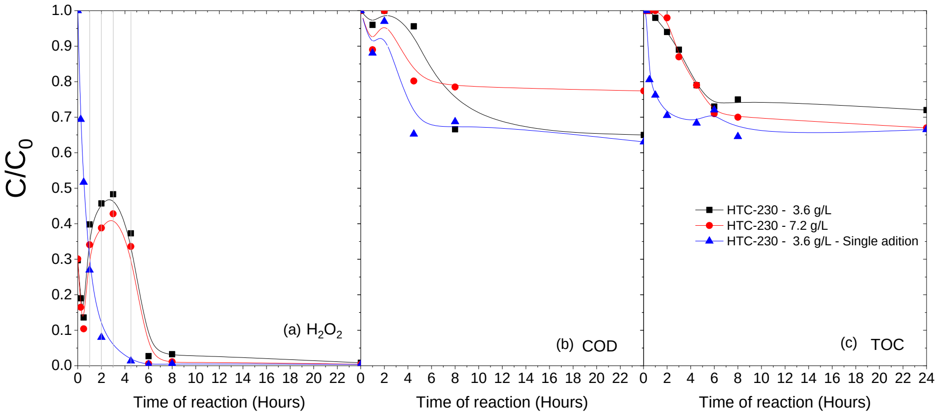

Figure 21: Normalized concentration of H_2O_2, COD and TOC upon time in CWPO runs performed with catalyst HTC-230 under the following experimental conditions: T = 80 ºC, pH = 6.00 ± 0.02, $C_{Catalyst}$ = 3.6 and 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1} in five equal stepwise additions (The grey vertical lines indicate the times where an addition was made) or with a single addition on t_0 (Blue line)

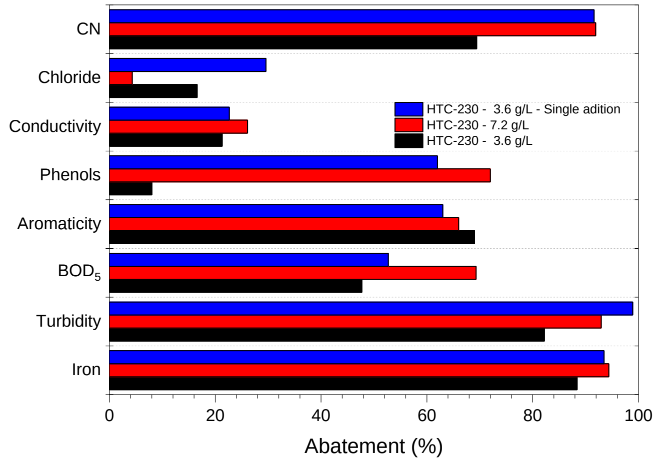

Figure 22: Abatement of CN, turbidity, BOD_5, aromaticity, phenols, conductivity, chlorides and iron after 24 h of reaction under the following experimental conditions: pH = 6.00 ± 0.02, $C_{Catalyst}$ = 3.6 and 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, T = 80 ºC, C_{H2O2} = 85.71 g L^{-1} in five stepwise additions of 17.14 g L^{-1} or a single addition of 85.71 g L^{-1} at t_0

For the runs performed at pH 6, it is shown in Figure 21 that all H_2O_2 was decomposed at the end of reaction. The conversion of hydrogen peroxide continues in 2 h after the final H_2O_2 addition was made. This was already expected at pH 6.0, since in the other CWPO runs performed under the same conditions a total consumption of H_2O_2 was observed after 6 h when totally added on t_0.

The run performed with 3.6 g L^{-1} of catalyst achieved removals of 36, 28, 82.9, 61, 28, 29, 23, 79, 70 and 88 % for COD, TOC, turbidity, aromaticity, phenols, chloride, conductivity and BOD_5, CN and iron concentration, respectively. When comparing this result with the run performed at the same experimental conditions, but with all H_2O_2 added on t = 0 h, the results are shown to be very similar, and the stepwise addition even resulted in worse conversion of TOC and COD. The CWPO run carried out with a catalyst load of 7.2 g L^{-1} revealed slight increase in conversion, mainly of BOD_5, phenols and TOC.

