

**Valorization of compost in the production of carbon-based materials  
for the treatment of contaminated wastewater**

**Caroline Martins Masso**

Thesis report submitted to  
**Escola Superior de Tecnologia e Gestão**  
**Instituto Politécnico de Bragança**  
Master Degree in  
**Chemical Engineering**

Supervisors:

**Prof. Dr. Helder T. Gomes**  
**Prof. Dr<sup>a</sup> Juliana M. T. de Abreu Pietrobelli**  
**Dr. Jose L. Diaz de Tuesta**

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“The biggest discovers are made when you  
step forward beyond your limits.”

**Caroline Masso**

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## Abstract

The municipal organic waste is typically treated by mechanical separation and then by anaerobic digestion and composting, in order to valorise the residues in a biogas stream for energy purpose and in compost that can be used in agriculture. However, the current waste management legislation in Europe and the expected developments on the coming directives regarding the application of the “*end-of-waste*” criteria, are leading to barriers on the use of fertilizers resulting from waste. The current work proposes an alternative strategy to the valorisation of compost through the production of low-cost materials to be used as catalysts in the treatment of wastewaters. The compost was supplied by a waste management company located in the North Est region of Portugal, and then subjected to thermal and hydrothermal treatments. Compost was mixed with water, filtered and washed in order to remove the soluble compounds and suspended solids. Then, materials were prepared with H<sub>2</sub>SO<sub>4</sub> (18 M) and different mass ratios of glycerol, the resulting products of reaction being calcined at 800 °C. The material that presented the highest conversion was washed with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), at room temperature and at 60 °C, and HCl (1 M). The prepared materials were sieved, and the samples obtained were tested in H<sub>2</sub>O<sub>2</sub> decomposition and in the remediation of waters containing one model pollutant with lipophilic character (4-nitrophenol) by catalytic wet peroxide oxidation (CWPO). The effluents of the CWPO and H<sub>2</sub>O<sub>2</sub> decomposition runs were analysed in order to quantify the pollutant, oxidant, TOC and the leached iron. In this sense, it was concluded that the materials produced shows activity through the analyses, and the conversions reached had a strong contribution of leached iron. Then, the amount of leached iron could be minimized while maintaining the conversions.

**Keywords:** catalytic wet peroxide oxidation, H<sub>2</sub>O<sub>2</sub> decomposition, activation, compost.

## Resumo

Atualmente, os resíduos orgânicos urbanos são tipicamente separados e tratados por digestão anaeróbia e compostagem, permitindo a sua valorização em biogás, para fins energéticos, e a produção de composto, usado na agricultura como fertilizante. No entanto, a legislação europeia em matéria de gestão de resíduos, e os desenvolvimentos esperados nas próximas diretivas sobre a aplicação dos critérios relativos a “fim do resíduo”, estão a limitar o uso de fertilizantes procedentes de resíduos. O presente trabalho propõe uma estratégia para a valorização de composto, convertendo-o em materiais de baixo custo capazes de serem utilizados como catalisadores em reações de oxidação no tratamento de águas residuais. O composto utilizado neste trabalho foi fornecido por uma empresa de gestão de resíduos localizada em Trás-os-Montes, sendo de seguida sujeito a tratamentos térmicos e hidrotérmicos. O material de partida foi misturado com água, filtrado e lavado para remover parte do conteúdo solúvel e os sólidos suspensos. Em seguida foram produzidos materiais por tratamento com  $\text{H}_2\text{SO}_4$  (18 M) e diferentes razões mássicas de glicerol. O material resultante da reação foi submetido a calcinação a uma temperatura de 800 °C. Destes materiais preparados, o que apresentou maior conversão, foi lavado com peróxido de hidrogénio, a temperatura ambiente e a 60 °C, e HCl (1 M). Os materiais preparados foram testados na decomposição catalítica de  $\text{H}_2\text{O}_2$  e na remediação de águas contaminadas com um poluente modelo de carácter lipofílico (4-nitrofenol), por oxidação catalítica com peróxido de hidrogénio (CWPO). Ao final da decomposição catalítica e CWPO foi feita análise para determinação de ferro lixiviado e análise de carbono orgânico total (TOC). Conclui-se que os materiais produzidos apresentam atividade através das análises feitas, sendo que as conversões alcançadas tiveram forte contribuição do ferro lixiviado. Foi possível de seguida minimizar-se a quantidade de ferro lixiviado mantendo as conversões.

**Palavras chave:** Oxidação com peróxido de hidrogénio, decomposição de  $\text{H}_2\text{O}_2$ , ativação, composto.

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*Caroline Martins Masso*

## **INTRODUCTION**

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## **1 INTRODUCTION**

### **1.1 MUNICIPAL SOLID WASTE MANAGEMENT**

The increase in world population implies the generation of large amounts of waste that results in socio-economic and environmental issues. In addition, new technologies and chemical products are released to the market every year, generating new solid waste for which treatments are not known yet. In order to increase the quality and durability of those products, some of them are non-biodegradable and are characterized to be more resistant and composed by several types of substances. In consequence, the management of Municipal Solid Waste (MSW) becomes a challenge, not only for the quantity of generated waste, but also for the complexity of new products. The Directive 2008/98/EC sets the basic concepts and definitions related to waste management, such as definitions of waste, recycling, recovery and the proposal to apply as a priority order the following waste management hierarchy: prevention, preparation for re-use, recycling, recovery and, as last instance, disposal of the waste on a landfill. However, several materials are difficult to re-use and, when a product is composed with different elements, recycling shows handicaps.

Nowadays, what drives and encourages the world economy is the consumer-based lifestyle where people generate waste, which is further destined most of the time to landfills, leading to its accumulation. In the year 2025, the accumulated waste is expected to reach a total of 2.2 million tons in the world, which means a huge credit for the generation of waste.<sup>1,2</sup> The MSW can be classified as organic, that is a solid part that can result in compost, and inorganic, materials that may be recycled, for example, paper, plastic, glass, metals and other materials. The quantity, composition and existence of waste depend on the culture, laws and policies of waste management, as well as on the economic activities practiced in each countries.<sup>1,2</sup>

Commonly, in advanced waste management systems, MSW passes through two separation processes, named mechanical and biological treatment processes. The

organic solid waste in general is conducted to management centers to be exposed to different biological treatments. A method of recycling waste based on the biological degradation of organic matter is by anaerobic digestion, whose main products are biogas and a solid digestate. The solid product obtained under these conditions is then stabilized by aerobic digestion and the resultant compost is properly sanitized. In more detail, in biological treatment processes, the composting process begins after the collection of MSW and mechanical treatment, used to separate the waste glass and plastic that are taken to the line of recyclable waste. Bulky materials and textiles are discarded on landfills. The remaining material goes to a rotary separation unit, which has the function of separating the mass of waste into organic matter, packaging and a mixture of waste that cannot be defined in the other categories. Each of these materials receives a type of treatment. The recycled materials are separated into PET, HDPE, metal (especially aluminum), ECAL, mixed plastic and rubbish. Later, the materials undergo a strict quality control and are placed in bales before being sent to the recycling companies. The organic matter goes to bioprocessing for methanization, where biogas is produced and used in the production of electric energy. Subsequently, in the composting stage, the resultant solid material, with granulometry from 40 to 90 mm, is degraded by a controlled aerobic process.<sup>3</sup> Next stage is the maturation process, where the material stays for a ripeness of previous steps. Then, matured organic waste goes to refinement in order to separate the plastics, glass and stones that compost contain, improving the quality of this organic material.<sup>3,4</sup>

The valorization of waste to generate products with added-value may be one of the key strategies to reach a circular economy. The circular economy is a type of economy in which the value of products, materials and resources is maintained for as long as possible, thus minimizing waste. One priority of the European Union (EU) is to achieve an economy based on those principles. For this reason, all Member States, including the European Environment Agency (EEA) countries need to develop new strategies for the treatment of MSW, avoiding the disposal of waste. In this regard, the EU requires that waste management activity to be transformed into sustainable materials management. Thus, future management strategies should seek the incorporation of the

principles of circular economy, thereby increasing the diffusion of renewable energies and also energy efficiency, both of which result in a reduction in the dependence of the EU in imported resources. In addition, these strategies should allow providing economic opportunities and long-time competitiveness.<sup>5</sup>

## 1.2 OBJECTIVES

In this work, the production of low-cost useful materials to be used as catalysts from stabilized composting waste (compost) provided by the company "*Resíduos do Nordeste, EIM*" is assessed. The company collects the MSW in the northeastern region of Portugal and forward it to a mechanical and biological treatment process, generating biogas and compost. This compost was used in the preparation of catalysts to be used in catalytic wet peroxide oxidation (CWPO) of 4-NP, as model pollutant, hence favoring a circular economy. To the best of my knowledge, there are not published works relying on the use of compost to produce catalysts to be used in CWPO.

*Caroline Martins Masso*

**STATE OF THE ART**

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## **2 STATE OF THE ART**

### **2.1 ACTIVATED CARBONS**

Activated carbons are present in human history in such a long time that its origin is impossible to be accurately determined. Nowadays, activated carbons are mainly used as adsorbents, with materials like wood char, coal char or simply a partially devolatilized carbonaceous material.<sup>6</sup>

Activated carbons are materials with high porosity, which makes them greatly suited for adsorption applications, with the main concern to remove species from the liquid or gas phases, so that the chemical substances are purified or recovered. Other applications of these materials are its use as catalyst support, chromatography columns and electrode materials for batteries and capacitors.<sup>7</sup> Another big important application of activated carbons is in treatment of air and water, because these materials have advantages in adsorption, even that the coal for activation comes from landfills.<sup>6-9</sup> In general, these materials are very flexible, and their physico-chemical properties can be easily tuned by proper treatments. For the final applications of activated carbons, its morphology must be taken into account. In this way, the material can be prepared in different conformations, including powdered activated carbons (PACs), granular activated carbons (GACs), activated carbon fibers (ACFs), carbon monoliths or spherical activated carbons.<sup>6-10</sup> Both of importance to take into consideration in the choice of an activated carbon are the criteria of techniques to apply in the activation of carbons and environmental issues. In this sense, the environmental questions are included and agricultural wastes appear as very important precursors because they are cheap, renewable, safe and available in large quantities. Besides, they have high carbon and low ash contents.