These results lead to conclude that for pH = 6.0 the stepwise addition of H_2O_2 is not a very interesting strategy, considering that when all hydrogen peroxide was added on t = 0 h, the catalyst was already able to degrade completely H_2O_2, and the changes on the results are almost immeasurable.

4.4.4.2 At pH 3

The same runs were performed at pH = 3.0, for the catalysts C-800 and HTC-230, using the catalyst loads of 3.6 and 7.2 g L^{-1}. The results are shown in Figure 23 and Figure 24.

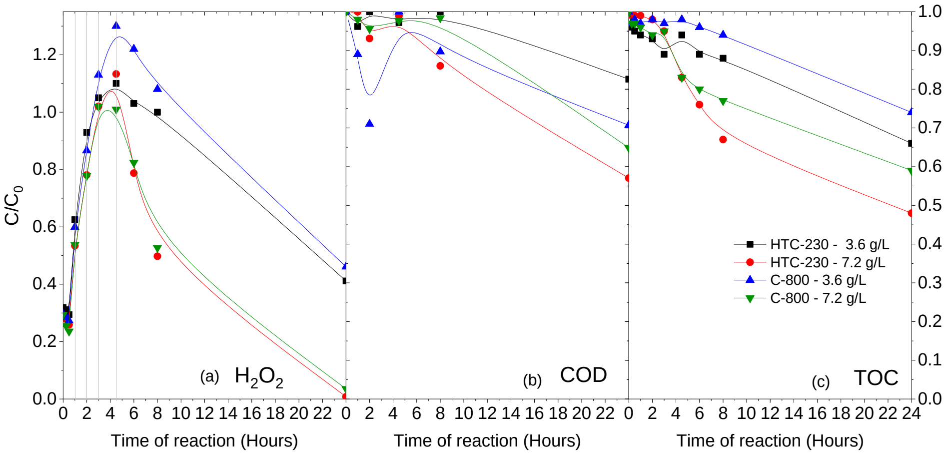

Figure 23: Normalized concentration of H_2O_2, COD and TOC upon time in CWPO runs with the catalyst: HTC-230 under the following experimental conditions: T = 80 ºC, pH = 3.00 ± 0.02, $C_{Catalyst}$ = 3.6 and 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1} in five equal stepwise additions (The grey vertical lines indicate the times where an addition was made)

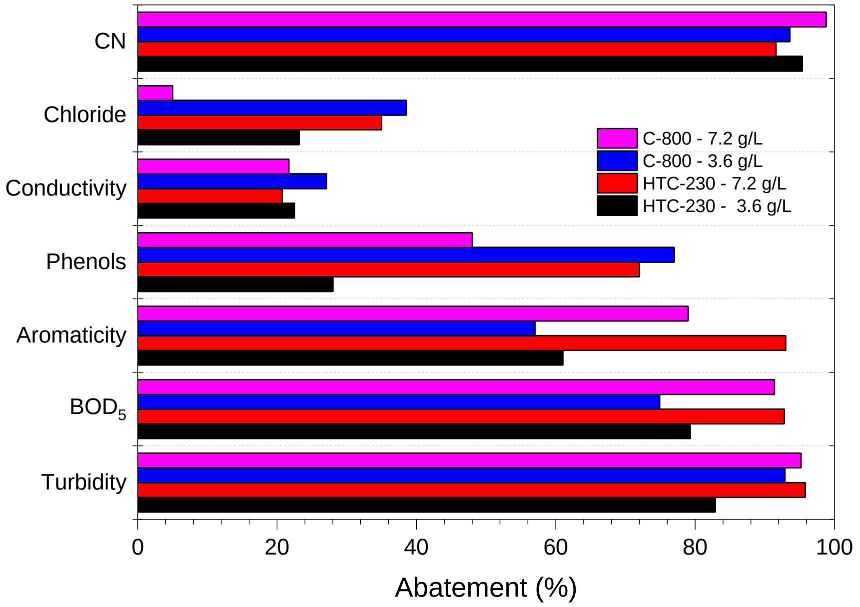

Figure 24: Abatement of CN, turbidity, BOD_5, aromaticity, phenols, conductivity, and chlorides after 24 h of reaction under the following experimental conditions: pH = 3.00 ± 0.02, $C_{Catalyst}$ = 3.6 and 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, T = 80 ºC, C_{H2O2} = 85.71 g L^{-1} in five stepwise additions of 17.14 g L^{-1}