The use of activated carbons in industrial processes implies the need to constantly reduce the costs of its production in order to maintain its competitiveness in relation to other technologies and materials. A reduction in production costs and an increase in its efficiency are possible through the substitution of raw materials by those with lower market values, avoiding waste of materials and also seeking to optimize production conditions.

### 2.1.1 APPLICATIONS OF ACTIVATED CARBONS

Activated carbons (ACs) have a versatile applicability. The first report about it consisted on its use as adsorbent, when Dr. D.M. Kehl applied wood char to mitigate the odors emanating from gangrene in 1793.<sup>6</sup> Nevertheless, the first time that an AC was applied in the industrial sector was in England in 1794, being used as a decolorizing agent in the industry of sugar production. In 1854, the London's Mayor ordered to remove nasty odors by using the mounting of wood char as filters in all the ventilation systems. Eighteen years later, gas masks with carbon filters were used in chemical industries, with the purpose to avoid inhalation of toxic vapors.<sup>6</sup> In the second half of the 20<sup>th</sup> century, the evolution of modern societies induces a fast growing production and utilization of ACs, due to the stricter environmental regulations regarding water resources, clean gas applications, air quality control, energy storage/conversion and economic recovery of valued chemicals.<sup>6</sup> The search for an alternative use of environmental correct material has increased and highlighted the search for ACs through renewable sources, which are known as biochar.<sup>11</sup>

The scientific community has interest in the development of activated biochars for two good reasons: cost-effective and environmentally-friendly carbon materials with great application prospect in many fields. The activated biochars have advantages when compared with traditional ACs, as the feedstocks of biochar production are abundant and low-cost, which can be found in agricultural biomass and solid waste. According to this, the activation of biochars is very attractive, because of renewable energy

generation, and their multiple applications, including water pollution treatment, CO<sub>2</sub> capture and energy storage.<sup>11</sup> Therefore, one of the applications of carbons is its use as adsorbent for the purification of gas streams or aqueous solutions with high efficiency for the removal of heavy metals from waters. In this regard, the trend is positive because metal ions form metal complexes with negatively charged acid groups.<sup>12,13</sup>

As environmental pollution has become a serious problem, this results in increased use of ACs for the adsorption of pollutants in industrial effluents. The adsorption performance and pore characteristics of ACs depend on the physical and chemical properties of the precursor as well as on the activation technique.<sup>6,9</sup>

The performance activated carbons as adsorbents depend strongly on its textural properties, such as, porosity, pore width, pore distribution and specific surface area. IUPAC has a classification for each type of pores using the diameter, as described in Table 1.

**Table 1. Classification of pores and functions (IUPAC Classification)<sup>14</sup>**

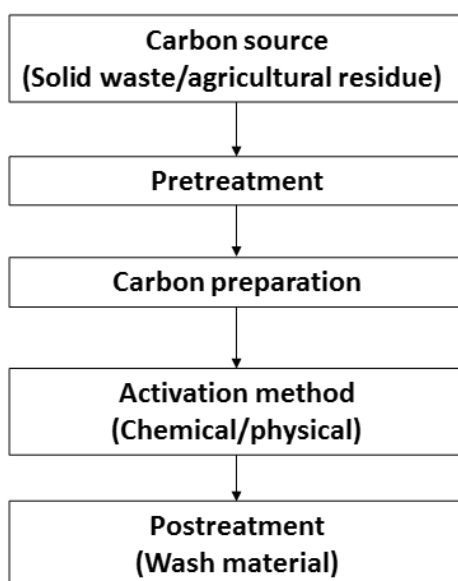
<b>POROUS CLASSIFICATION</b>	<b>POROUS DIAMETER</b>	<b>FUNCTION</b>
Microporous	$\theta_m < 2\text{nm}$	Provides a high adsorption capacity for small molecules such as common gases and solvents.
Mesoporous	$2\text{nm} < \theta_m < 50\text{ nm}$	Used in the adsorption of large molecules, such as dyes. In addition, it provides part of the surface area for carbons impregnated with chemicals.
Macroporous	$\theta_m > 50\text{ nm}$	It has the function of transport medium for gas molecules.

In this context, the physisorption capacity for the adsorption of larger molecules is dependent on the surface of mesoporous.<sup>15</sup> The properties of chemisorption on porous carbons are very influenced by the surface chemistry, which depends on the presence of surface oxygen groups or surface heteroatom groups, as well as on the

presence of doping elements and the own structure of the carbonaceous material and its crystallinity. The charge of the surface is determined by both its hydrophobicity and the electronic density of the graphene layers.<sup>16</sup> In this context, all the properties mentioned explain the facile and efficient surface of the porous types in adsorption. The adsorption of a substance (adsorbate) on activated carbons may be physical (weak van der Waals forces) or chemical (chemical bonding) adsorption, depending on the physicochemical properties of the AC and the affinity of the adsorbate.<sup>15</sup> Therefore, activated carbons are versatile adsorbents, which can remove diverse types of substances from a gas or water effluent, making themselves great candidates to be used in environmental applications for the removal of pollutants as the priority substances announced by the Directive 2013/39/EU (metal ions, dyes, phenols, detergents, pesticides, chlorinated hydrocarbons) and many other chemicals and organisms, that are important in many types of treatment of wastewater or gas effluents as well.<sup>9</sup>

#### 2.1.2 METHODS OF PREPARATION

Figure 1 shows a diagram flow of the entire process for the production of activated carbons, so that it is easier to visualize the preparation process.



**Figure 1. Process for the production of activated carbons**

In this context, it is possible to prepare activated carbons by using different methods and carbon sources.

At first, the material is submitted to a treatment, named carbonization. In this process, solid wastes with a significant carbon content are obtained from organic material by pyrolysis in an inert atmosphere. Pyrolysis is a process that occurs at a high temperature ( $> 300\text{ }^{\circ}\text{C}$ ), which has a significant effect.<sup>17</sup> Other factors that must be taken into account in the pyrolysis are the heating rate, the nitrogen flow rate (this is generally used to assure the inert atmosphere) and the time of pyrolysis. The decrease in the yield of coal with the increase of temperature occurs due to a greater primary decomposition of matter occurring at higher temperatures or also through the secondary decomposition of coal residues. The increase of the temperature can result in a decrease of the solid yield, leading to the production of great quantities of a liquid and gas fraction. In another hand, higher temperatures result in the production of higher quality coals.<sup>17-19</sup> ACs can be activated by two different processes: "physical" or "thermal" activation and "chemical" activation.

### 2.1.2.1 CARBON ACTIVATION

Activation is a process to develop a better porous structure, create new porous or create functional groups in surface of the carbon. The types of activation conditions, for example the different agents, temperature and time of the process, precursor, additives and others, affects the structure, elemental content and the disposition of those elements of the produced activated carbons. The treatments to activate a carbon may be classified as Chemical and Physical depending of the activating agent, as summarized in Table 2.<sup>20,21</sup>

**Table 2. Activation methods with agents.**

Activation Method	Agent	Reference
Chemical	H <sub>3</sub> PO <sub>4</sub>	22
	H <sub>2</sub> SO <sub>4</sub>	23
	KOH	24
	NaOH	25
	ZnCl <sub>2</sub>	26
	K <sub>2</sub> CO <sub>3</sub>	27
Physical	Steam	28
	CO <sub>2</sub>	29
	CO <sub>2</sub> /N <sub>2</sub>	30
	Steam/CO <sub>2</sub>	31
Physiochemical	KOH/CO <sub>2</sub>	32,33

#### *Physical Activation*

A precious step of the activation is the carbon synthesis, where the carbon rich material is pyrolyzed at low temperature in an inert atmosphere and the produced coal is a material with a surface area considered to be medium, which is reflected in a low

capacity for the sequestration of pollutants. The second stage consists on the activation of the coal obtained from the previous stage, typically using water steam, carbon dioxide or, less frequently, air, as activating agent. The resultant material is subjected to an oxidizing atmosphere, increasing substantially its porosity and, in consequence, its surface area, leading to an improved uptake capacity for adsorption applications.

The physical activation process may be done in a single stage, where the pyrolysis reaction occurs under oxidative gas flow, generally steam, carbon dioxide, air or a mixture of these gases. Steam and carbon dioxide are the most preferred options. Due to the release of heat from the exothermic reaction between carbon and oxygen, the use of air further difficult controlling of the reaction temperature.<sup>34</sup> The process temperature affects the kinetics of the activation reaction, due to the endothermic character of this reaction, since that the temperature is determinant for the reaction and the development of the porous structure. Thus, the temperature of the process must be high. Using the proper temperature in the reaction, that is, the temperature to which the reaction occurs most efficiently. The process of activation occurs on the inner surface of the material, implying that the coal is removed from the walls of the pores during the process of the activation, resulting in an expansion of the pores. The development of the porosity by this way, implies a mass loss that can reach values of 40% to 50% of burned matter. The evolution of microporosity is relatively similar for CO<sub>2</sub> and steam as activators, with a maximum of about 40 to 50% mass burn. Additional gasification results in a decrease in micropore volume for the case of CO<sub>2</sub>. The steam produces a continuous increase with the burn-off, which indicates the increase of the micropores and the change of size for the mesopore.<sup>34,35</sup>

Furthermore, the carbonization burns off in an uncontrollable method that results in the development of porous structure and losing part of the material, generating considerable quantities of oxygen surface groups on the carbon. Some activating agents, even small amounts of specific compounds, can significantly accelerate the process in physical activation.<sup>34</sup> The main advantages of physical activation are the relatively low cost of activated carbon production and the possibility of preserving the shape and texture of the raw material, as for example, the production of tissues and activated

carbon cloths. In the other hand, the specific surface area of the carbons produced by physical activation is less than 2000 m<sup>2</sup>/g. Other factors are the mass of the raw material that decreases up to approximately 70% in the process and the high temperature of carbonization, which results in high energetic costs.<sup>34</sup>

### Chemical activation

The process of chemical activation consists on the treatment of the material used as carbon source with a chemical activating agent, as summarized in Table 3. There is only one step to make a chemical activation, where the material has to be charred and after this process it is subjected to the activation.<sup>34</sup>

**Table 3. Activation agent with possible reaction temperatures**

Activation Agent	Temperature range	Reference
ZnCl <sub>2</sub>	500-850 °C	36,37
H <sub>2</sub> SO <sub>4</sub>	500-700 °C	38,39
KOH	400-750 °C	40,41
NaOH	500-700 °C	42,43
K <sub>2</sub> CO <sub>3</sub>	300-800 °C	44,45
H <sub>3</sub> PO <sub>4</sub>	600 °C	46

One way to perform chemical activation is by acid treatment of the charred carbon. This method is generally employed to oxidize the porous carbon surface as it increases the acidic property, removes the mineral elements and improves the hydrophilic nature of surface.<sup>20</sup> The acidic functional groups, which denote functional oxygen groups containing proton donors, are found on the carbon surface. On the other hand, the alkaline treatment of the charred carbon produces a positive surface charge, which may be beneficial when the resultant activated carbon is used as adsorbent to

remove the negatively charged species in greater amounts. The easiest and most used method to produce porous carbons with basic surface properties is by high temperature treatment in an inert atmosphere.<sup>20</sup>

Factors affecting the formation of the porous structure during chemical activation include the type of raw material, process temperature, atmosphere of the activation process and the proportion of the activating agent to the raw material, which has an impact on pore quality and pore size distribution. The application of a higher impregnation ratio generally produces greater pore capacity and greater surface area of the activated products.