In Figure 23 it is possible to observe that the use of the strategy of stepwise additions of H_2O_2 enhanced the degradation of this molecule, since in the first runs performed at pH = 3.0 (in Figure 15), the catalysts C-800 and HTC-230 were able to degrade 64 and 39 %, respectively, while with the new strategy, H_2O_2 degradation values of 99.2 and 96.5 % were achieved. The slow addition of H_2O_2 leads to higher process efficiency, since it was expected that the catalysts would be less overloaded, allowing a better degradation of hydrogen peroxide while maintaining the slower kinetics when compared to other pHs.

The higher removals of COD and TOC were obtained with a catalyst load of 7.2 g L^{-1}. For the catalyst HTC-230, values of 43 and 52 % were respectively reached, although for the catalyst C-800, the removals reached 34 and 41 %, results much better than those shown in Figure 15 with COD and TOC removals between 2 and 28%, proving the success of the adopted strategy at pH = 3.0.

The good results obtained with HTC-230 at [Cat] = 7.2 g L^{-1} were also observed on other parameters, such as turbidity, aromaticity, phenols, chlorides, BOD_5 and CN, where the conversions achieved 95, 93, 72, 35, 93 and 91 %, much higher removal results than those obtained with the previous conditions reported, highlighting the importance of optimizing the several variables for the enhancement of the CWPO efficiency.

For further runs, it was decided to consider the initial operating pH = 3.0, in which the stepwise addition of H_2O_2 showed improved performance of the CWPO process.

In order to prove that all the organic matter removal was carried out by CWPO, and not due to adsorption, two adsorption runs were performed under the same conditions considered in the CWPO runs, but without any catalyst. After 24 h, the sample was taken and analyzed to determine TOC and COD, and the removals obtained were 0 and 0.5 % for the catalyst C-800 and 0 and 2.1 % for the catalyst HTC-230, respectively, showing that the removals by adsorption in the materials are negligible.

In the work of Galeano *et al.* (2011), the study of hydrogen peroxide rate addition was performed and it was concluded that for CWPO of leachate under acid pH (3.7), high catalyst loadings and moderate hydrogen peroxide dosages, with low addition rates, promote better use of the H_2O_2 in this catalytic system, providing a significant COD removal [46], an observation that supports and justify the results obtained with the adopted methodology of hydrogen peroxide stepwise additions.

4.4.5 Sequential treatment with ionic exchange resins and CWPO

4.4.5.1 Treatment with ionic exchange resins

The leachate waters were pretreated with cationic or anionic ion exchange resins, to remove some of the ions of the leachate that could be acting as scavengers of hydroxyl radicals.

The characterization of the leachate waters after the three pre-treatments evaluated in this work is showed in Table 9.

Table 9: Characterization of the leachate after the resin pre-treatment

Parameter	**Unity**	**TP – 207**		**IRA 402**		**D.T.**	
		VALUE	**S.D.***	**VALUE**	**S.D.***	**VALUE**	**S.D.***
COD	mg L^{-1}	51340	2667	49870	495	43912	1563
BOD_5	mg L^{-1}						
pH at 25 ºC	-	8.53	NA	3.42	NA	2.99	NA
Conductivity	mS/cm	34.1	NA	38.7	NA	38.3	NA
Turbidity	NTU	304	4	634	3	991	5
Chlorides	mg L^{-1}	5625.37	48.21	6192.63	66.85	6975.58	146.24
Phenol	mg L^{-1}	783.11	19.34	558.99	24.38	593.47	24.38
Aromaticity	mg L^{-1}	13606	93	6495	90	7291.23	75.05
TOC	mg L^{-1}	26425	36	23103	341	21424	1165
Iron	mg L^{-1}	21.37		15.18		15.82	
CN	m^{-1}	100.33	NA	27.16	NA	36.04	NA

*S.D. = standard deviation; NA = not available

The leachate waters after the treatment with all resins, when compared to the raw leachate waters, presented a reduction in the initial COD value, indicating that all pre-treatment tested were able to adsorb some compounds.

For the treatment with the cationic adsorption resin, TP-207, the major change occurred in the conductivity and turbidity, indicating that the resin was able to adsorb some cations, reducing the conductivity value. The iron content is also lowered. This removal could be promising for the CWPO runs, where the leachate complexity decreases.

The leachate waters were after subjected to a double treatment, first with the cationic resin, followed by the anionic resin. In this run it was observed a drop of COD concentration around 25%. However, the concentration of chlorides increased even more than when considering the single treatment with the resin IRA-402 Cl^-. It was expected that the leachate would have lower complexity after the double treatment. However, this was not observed, since while COD, TOC, aromaticity, phenols and iron concentration dropped, the turbidity and chlorides concentration increased.

4.4.5.2 CWPO of the leachate waters treated with ionic exchange resins

The CWPO runs were performed with the leachate waters after the pre-treatment with resin, at pH = 3.0, considering the catalysts C-800 and HTC-230, using the catalyst load of 7.2 g L^{-1}. The results are shown in Figure 25 and Figure 26.

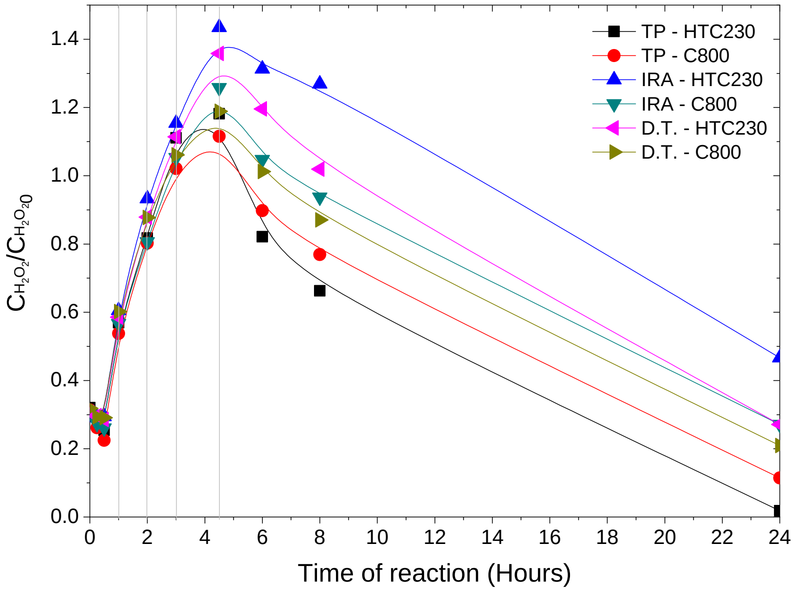

*Figure 25: Normalized concentration of H_2O_2 upon time in CWPO runs performed with the catalysts HTC-230 and C-800 under the following experimental conditions: T = 80 ºC, pH = 3.00 ± 0.02, $C_{Catalyst}$ = 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1} in five equal stepwise additions (The black vertical lines indicate the times where an addition was made). *D.T. = Double resin pre-treatment*

For the CWPO runs performed in the leachate waters after treatment with the anionic resin (IRA 402 Cl^-), and after the double resin pre-treatment, the results of the H_2O_2 decomposition show that the catalysts were not able to decompose completely the H_2O_2. At the same time, the CWPO of the leachate waters treated by the cationic resin (TP 207) was able to achieve 98 and 90 % of H_2O_2 decomposition, for the HTC-230 and C-800 catalysts, respectively, highlighting that the higher concentration of chlorides affects the decomposition of hydrogen peroxide.

In all cases, the decomposition of H_2O_2 maintained the same pattern at pH = 3.0, a linear tendency, with a slower decomposition rate than at pH = 6. In Figure 26, the COD and TOC removals upon reaction time is shown.