In comparison to physical activation, chemical activation processes have numerous advantages. One advantage results from the fact that chemical activation reduces tar production during pyrolysis, increasing the efficiency of the production process. Another very relevant and advantageous point in chemical activation is that it can be performed at lower temperatures and relatively shorter times when compared with the physical activation, besides that a larger porous structure may be obtained in the process. Due to all these factors, the amount of energy and the production costs of this process are smaller. In contrast, there are some drawbacks in the chemical activation methods, such as the need of a second phase after the main activation reaction, because the reaction requiring the material to be basically washed, depending on the reactants used in the activation reaction and continued washing with water. This step is important because of the high concentration of the activating agent and the likelihood that impurities from the activating agent will continue in the material produced and beyond the possible presence of additional reactants. Then, with the development of technology, it is already possible to combine the advantages and disadvantages of the two methods of activation, the physical and chemical.<sup>34,47</sup>



### 2.1.2.1 SOURCES OF CARBON

For the preparation of activated carbons, there is a wide variety of raw materials that may be used and whose main properties should include abundant, cheap, high carbon content and a low presence of inorganic substances. Additionally, some characteristics are important for the raw material, such as the easiness of activation, inherent porosity and high filterability. There are two main sources of activated carbon production: coal and agricultural residues, or lignocellulosic materials. Among the most commonly used raw materials are coal, mainly due to its low cost and large quantity. Another type of commercially activated charcoal source basically uses precursors, such as petroleum, wood, coal, peat and lignite residues, which are very expensive and non-renewable.<sup>47</sup> The adsorption characteristics of each type of coal are determined by two important factors: the nature of the plant material and its extent of the physico-chemical changes that occur during the formation of coal.<sup>47,48</sup> In Table 4 are shown the analysis of different materials coming from agricultural waste, containing some materials that are commonly used to produce activated carbon. It can be observed that the value of carbon when compared with oxygen is not too high.

**Table 4. Analysis of components in agricultural waste.**

Agricultural Waste	Component Analysis (w/w%)				Reference
	C	N	H	O	
Palm shell	50.01	1.90	6.9	41.00	49
Coconut shell	48.63	0.14	6.51	44.64	50
Olive stone	44.80	0.10	6.00	49.09	51
Corn cob	46.80	0.90	6.00	46.3	52
Almond shell	50.50	0.20	6.60	42.69	51
Bamboo	45.53	0.22	4.61	49.65	53
Grape stalk	46.14	0.37	5.74	36.6	54

The preparation of activated carbons from waste materials has several advantages, mainly of economic and environmental nature. It is because a wide variety of activated carbons have been prepared from different waste materials; conventional

wastes, from agriculture and wood industry, as well as non-conventional wastes, from municipal and industrial activities, have been used.<sup>48</sup>

Disposal of plastic waste, industrial waste, tires, sewage sludge and fertilizers are a very significant waste management problem. In this way, the alternatives to recycle these materials, using environmentally sustainable procedures, are very important. The use of waste as a source of carbon for the production of activated carbon may be an alternative, since it would also have a low cost and would solve a portion of the waste management challenges.<sup>48</sup>

Table 5 summarizes the carbon source, activation method and the agent or agents of activation used in different studies in regard to the preparation of activated carbons from MSW or agricultural wastes.

In this way, the variety of carbon sources is evident, many of which present a low cost, such as agricultural waste and municipal solid waste. In addition, there are several types of carbon activation, each of which has a characteristic of interest for its final use, such as greater or lesser surface area, for the type of adsorption in which it is desired to study.

**Table 5. Relation of material and activation methods (continue)**

<b>Material</b>	<b>Activation Method</b>	<b>Agent of activation</b>	<b>Technique</b>	<b>Reference</b>
Corn stalks	Physical Activation	CO <sub>2</sub>	Activation with CO <sub>2</sub>	55
Broiler litter	Physical Activation	Steam	-	56
Cactus fibers	Chemical Activation	HNO <sub>3</sub>	Nitration and reduction	57
Cherry stones	Chemical Activation	NaOH	-	58
Municipal Solid Waste	Chemical Activation	KOH/H <sub>2</sub> SO <sub>4</sub>	-	59
Peanut hull	Chemical Activation	H <sub>2</sub> O <sub>2</sub>	Modified by H <sub>2</sub> O <sub>2</sub>	60
Rice straw	Chemical Activation	HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	Oxidized with mixed of HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	61

**Table 5. Relation of material and activation methods**

<b>Material</b>	<b>Activation Method</b>	<b>Agent of activation</b>	<b>Technique</b>	<b>Reference</b>
Peach stones	Chemical Activation	H <sub>3</sub> PO <sub>4</sub>	-	62
Olives stones	Chemical Activation	H <sub>3</sub> PO <sub>4</sub> /ZnCl <sub>2</sub> /KOH	-	63
Eucalyptus wood	Chemical Activation	KOH/NaOH	-	64
Waste tea	Chemical Activation	K <sub>2</sub> CO <sub>3</sub>	Activation with K <sub>2</sub> CO <sub>3</sub>	65
Coconut pith	Chemical Activation	KOH	-	66
Tabaco	Chemical Activation	HNO <sub>3</sub>	-	67
Starch-rich banana	Chemical Activation	H <sub>3</sub> PO <sub>4</sub>	Activation with H <sub>3</sub> PO <sub>4</sub>	68
Coir fiber	Chemical Activation	ZnCl <sub>2</sub>	-	69

## 2.2 ADVANCED OXIDATION PROCESSES IN WASTEWATER TREATMENT

There are a large variety of treatment technologies to be use in wastewater treatment, to control or minimize water pollution. In this regard, one type of treatment is the advanced oxidation processes (AOPs), which are based on the action of hydroxyl radicals (HO<sup>•</sup>) to oxidize organic pollutants from waters and wastewaters. These processes are very efficient, promising and environmental-friendly. One of the main AOPs advantage is use of oxidizers with a strong non-selective oxidation power, which allow the oxidation of many organic components, including non-biodegradable and toxic, which are difficult to treat by cheaper methods such as biological processes. In this context, the AOPs applied in the treatment of wastewater show high stability and low biodegradability. Even when operating with near ambient pressure and temperature, it results in the generation of the strong oxidation agent, the hydroxyl radicals. That enables waters decontamination, allowing the complete degradation of organic pollutants into nontoxic products.<sup>70-72</sup>

AOPs include many techniques, such as methods based on ultrasound, plasma, photolysis, photocatalysis and electro-hydraulic discharge along with processes based on hydrogen peroxide, such as wet peroxide oxidation (WPO), Fenton, and Fenton-like

processes (intensified Fenton with another energetic source or with a heterogeneous catalyst). Among them, another AOP that uses H<sub>2</sub>O<sub>2</sub> is catalytic wet peroxide oxidation (CWPO). When iron ions (Fe<sup>2+</sup>) are used to catalyze the formation of HO• from H<sub>2</sub>O<sub>2</sub>, the process is usually known as the Fenton process. In the particular case of CWPO with activated carbons, AC and AC<sup>+</sup> act as reduced and oxidized catalyst states leading to the formation of HO• and HOO•, respectively.<sup>73</sup>

The main reactions of the Fenton process involved in the catalytic cycle can be described by Eqs. (1) and (2). Briefly, the interaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> in acidic media results in the decomposition of H<sub>2</sub>O<sub>2</sub> through the oxidation of Fe<sup>2+</sup> to ferric ion (Fe<sup>3+</sup>), with the formation of hydroxide ions (OH<sup>-</sup>) and HO•, as described by Eq. (1). Afterwards, the regeneration of Fe<sup>2+</sup> from Fe<sup>3+</sup> is mainly accomplished through the reaction of Fe<sup>3+</sup> with H<sub>2</sub>O<sub>2</sub>, as described by Eq. (2). For instance, the regeneration of Fe<sup>2+</sup> from Fe<sup>3+</sup> can also proceed through the reaction of Fe<sup>3+</sup> with hydroperoxyl radicals (HOO•), as described in Eq. (3)<sup>74</sup>:



The Fenton process is carried out with a homogeneous catalyst (an iron salt), but the last decades the scientific community has shown an interest for the development of heterogeneous catalysts in order to avoid the iron sludge formation observed with Fenton. In Fenton it is not possible to remove the catalyst from the effluent of the process without an additional separation step. In many cases, the iron is found in amounts exceeding the limits allowed by EU directives for discharge of treated water into natural receiving water bodies (2 mg·L<sup>-1</sup>), which in turn leads to the undesired production of large amounts of iron sludge.<sup>74,75</sup>

### 2.2.1 CATALYTIC WET PEROXIDE OXIDATION

CWPO is a low-cost type AOP usually studied in soft pressure and temperature conditions. Additionally, the oxidant used in the process ( $\text{H}_2\text{O}_2$ ) is eco-friendly when compared with, for example, persulfate agent and is safer to use  $\text{H}_2\text{O}_2$  when compared with other oxidants, such as  $\text{O}_3$ . In this process, an adequate solid catalyst is used generate hydroxyl radicals from the decomposition of hydrogen peroxide, which will further oxidize the organic matter present in a wastewater effluent.<sup>74,76</sup>

When CWPO is carried out with heterogeneous catalysts, some possible materials are employed as catalyst support, for example, alumina, silica, zeolites, pillared clays and activated carbon, among metal catalysts that are supported on metals oxide surfaces. Those materials have been shown an activity and stability on catalysis. It has been studied that carbon materials, for example, activated carbons, without any supported phase, are active catalysts for CWPO of water organic pollutants.<sup>77,78</sup> The development of metal-free catalysts for the CWPO process is of great interest in order to avoid iron leaching, deactivation and the use of high-cost metals. In this sense, it is important that the catalyst used presents a stable behavior. The activated carbon is a type of material that may be used and has shown activity and stability. Furthermore, as commented previously, this material can be produced from different sources.<sup>79-81</sup>

The advantage of using CWPO, which can be made with homogeneous or heterogeneous catalysts, is that it has been extensively used for the degradation and mineralization of various organic pollutants in water treatment.<sup>77</sup> The catalyst used in the CWPO must be active and stable because during the reaction it cannot be deactivated and cannot react with the aqueous phase (reaction components).<sup>78</sup>

To the best of my knowledge, this is the first work regarding the production of biochar materials from compost obtained in excess as by product after the treatment of the organic fraction of municipal solid waste, then this material is subjected to CWPO of 4-nitrophenol, that was used as non-biodegradable model pollutant.

## **MATERIALS AND METHODS**

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### 3 MATERIALS AND METHODS

#### 3.1 REACTANTS

The reactants used in this work follow below, according to the application for which they were used.

##### *Activated carbons*

- Sulphuric acid (98%). Labkem; Formula: H<sub>2</sub>SO<sub>4</sub>
- Glycerol (> 99%). Cymit Quimica, S.L; Formula: C<sub>3</sub>H<sub>8</sub>O
- Cyclohexane (99%). Fischer Chemical; Formula: C<sub>6</sub>H<sub>12</sub>
- Compost (its characterization is summarized in Table 6):

**Table 6. Properties provided by the company "Resíduos do Nordeste, EIM" and based on standard analytical techniques (continue)**

<b>Moisture</b>	<b>29.6 %</b>
<b>Organic Matter</b>	<b>48.8 %</b>
<b>Organic Carbon</b>	<b>27.1 %</b>
<b>Nitrogen (N)</b>	<b>1.3 %</b>
<b>Phosphorus (P<sub>2</sub>O<sub>5</sub>)</b>	<b>1.1 %</b>
<b>Potassium (K<sub>2</sub>O)</b>	<b>1.4 %</b>
<b>Calcium (Ca)</b>	<b>4.9 %</b>
<b>Magnesium (Mg)</b>	<b>0.8 %</b>
<b>Sulphur (S)</b>	<b>0.6 %</b>
<b>Boron (B)</b>	<b>43.4 mg/kg</b>
<b>Cadmium (Cd)</b>	<b>0.9 mg/kg</b>
<b>Chromium (Cr)</b>	<b>130 mg/kg</b>
<b>Copper (Cu)</b>	<b>209.7 mg/kg</b>
<b>Mercury (Hg)</b>	<b>0.4 mg/kg</b>
<b>Nickel (Ni)</b>	<b>49 mg/kg</b>
<b>Lead (Pb)</b>	<b>110 mg/kg</b>

<b>Zinc (Zn)</b>	<b>453 mg/kg</b>
<i>Salmonella spp.</i> (in 25 g of fresh matter) fresca)	<b>off</b>
<i>Escherichia coli</i> (n°/g of fresh matter)	<b>460</b>
<b>Density</b>	<b>0.45 kg/dm<sup>3</sup></b>
<b>Electric Conductivity</b>	<b>2.5 mS/cm</b>
<b>pH</b> (in fresh matter)	<b>8.0</b>

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### *Analytical techniques*

- Hydrogen peroxide (30% w/v). Fischer Chemical; Formula: H<sub>2</sub>O<sub>2</sub>
- Distilled water
- 4-Nitrophenol (99%). Acros Organics; Formula: C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>
- Sodium Sulphite anhydrous (98%). Panreac; Formula: Na<sub>2</sub>SO<sub>3</sub>
- Titanium (IV) oxysulfate (99.99%). Aldrich; Formula: TiOSO<sub>4</sub>
- Acetonitrile. Carlo Erba Reagents; Formula: C<sub>2</sub>H<sub>3</sub>N
- Acid ortho-phosphoric (85%). Riedel-de Haën; Formula: H<sub>3</sub>PO<sub>4</sub>
- Methanol. Fischer Chemical; Formula: CH<sub>3</sub>OH
- Ultrapure water
- 2-Nitrophenol (98%). Aldrich Chemistry; Formula: C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>
- 2-Nitroresorcinol (98%). Alfa Aesar; Formula: C<sub>6</sub>H<sub>5</sub>NO<sub>4</sub>
- Resorcinol (99%). Alfa Aesar; Formula: C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>
- 1,4-Benzoquinone (99%). Acros Organics; Formula: C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>
- Hidroquinone (99%). Merek KGa; Formula: C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>
- 4-Nitrocatechol. Fluka (≥ 98%); Formula: C<sub>6</sub>H<sub>5</sub>NO<sub>4</sub>
- Pyrocatechol. Fluka (99%); Formula: C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>
- Phenol crystallized (99.5%). Panreac; Formula: C<sub>6</sub>H<sub>5</sub>OH
- Ascorbic acid (99%). Fischer Chemical; Formula: C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>
- Acetic acid glacial (99,8%). Fischer Chemical; Formula: C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>
- Ammonium acetate (98%). Pronalab; Formula: C<sub>2</sub>H<sub>7</sub>NO<sub>2</sub>
- O-phenanthroline. Homemade. Formula: C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>



### 3.2 PREPARATION OF MATERIALS

In this work, the activated carbons were prepared by treatment with H<sub>2</sub>SO<sub>4</sub> and carbonization at 800 °C, adapting the procedure reported elsewhere<sup>82</sup>, exploring four methods to avoid the leaching of iron in the liquid-phase catalytic application to be used (CWPO). The strategies approach were:

(1) the preparation of material was made using 20 g of compost from the organic waste obtained and 100 mL of cyclohexane at 50 °C for 24 hours under stirring and further separation by evaporation (C-cC6 material), but it was found that the organic part did not separate in the evaporation.

(2) the preparation of C1G3S, C2G2S, C3G1S and CS from a mixture of compost and glycerol during 20 minutes at 180 °C under stirring, aiming to encapsulate the inorganic content;

(3) washing a CS material prepared directly from compost with H<sub>2</sub>O<sub>2</sub> 0.5 M at room temperature and 80 °C (CSHP and CSHPW material, respectively) using vacuum filtration;

(4) washing a CS material prepared directly from compost with HCl 1 M at 60 °C (CSAH material) under stirring.

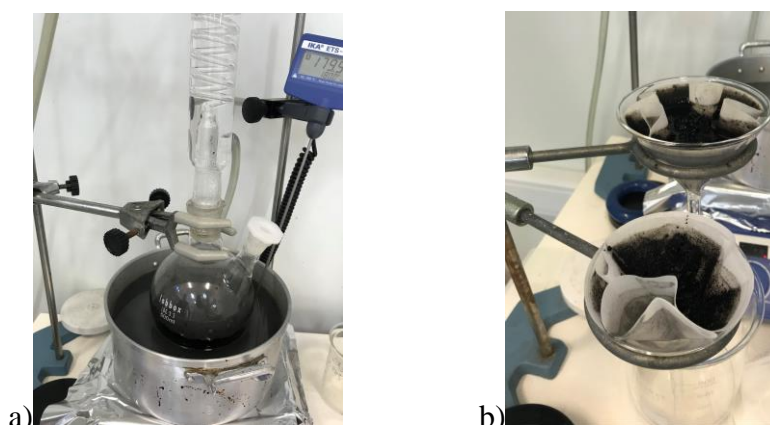
In preparation of the AC materials from compost, the materials referred in (2), named glycerol-based carbon materials, a mixture of glycerol, compost and sulphuric acid (40 g) was gently heated and exposed to 180 °C for 20 min to allow in situ partial carbonization. The mass ratios of glycerol and compost were varied in 4 reactions, with the amounts of these components resulting in 20 g.

Table 7 contains the mass ratios of reactions with glycerol and compost.

**Table 7. Mass ratios compost-glycerol.**

Material	Ratios
Compost-Glycerol	3:1
	2:2
	1:3
	4:0

The fourth reaction happened in the same conditions described but was used just 20 g of compost and sulphuric acid. After that reaction, the resulting material was filtrated with distilled water until the rising water reach a pH approximately of 6, then the materials were leaded to a furnace at 60 °C for 24 h. After that stage, the material was calcined under a nitrogen flow ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) at 120, 400 and 600 °C during 60 min at each temperature, and then at 800 °C for 240 min, defining a heating ramp. To obtain particle sizes in the range 0.160–0.053 mm, the calcined material was ground and sieved. Materials were named according to the mass ratio, so, following the order of Table 7, C3G1S, C2G2S, C1G3S, CS. Figure 2 shows the compost reaction and the materials being filtered to wash.



**Figure 2. a) Material preparation and b) Filtration**

The CS material used to prepare material (3), was a result of compost-sulphuric acid reaction. First, 15 mL of  $\text{H}_2\text{O}_2$  were mixed in 250 mL of distilled water (concentration of  $17.8 \text{ g L}^{-1}$ ) and wash the AC using a vacuum filtration, then the material was placed in furnace at 60 °C for 24 h to dry, resulting in the material CSHP. Another way of wash AC was preparing with the same procedure described, but the compounds was mixed at 80 °C for 40 min. This results in the CSHPW material.

In the production of material (4) AC from the compost-sulphuric acid reaction was used. It was washed with 100 mL of HCl 1 M per gram of solid during 24 h to

remove the activating agents. Final rinsing with distilled water at 60 °C until neutral pH. The resulting activated carbons were dried at 60 °C. This results in CSHA.