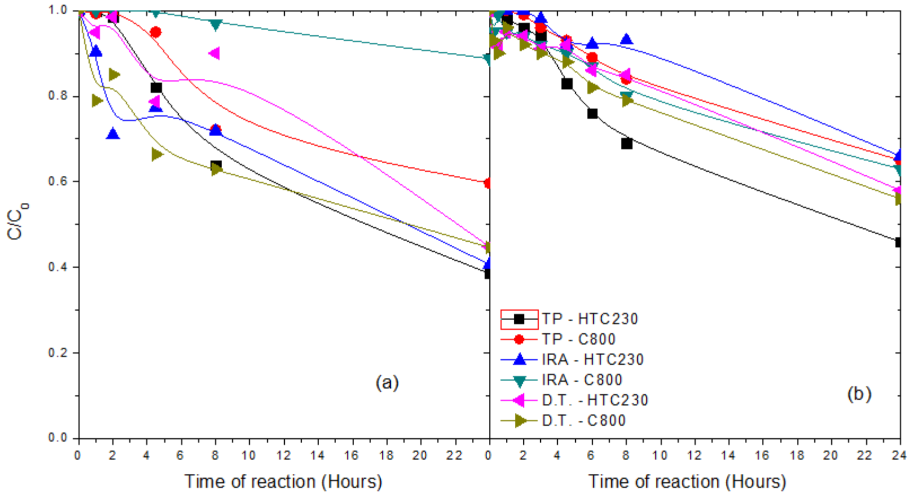

Figure 26: Normalized concentration of (a) COD and (b) TOC upon time in CWPO runs, with the catalysts HTC-230 and C-800, performed under the following experimental conditions: T = 80 ºC, pH = 3.00 ± 0.02, $C_{Catalyst}$ = 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1} in five stepwise additions of 17.14 g L^{-1}.

**D.T. = Double resin pre-treatment*

As observed, the removals of COD and TOC were 62 and 55 %, respectively, in the CWPO of the leachate waters treated with the cationic resin (TP 207), considering the catalyst HTC-230 (considered the optimized experimental condition), result at least 10% better than any other obtained with resin pre-treatment. The results of COD and TOC are similar, showing the reliability of the data.

Another satisfactory result was achieved with the catalyst C-800 after the double resin pre-treatment, in which COD and TOC removals were 56 and 41% respectively. The result is worth to highlight since the leachate after the double resin pre-treatment had a higher concentration of chlorides (acting as radical scavengers), a condition that is not favorable to a CWPO run.

Other CWPO runs resulted in TOC removal values between 22 and 40%. However, an interesting result was obtained with the catalyst HTC-230 in the CWPO run carried out with the leachate waters pre-treated with the anionic resin, where only 70% of H_2O_2 was decomposed while the consumption of COD was 50%.

The other parameters abatement for the CWPO runs are shown in Figure 27.

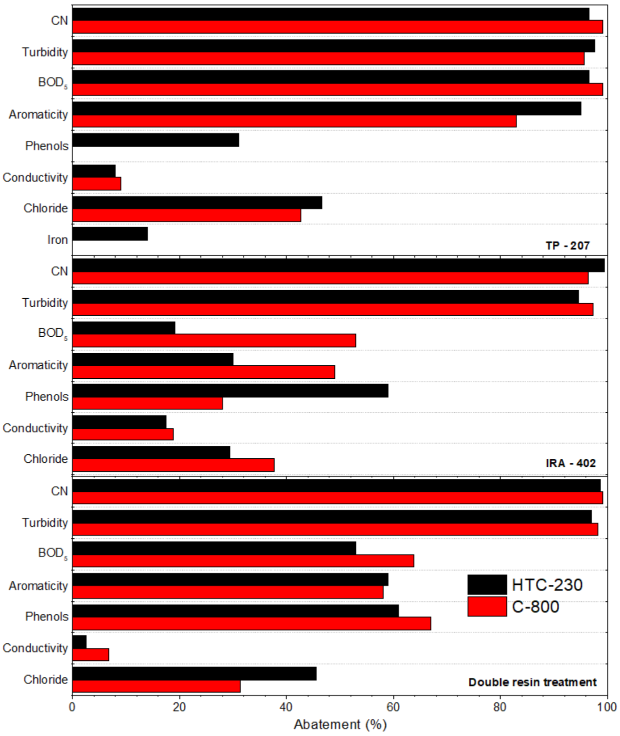

*Figure 27: Final removals of turbidity, aromaticity, phenols, chlorides, conductivity and BOD_5 in CWPO runs of leachate waters afte pre-treatmemt with resins, performed under the following experimental conditions: pH = 3.00 ± 0.02, $C_{Catalyst}$ = 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, T = 80 ºC, C_{H2O2} = 85.71 g L^{-1} in five stepwise additions of 17.14 g L^{-1}. *D.T. = Double resin pre-treatment*