### 3.3 CHARACTERIZATION TECHNIQUES

Elemental analysis (CHNS) of the prepared materials was performed in a Carlo Erba EA 1108 Elemental Analyser. The textural properties were determined from N<sub>2</sub> adsorption-desorption isotherms at 77 K obtained in a Quantachrome instrument NOVA TOUCH LX<sup>4</sup> using long cells with a bulb and an outer diameter of 9 mm. The method of outgassing run at 120 °C during 16 h, according to the time proposed by IUPAC. The specific surface area ( $S_{BET}$ ) was calculated using the BET method in the range of  $p/p_0$  0.05 – 0.15. The external surface area ( $S_{ext}$ ) and the micropore volume ( $V_{mic}$ ) were obtained by the  $t$ -method (thickness was calculated by employing ASTM standard D-6556-01). The total pore volume ( $V_{Total}$ ) was calculated at  $p/p_0 = 0.98$ . The microporous surface area ( $S_{mic}$ ) was determined as the subtraction of  $S_{ext}$  from  $S_{BET}$ .<sup>83</sup>

### 3.4 CWPO OF 4-NP AND H<sub>2</sub>O<sub>2</sub> DECOMPOSITION

The oxidation reactions were performed in a 250 mL well-stirred (600 rpm) glass reactor, equipped with a condenser, a temperature measurement thermocouple, a pH measurement electrode and a sample collection port. The reactor was loaded with 50 mL of a 5 g/L 4-NP solution and heated by immersion in a water bath monitored by a temperature controller. Upon stabilization at the desired temperature, the solution pH was adjusted by means of an H<sub>2</sub>SO<sub>4</sub> solution (1 M). A calculated volume of H<sub>2</sub>O<sub>2</sub> (6 wt.%) was then injected into the system, in order to reach a H<sub>2</sub>O<sub>2</sub> concentration [H<sub>2</sub>O<sub>2</sub>] of 17.8 g/L, which is the stoichiometry concentration needed for mineralization (complete oxidation of organic matter). After its complete mixing, the catalyst was added to the solution, that moment being considered as  $t_0 = 0$  min. Typical experiments were performed during 1440 min, at T = 50 °C pH = 3 and catalyst concentration =

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2.5 g/L. The samples for analysis were periodically withdrawn following selected times: 5, 15, 30, 60, 120, 240, 360, 480 and 1440 min and placed in two eppendorf cliparts for  $H_2O_2$  and organic content determination. The evolution of  $H_2O_2$  was followed taking 0.4 mL of samples and then centrifuged to separate the catalyst from the dilution. After 24 h of reaction, the catalyst was separated by filtration (47 mm, MS Nylon Membrane Filter), washed with distilled water and dried at 60 °C. Figure 3 shows the bath and the reactor used in the described experiments.



**Figure 3. Bath and reactor used in the CWPO and  $H_2O_2$  decomposition experiments**

Tests of  $H_2O_2$  decomposition were made in the absence of 4-NP following the same procedure described in the oxidation for the quantification of  $H_2O_2$ .

### 3.5 ANALYTICAL METHODS

#### *$H_2O_2$ determination*

To monitor the decomposition of  $\text{H}_2\text{O}_2$ , 1 mL of diluted sample was added in a 20 mL volumetric flask with the solution of  $\text{H}_2\text{SO}_4$  (1 mL/0.5M) and  $\text{TiOSO}_4$  (0.1 mL) and diluted again with distilled water. Then, samples were analysed by UV-Vis spectrophotometry (T70 spectrometer, PG Instruments, Ltd.) at the wavelength of 405 nm to determine its absorbance. Previous calibration of the equipment with different aliquots is represented in Figure 4.

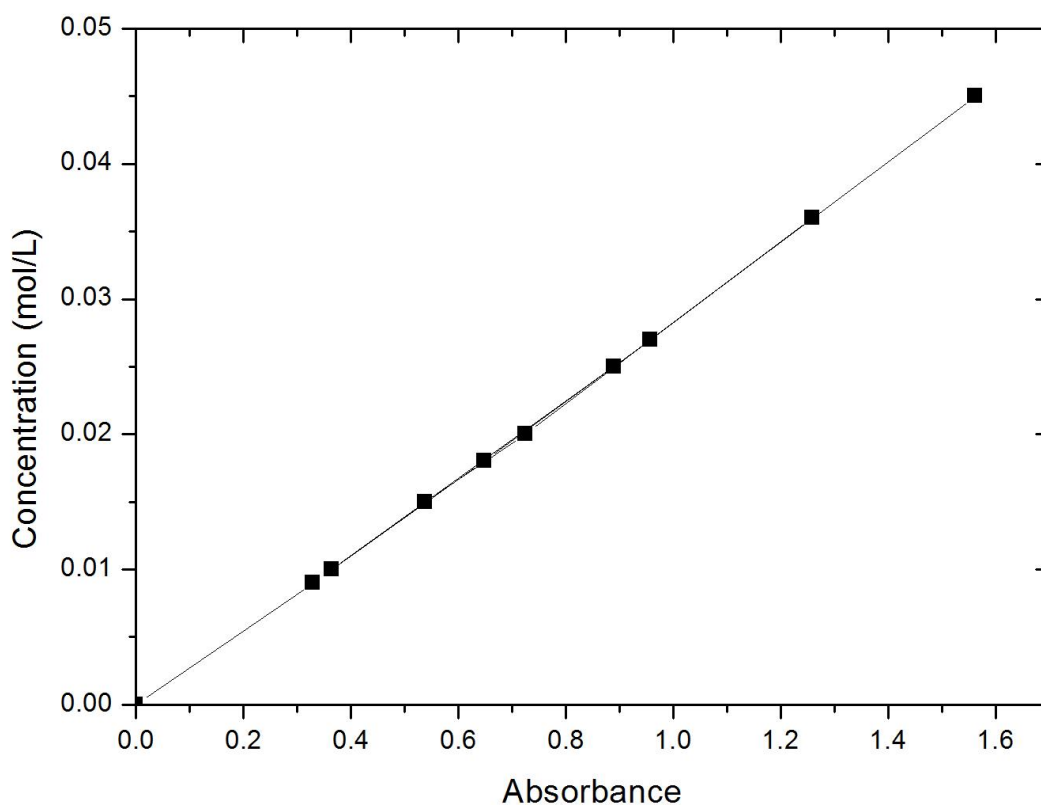


Figure 4. Calibration curve for  $\text{H}_2\text{O}_2$  concentration

The values of  $R^2$  is close to 1 and the 9 points of calibration have a good adjust. This result allows the quantification of  $\text{H}_2\text{O}_2$  concentration from the absorbance of the samples.

### *HPLC measurements*

A Jasco HPLC system equipped with an UV-vis detector (UV-2075 Plus), a quaternary gradient pump (PU-2089 Plus) for solvent delivery ( $1 \text{ mL min}^{-1}$ ) and a RES ELUT  $5 \mu \text{ C18 90A}$  column ( $150 \text{ mm} \times 4.6 \text{ mm}$ ) of AGILENT was used.

Different mobile phases were assessed in isocratic and non-isocratic methods considering different mix mixture of ultrapure water with phosphoric acid, which pH should be 2 (A) and acetonitrile (B), in the range A:B = 90:10-75:25. It was possible to analyze the model pollutant (4-NP) and its possible oxidized intermediates, namely hydroquinone, 1,4-benzoquinone, 4-nitrocatechol, catechol and phenol. The wavelength used to measure the peaked absorbance of the compounds was 277, for 2-nitrophenol, 2-nitroresorcinol, resorcinol, 4-nitrophenol, hydroquinone, pyrocatechol and phenol compounds, and 244 nm for 1,4-benzoquinone and 4-nitrocatechol compounds.

### *Total Organic Carbon analyzer*

The quantification of the Total Organic Carbon (TOC) of the liquid aliquots was performed by using a Shimadzu Equipment TOC-L CSH/CSN. The samples were placed in an eppendorf clipart with 0.2 g of  $\text{Na}_2\text{SO}_3$ , centrifuged and diluted considering 0.8 mL in 20 mL volumetric flask and diluted again taking 10 mL from there to place in a 20 mL volumetric flask.

### *Iron determination*

The quantification of the iron in the remaining solution of CWPO and  $\text{H}_2\text{O}_2$  decomposition experiments was performed in order to determine the leached iron from prepared materials to the reaction media, according to ISO 6332.<sup>84</sup> First, the samples were filtered, and then the Fe content determined by absorption, using an UV/VIS absorption spectrometer (T70 UV/VIS Spectrometer, PG Instruments). It was used 4 mL of reaction solution for blank and sample. 0.5 mL of ascorbic acid ( $12.5 \text{ g L}^{-1}$ ) was

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the then added. After 30 min 0.5 mL of o-phenanthroline ( $2 \text{ g L}^{-1}$ ) was added in sample and 0.5 mL of distilled water in blank and, in both, 1 mL Ac<sup>-</sup>/AcH, that was prepared with 12.5 g of ammonium acetate, 35 mL of acetic acid and completed with ultrapure water in a volumetric flask of 50 mL. Finally, the solutions were aged for 24 h and the absorbance was determined at 510 nm. The blank was prepared without o-phenanthroline, the reactant that shows the iron presence in the sample. Thus, the value obtained in the blank analysis is subtracted from the value of a sample measured with o-phenanthroline.

## **RESULTS AND DISCUSSION**

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## 4 RESULTS AND DISCUSSION

### 4.1 YIELD IN MATERIALS PREPARATION

The yields obtained in the reactions carried out to prepare the materials using the compost as source are present in **Erro! Fonte de referência não encontrada..**

**Table 8. Yield obtained in the production of materials from compost**

Material	Initial Weight (g)	Weight after reaction (g)	Weight after pyrolysis (g)	Yield (%)
CS	30.19	13.92	9.22	30
C2G2S	20.00	9.53	5.97	29
C1G3S	20.00	8.81	5.48	27
C3G1S	20.03	8.23	5.61	28

The yield was calculated using Equation 4:

$$Yield = \frac{W_F}{W_0} * 100 \quad (4)$$

Where  $W_F$  is the mass after pyrolysis and  $W_0$  is the initial weight. The mass loss after reaction with  $H_2SO_4$  was not considered to calculate the yields represented in Table 8.

The yield in the preparation of the materials was higher than 27 % for all samples. The greatest mass loss was after the reaction of compost, glycerol and  $H_2SO_4$ , because the material undergoes to washing process and an amount of the material remaining in the paper filter is lost. Another factor that explains this loss of mass is the volatilization of organic matter, which is largely present in the material prepared from the reaction of compost and glycerol (as shown in Table 6).

The yield obtained is higher when compared to other works<sup>85,86</sup> regarding the preparation of activated carbons from tyres<sup>85</sup> and grapevine rhytidome<sup>86</sup>. In this last

study<sup>86</sup>, the production of activated carbon was performed by using chemical activation with phosphoric acid, and the best yield obtained was 25 %. In this sense, the yield obtained in this work by chemical activation and calcination from compost was better when compared with literature. There are only a few works regarding the production of activated carbons from waste with the yield reported.

## 4.2 MATERIALS CHARACTERIZATION

### 4.2.1 ELEMENTAL ANALYSIS

The composition of nitrogen, carbon, hydrogen and sulphur was assessed by elemental analysis. The results of the materials prepared with glycerol is summarized in Table 9.

**Table 9. Elemental analysis of the materials prepared**

Material	N (%)	C (%)	H (%)	S (%)	Remaining (%)
CS	0.46	18.29	0.25	5.28	76.2
C3G1S	0.02	33.87	0.28	2.30	63.5
C2G2S	0.60	53.25	0.94	1.40	43.7
C1G3S	0.02	74.44	0.65	0.99	23.8
C1G3S Recovered	0.02	67.06	0.98	0.67	34.5

Firstly, the hydrogen and nitrogen have low values in all the samples prepared and presents no linear relation with the mass ratios of glycerol used in the materials.

In one hand, the quantity of carbon is higher in materials prepared with glycerol. That is because glycerol precursor has a large amount of carbon when compared to the compost supplied for the waste management company (as shown in Table 6). The presence of the sulphur in the samples is due to the chemical activation with H<sub>2</sub>SO<sub>4</sub>. As can be seen, the high quantity of sulphur was found for the material prepared without glycerol. In fact, it is possible to observe a tendency in the S-content

of the samples with the glycerol to compost ratio used. Thus, the sulphur is best fixed on the materials when compost is used, likely because sulphur react with some metals presents in compost and sulphur stay anchored to the material framework, even when is washed. Other reason is the presence of sulphur in compost (Table 6), that is 0.6 wt. % with dry matter. It is also observed that when recovering the material C1G3S from the oxidation reaction, the quantity of carbon is still high.

The high loads of sulphur observed in this work is in line that study activated carbon with different treatment <sup>83</sup>, where the preparation of one material reported was employing sulphuric acid in the activation of carbon, lead to higher quantities of sulphur when compared with other materials.

The remaining composition (unknown) presented in this work is associated with oxygen and ash contents of the materials. Table 9 shows a tendency related with the ratio compost/glycerol, with the values of remaining composition decreasing as the quantity of glycerol increase. Those results show that the material prepared without glycerol has higher yield, which was ascribed to the inorganic content of the raw material.

#### 4.2.2 ADSORPTION ISOTHERMS

IUPAC grouped adsorption isotherms in six types, in 1985. However, various new characteristic types of isotherms have been identified and shown to be closely related to particular pore structures. Thus, IUPAC has to consider it expedient to refine the original IUPAC classifications of physisorption isotherms and associated hysteresis loops.<sup>87</sup> The new classification follows in Figure 5.

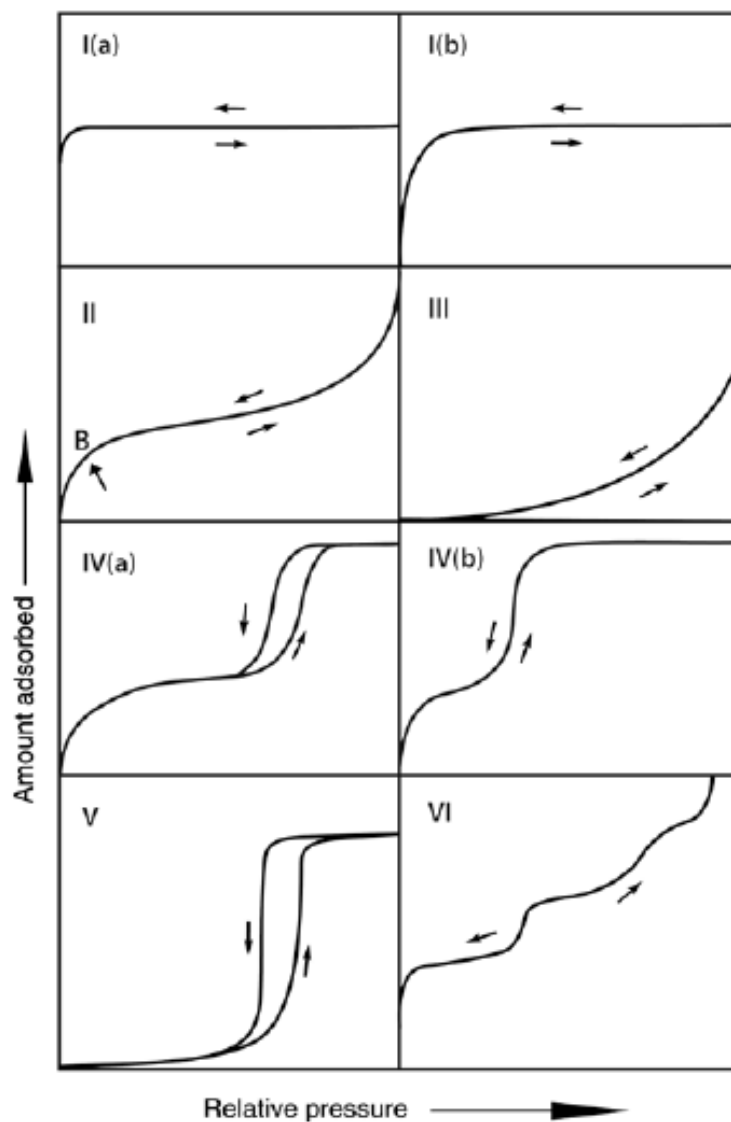


Figure 5. Classification of physisorption isotherms IUPAC<sup>87</sup>

The adsorption and desorption isotherms of N<sub>2</sub> on prepared samples obtained by the Quantachrome instrument is depicted in Figure 6.

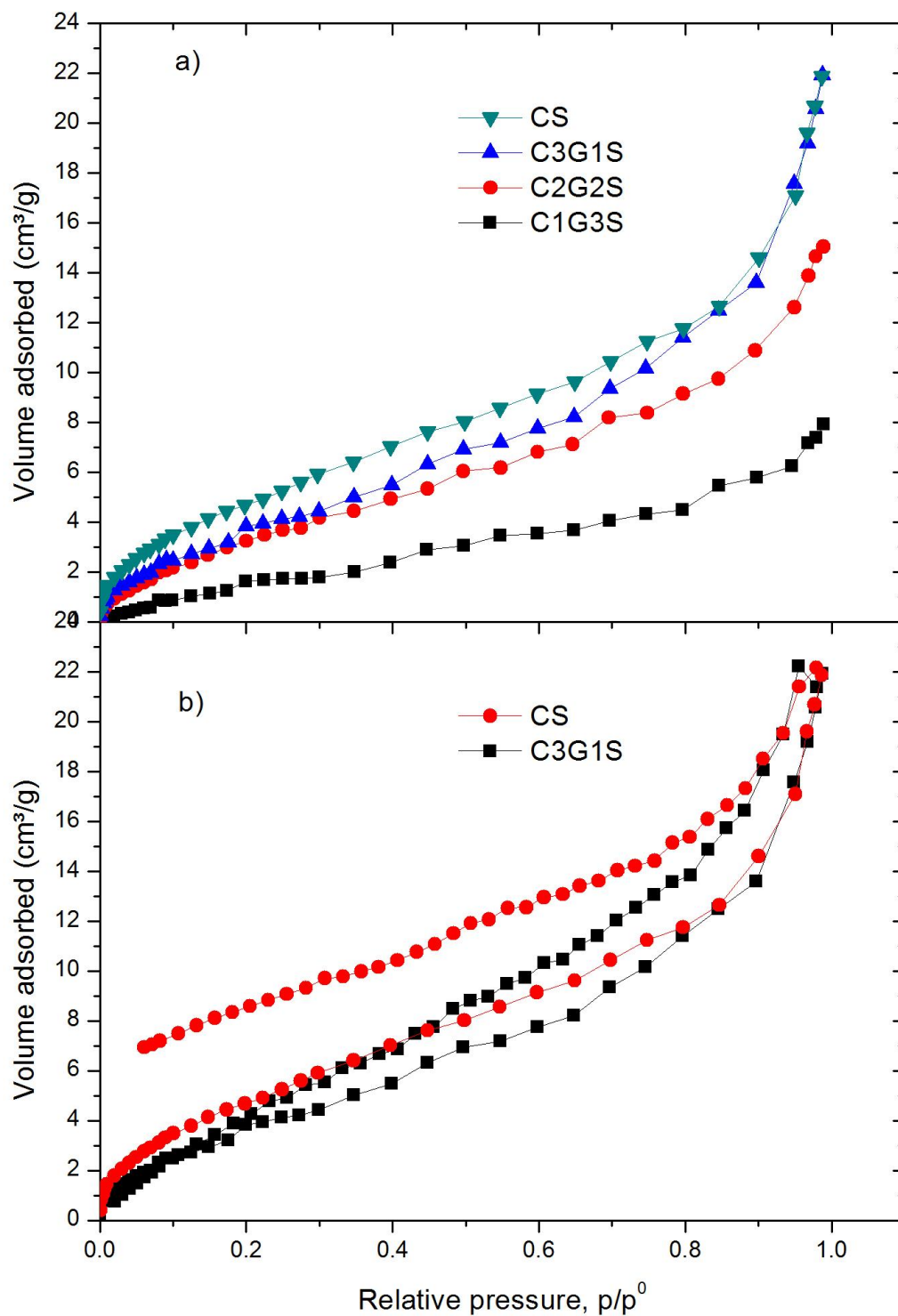


Figure 6. Adsorption isotherms at 77 K of the materials prepared a) Adsorption of materials b) Adsorption-desorption of materials with high  $S_{BET}$ .