In Figure 27, the confirmation of the good results obtained in the CWPO of the leachate waters after cationic resing (TP-207) using the catalyst HTC-230 is obtained, where the conversion of turbidity, aromaticity, chlorides, BOD_5 and CN is 97, 95, 46.5, 97 and 99 %, results that outperform all other CWPO performed during this work and highlighting the efficient consumption of H_2O_2, being able to convert all those parameters along with COD and TOC.

Figure 28 illustrates the visual difference of the leachate before and after the CWPO treatment.

*Figure 28: Picture of the raw leachate (right flask) and the leachate after the CWPO (left flask) using HTC-230 under the following experimental conditions: T = 80 ºC, pH = 3.00 ± 0.02, $C_{Catalyst}$ = 7.2 g L^{-1}, $V_{Leachate}$ = 25 mL, C_{H2O2} = 85.71 g L^{-1} in five stepwise additions of 17.14 g L^{-1}. *Leachate after the TP-207 pretreatment*

Moravia *et al.* (2012) [45] combined a Fenton process with a membrane separation process (MSP) using microfiltration (MF) and nanofiltration (NF) to treat leachate waters with 2.5 g L^{-1} and 0.85 g L^{-1} for COD and TOC, under optimized conditions (1.7 g H_2O_2/g COD; $FeSO_4 \cdot 7H_2O:H_2O_2$ = 1:5.3; pH = 3.8; reaction conditions = 115 rpm/28 min) and achieved 65% of COD removal and 72% of TOC removal. Although good results, the leachate waters used had 20 and 30 times lower COD and TOC concentrations when comparing to the one used in this work and, yet, the result is similar to the CWPO performed with optimized conditions, displaying the satisfactory treatment of the leachate waters.

Galeano *et al.* (2011) reported the use of CWPO with an Al/Fe-pillared clay catalyst in the treatment of landfill leachate (COD = 5–7 g L^{-1}; BOD5 ~ 0.8 g L^{-1}; BOD5/COD = 0.11–0.16). COD removals up to 50% were achieved in 4 h of reaction at mild conditions (291 K; 72 kPa), and it was found that extremely high concentrations of organic matter featuring leachates of landfill may prevent the oxidizing molecules to reach the active sites on the solid catalyst during the early stages of reaction [46]. In our study, besides using a carbon-based catalyst and treating a leachate with a COD concentration up to 10 times higher, that prevents, even more, the hydroxyl radicals to reach the active sites of the solid catalyst a better COD removal was achieved (62%).

CONCLUSION AND FUTURE WORK

5 CONCLUSIONS AND FUTURE WORK

The treatment of real leachate waters by CWPO, using carbon-based catalysts prepared from compost of MBT plants proved to be a viable option. Seven catalysts were prepared, five by pyrolysis and two by HTC, the carbon-based catalysts proven to be active on the decomposition of H_2O_2 at 50 ºC and in a range of tested pHs. Two catalysts were selected for CWPO, both being able to degrade completely the H_2O_2, the first catalyst, synthesized after pyrolysis of the mature compost (C-800), with quicker decomposition rates than the second, the HTC-230, synthesized by hydrothermal treatment of the mature compost.

Blank CWPO runs and adsorption runs were performed and, in both cases, the COD and TOC removals were negligible, proving the activity of the catalysts and the main role of CWPO in the mineralization of the leachate waters. Under several conditions, the CWPO treatment was tested and grouped into three main studies.

In the first studies were tested experimental variables, such as temperature, pH and catalyst load. The best result was obtained at T = 80 ºC, pH = 6.0, using 3.6 g L^{-1} of catalyst HTC-230, being able to fully decompose the H_2O_2 and achieving COD and TOC removals of 37 and 34 %, respectively.

The second group of studies considered the stepwise addition of H_2O_2, to promote a slower H_2O_2 decomposition, minimizing undesirable side reactions and less chance of overloading the catalyst capacity. The best result in this group of studies was obtained using T = 80 ºC, pH = 3.0, 7.2 g L^{-1} of catalyst HTC-230, being able to achieve removals of 43, 52, 95, 93, 72, 35 and 93 % for COD, TOC, turbidity, aromaticity, phenols, chlorides and BOD_5, respectively, proving the success of this strategy at pH = 3.0.

Lastly, applying pre-treatment of the leachate waters with a resin and using the methodology of stepwise H_2O_2 additions, the best result in this group of studies was obtained using T = 80 ºC, pH = 3.0, 7.2 g L^{-1} of catalyst HTC-230, for the leachate waters treated with the cationic ion exchange resing, being able to achieve removals of 62, 55, 97, 95, 46.5 and 97 % for COD, TOC, turbidity, aromaticity, chlorides and BOD_5.

The best result was obtained using the pre-treatment with resin, however, the enhancement of removals was not significant when compared to the results obtained without pre-treatment, making the last option economically more viable, needing less investment of money and time to treat the leachate waters.

Future works can be developed using mathematical and statistical tools, such as response surface methodology, which have been very explored lately to optimize experimental conditions [86]. The catalyst reuse and stability shall be explored as well.

Other possibilities to improve the efficiency of the CWPO process includes exploring more options to pre-treat the leachate waters since its complex matrix is harmful to the CWPO process, using other adsorption resins or other pre-treatment techniques, such as sedimentation and flocculation.

There is also room to explore the catalysts applied, where the carbon-based materials could be mixed with some metals usually applied in catalysis, using, in this case, the carbon material as support for the metallic centers. Another possibility can be the refinement of these catalysts, synthesizing several nanoparticles and nanomaterials from the compost originated in the MTB plants.

Since in this work, it was proved the important influence of the pH on the CWPO efficiency, it is also suggested as future work the pH monitorization and control during all the run duration, maintaining always the optimal condition. Further runs at a larger scale should be explored to study the viability of this treatment on an industrial scale.

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Appendix

Congress Presentation

This work generated a congress oral presentation, on the VI CIEEMAT 2020 - Congresso Ibero-americano de Empreendedorismo, Energia, Meio Ambiente e Tecnologia – this congress general objective is to promote a wide discussion of key topics within the areas of R&D, Entrepreneurship, Energy (conventional and renewable), Environment, Sustainability and Energy Efficiency. This debate has the opinion of experts and cooperation between institutions/companies in Ibero-American countries, represented by professors, researchers, professionals and students, contributing to the greater dissemination of an entrepreneurial culture and disseminating technical and scientific knowledge.

The presentation abstract is shown below.

Valorization of compost obtained from the mechanical and biological treatment of municipal solid waste: catalysts for wet peroxide oxidation of landfill leachates

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ABSTRACT

Since humanity started living in communities and towns, the generation of solid waste has largely increased and, in 2017, each European citizen generated 480 kg of municipal solid waste (MSW). The main concern with MSW is its management and final destination since in many cases MSW is just thrown in landfills. In mechanical and biological plants, MSW is first sorted into discarded, recyclable, and organic waste streams. This organic fraction goes to the biological treatment stage, generating biogas, and as by-products, leachate, and compost are obtained, the compost being mainly used as an agriculture fertilizer. However, the amount of compost produced is higher than its demand, resulting in an excess that is currently accumulated in landfills. This work deals with the valorization of compost to produce hydrochairs, and pyrochars, through hydrothermal carbonization (HTC) and pyrolysis, respectively, with suitable properties as catalysts for the catalytic wet peroxide oxidation of the landfill leachate. Up to seven catalysts were synthesized under several conditions, 2 from HTC and 5 from pyrolysis. The catalysts were characterized to determine the ash content and elemental analysis. All materials were assessed in the degradation of H_2O_2, leading to its complete degradation after 2 h of reaction time. Some selected catalysts were further tested in the CWPO of the landfill leachate (TOC = 27 g L^{-1}, COD = 60 g L^{-1}, 38.8 mS/cm, and 5 g L^{-1} of chloride ions) 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.

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