Observing the results given in Figure 6 it is concluded that the material CS show the highest adsorption, and that a decrease is observed upon incorporation of glycerol in the materials. However, similar N<sub>2</sub> sorption isotherms were obtained for these all materials, with a hysteresis loop of the H1 type (according to the current IUPAC<sup>87</sup>, following the revisions of 1985 IUPAC recommendations on physisorption isotherms), which is typically found for mesoporous carbon materials. This type of hysteresis loop is found in materials which exhibit a narrow range of uniform mesopores and usually, the network effects are minimal, and the steep, narrow loop is a clear sign of delayed condensation on the adsorption branch.<sup>87</sup>

Comparing the type of the adsorption isotherms obtained in this work with IUPAC is possible to conclude that it fits in type V. The type V has an isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent–adsorbate interactions of mesoporous.<sup>87</sup>

In this context, the results of the isotherm analysis are given in Table 10, where the values were calculated by the Quantachrome software.

**Table 10. Textural properties of the materials determined from BET and *t*-plot methods.**

Material	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{EXT}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{mic}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_T$ (cm <sup>3</sup> g <sup>-1</sup> )
C1G3S	8.9	8.43	0.51	7.92
C2G2S	14.03	14.03	0	15.04
C3G1S	14.13	14.13	0	21.92
CS	19.15	17.87	1.28	21.86

The results of these materials show that BET surface areas are not high as in typical activated carbons showed in study with commercial activated carbon<sup>83</sup>. All the materials undergone a reaction with sulphuric acid, which may not represent difference for materials in terms of surface area. In this context, the ratio of glycerol in materials apparently makes differences in the surface area values obtained. As long as the glycerol mass ratio decrease, the surface area increases. This behavior may be explained due to the fact that the material prepared with glycerol is not activated after the

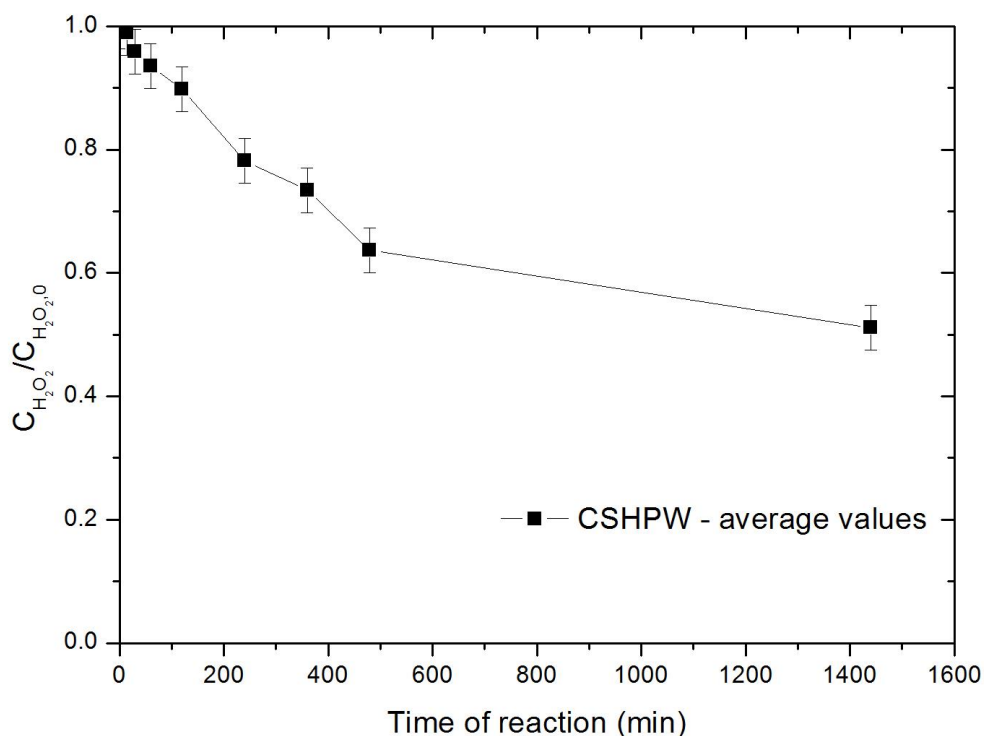
carbonization, such as reported in work<sup>82</sup>, where was produced materials with glycerol. Thus, the material with more ratio of glycerol, has a lower  $S_{BET}$  when compared with other materials.

It is possible to observe that  $S_{BET}$  and  $S_{EXT}$  of all materials is low for all because of the low quantity of microporous. Thus, this material may present more quantity of mesoporous, which is represented in the total volume and low values in microporous surface area. In some works reported in the literature of the textural properties as in carbon xerogels<sup>74</sup> and in work with study of different treatment of activated carbon to water treatment shows that these materials have microporous in high quantity. In consequence, the BET surface area is different of external and the  $S_{mic}$  shows values higher than presented in this work. Thus, the materials prepared may present mainly mesoporous and C1G3S and CS have a low quantity of microporous, leading to a non-uniform distribution of porous in the materials.

### 4.3 EXPERIMENTAL REACTIONS

#### 4.3.1 REPRODUTIBILITY

The reactions were repeated two times to test the reproducibility of CWPO with material CS washed with hydrogen peroxide at 80 °C. The results of the reactions carried out are represented in Figure 7 with average of normalized concentration values, and the standard error calculated shows that has a minimum difference between reactions.



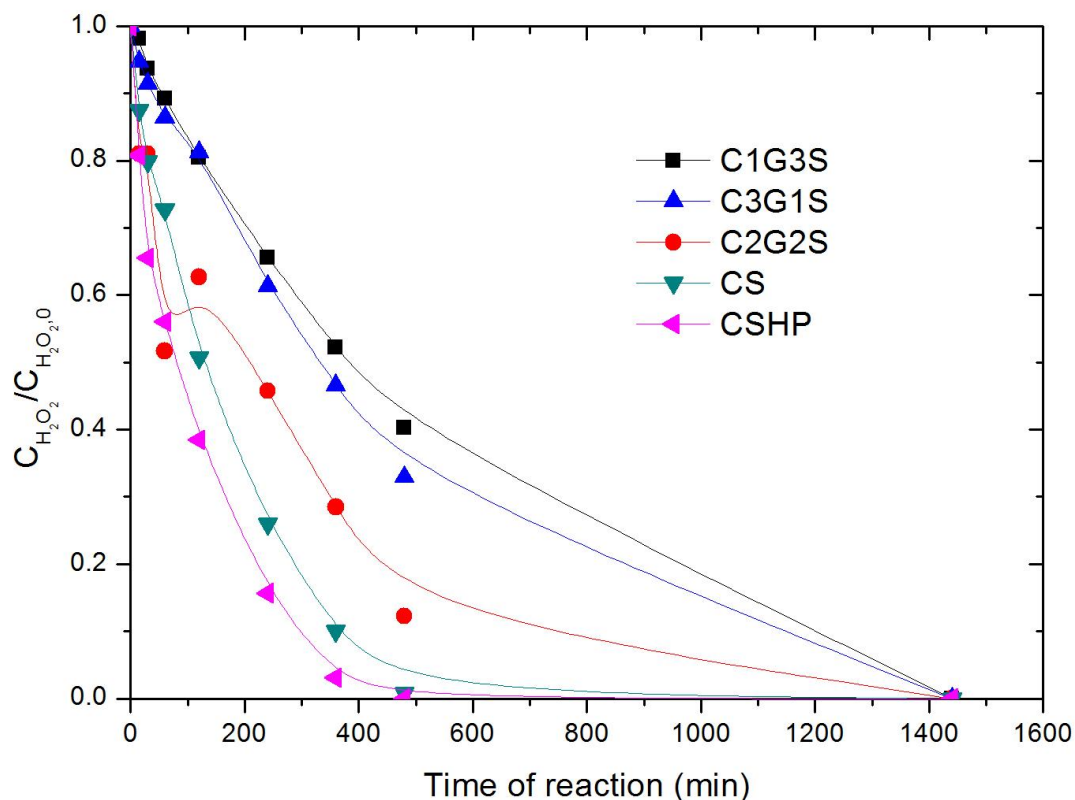
**Figure 7. Reproducibility of the CWPO reaction with standard error bars carried out under the operating conditions:  $C_{A.NP} = 5 \text{ g L}^{-1}$ ,  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $\text{pH} = 3$  and  $T = 50 \text{ }^\circ\text{C}$**

Though the error presented low values, it may be explained by the heterogeneous nature of the materials, because compost has different quantities of components in its composition. In addition, the compost is not homogenized. Thus, the presented values show that the obtained results have veracity to be used in the other calculations of this work.

#### 4.3.2 DECOMPOSITION OF HYDROGEN PEROXIDE

Concentration of  $\text{H}_2\text{O}_2$  was calculated through the values obtained in UV-Vis analysis, that was measured by the samples taken during the time of decomposition reaction, where it is possible to analyze the conversion and behavior of the activated carbons prepared (Figure 8).





**Figure 8.** Normalized concentration of  $H_2O_2$  as a function of time during the decomposition experiments (normalized for the corresponding initial concentrations) under the operating conditions:  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $\text{pH} = 3$  and  $T = 50 \text{ }^\circ\text{C}$ .

The experiments of  $H_2O_2$  decomposition were done following the conditions of  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $\text{pH} = 3$  and  $T = 50 \text{ }^\circ\text{C}$ . The results presented in Figure 8 show that all materials are active in the process studied and represented. The iron values were calculated preparing the sample according to the method ISO 6332<sup>84</sup>, and using the absorbance values measured in UV/Vis. To calculate the concentration, first calibration was performed to obtain the concentration values in the samples took at the end of reaction.

Table 11 shows the determination of iron at the end of the  $H_2O_2$  decomposition experiments in terms of leached percentage, calculated using the leached concentration divided by the catalyst concentration used in the reaction ( $2.5 \text{ g L}^{-1}$ ).

**Table 11. Measurement of Fe leached at the end of the H<sub>2</sub>O<sub>2</sub> decomposition experiments**

Material	Fe Leached (%)
C1G3S	0.2
C2G2S	1.1
C3G1S	0.4
CS	0.3
CSHP	2.10

In this sense, the values of iron leached show that the higher quantity of leached iron was obtained with the material CSHP, which may explain the high conversion, because in this situation the iron act like in Fenton process. Thus, the iron present also acts as a homogeneous catalyst, in addition of these contribution, material has functional groups in surface that may be obtained from the wash with hydrogen peroxide.

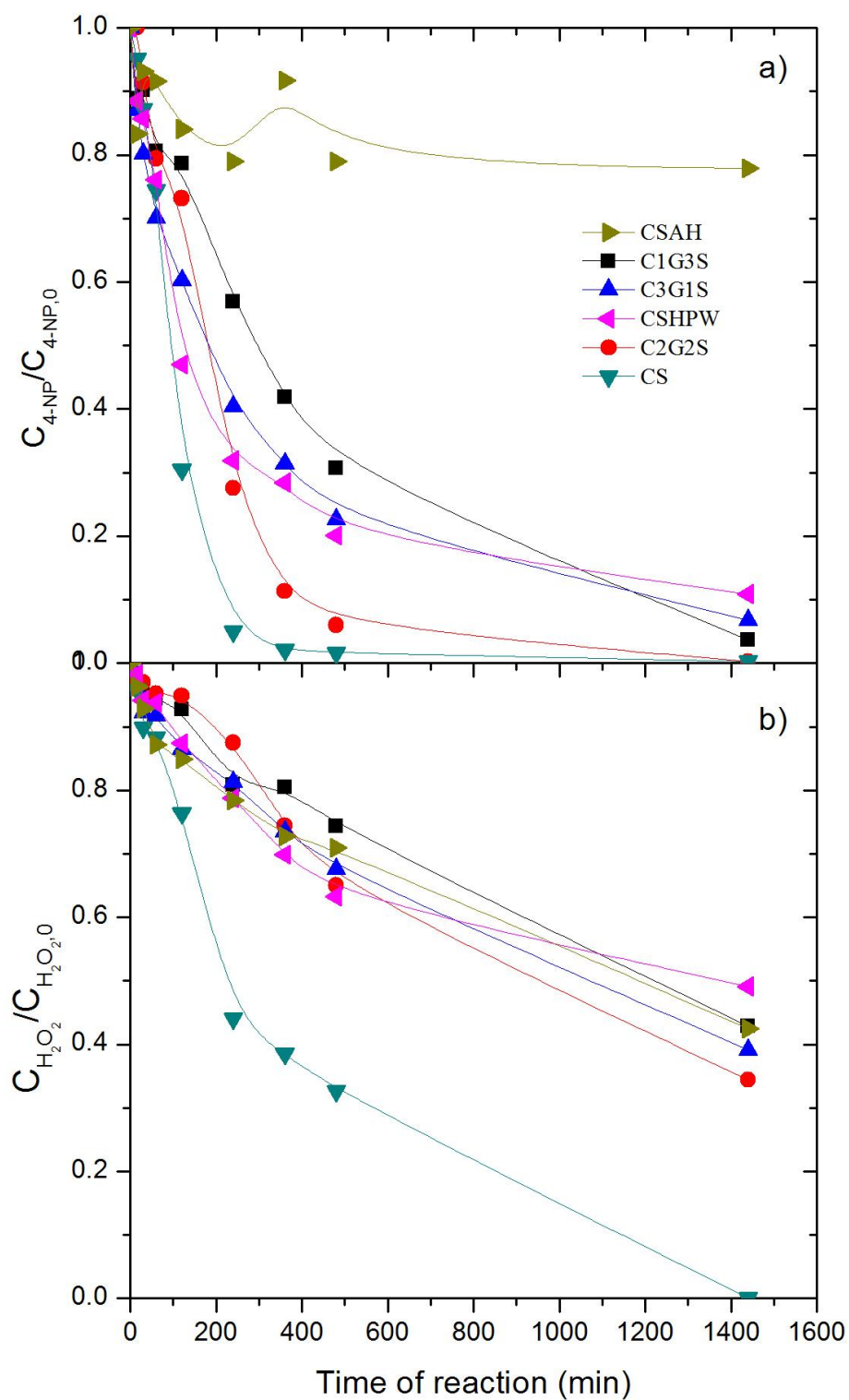
The conversion presented by the material prepared was acceptable by the fact that all of them results in 100 % decomposition of H<sub>2</sub>O<sub>2</sub>. In other works reported in literature<sup>88</sup> where was studied the decomposition of H<sub>2</sub>O<sub>2</sub> as in this work. The decomposition percentage obtained not happened as in this work. Furthermore, the best material used in this work show a decomposition of 61 % in 120 min, while in results studied in work that made the decomposition of H<sub>2</sub>O<sub>2</sub><sup>88</sup> the best materials lead to a decomposition value of 63 % in 150 min. The material with high mass ratio of glycerol has a low percentage of iron leached and lower conversion, suggesting that iron may closely influence the reaction.

#### 4.3.3 CATALYTIC WET PEROXIDE OXIDATION

The materials prepared were assessed in the CWPO of 4-NP. The conditions used in this reaction were  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $C_{4-NP} = 5 \text{ g L}^{-1}$ , pH = 3 and T = 50 °C. Figure 9 shows the concentration as a function of time during the reaction. The H<sub>2</sub>O<sub>2</sub> decomposition reaction was made first and the materials tested shows activity. The materials washed with hydrogen peroxide (at different temperatures) and hydrochloric acid were prepared to test if it was possible to increase the activity in the CWPO reaction. Then, all materials were used as catalyst in CWPO

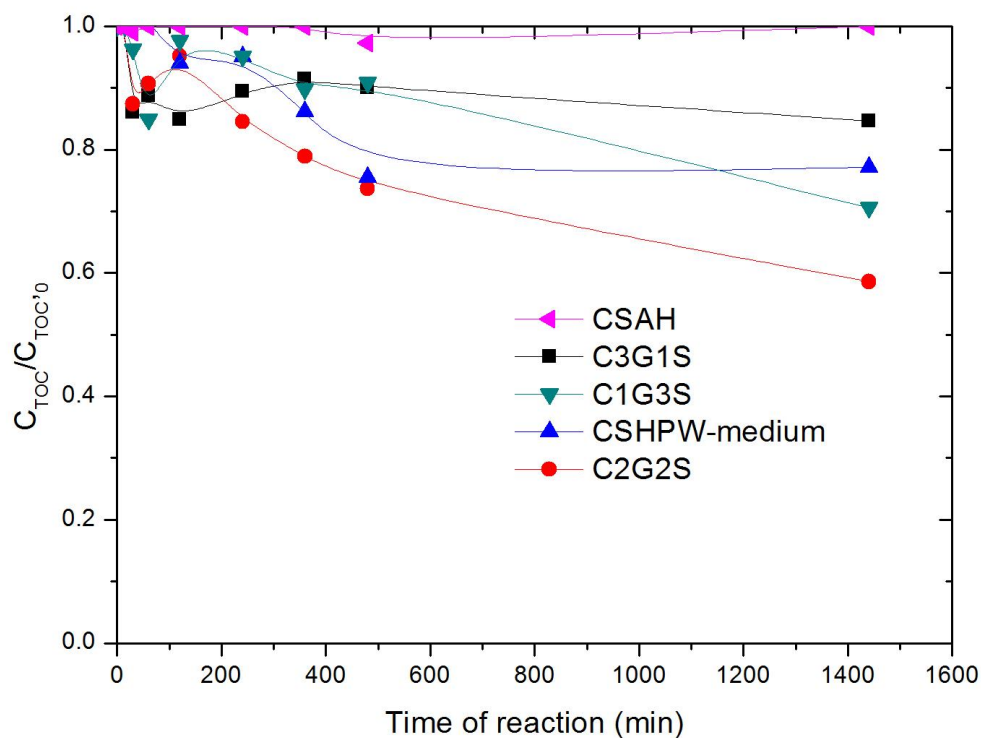
reaction to compare the activity with 4-NP oxidation and H<sub>2</sub>O<sub>2</sub> decomposition. The material CS present a higher oxidation of 4-NP (Fig. 9a). Figure 9b shows that material CS decomposes H<sub>2</sub>O<sub>2</sub> at a much higher rate than the other materials, namely 84% of conversion in 1440 min. In this sense, the behavior demonstrated for material CS may be explained due to iron leaching. The determination of this metal present in Table 11 shows a presence of iron. Thus, the iron acts as a homogeneous catalyst in the reaction, as in the Fenton process. Furthermore, in this process has the contribution of iron catalyst and the activity of the material, resulting in a conversion of 99 % 4-NP and 84 % H<sub>2</sub>O<sub>2</sub> at time 1440 min.

Previous works that analyze activity of activated carbon produced with carbon xerogels<sup>74</sup> and graphene<sup>76</sup> show the oxidation of 4-NP in CWPO process. After 1440 min the normalized concentration of the best material results around 0.4. In this work, the normalized concentration of CS material results around 0 (100% conversion).



**Figure 9.** Normalized concentration of a) 4-NP and b) H<sub>2</sub>O<sub>2</sub> as a function of time during the CWPO experiments under the operating conditions:  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $C_{4-NP} = 5 \text{ g L}^{-1}$ , pH= 3 and T = 50 °C.

The analysis of TOC was performed with the samples taken from the CWPO reaction. The results are presented in Figure 10.



**Figure 10. Normalized concentration of TOC as a function of time during the CWPO experiments (normalized for the corresponding initial concentrations) under the operating conditions:  $C_{H_2O_2} = 17.8 \text{ g L}^{-1}$ ,  $C_{cat} = 2.5 \text{ g L}^{-1}$ ,  $C_{4-NP} = 5 \text{ g L}^{-1}$ ,  $\text{pH} = 3$  and  $T = 50 \text{ }^\circ\text{C}$ .**

The materials presented appreciable conversion, in this case, C2G2S has results between 40 % and 50 %. This result agrees with Figure 10, how was explain, show a conversion in reaction for the behavior of the 4-nitrophenol and  $\text{H}_2\text{O}_2$  normalized concentration. The material CSAH, do not show conversion of TOC, probably because is not activated as the other materials, show the same behavior in Figure 9.

The results presented in other works with different activated carbon, one prepared with xerogels<sup>74</sup> and other used commercial carbon black<sup>78</sup> are in line with the results obtained in this work. The determination of iron was made at the end of each

CWPO reaction, and the materials with better conversion values have shown higher iron leaching values. This also happened in the H<sub>2</sub>O<sub>2</sub> decomposition runs, where better decomposition values were associated to iron leaching in larger amounts.

The TOC, 4-NP, H<sub>2</sub>O<sub>2</sub> concentration and leached iron are depicted/represented in Figure 11.

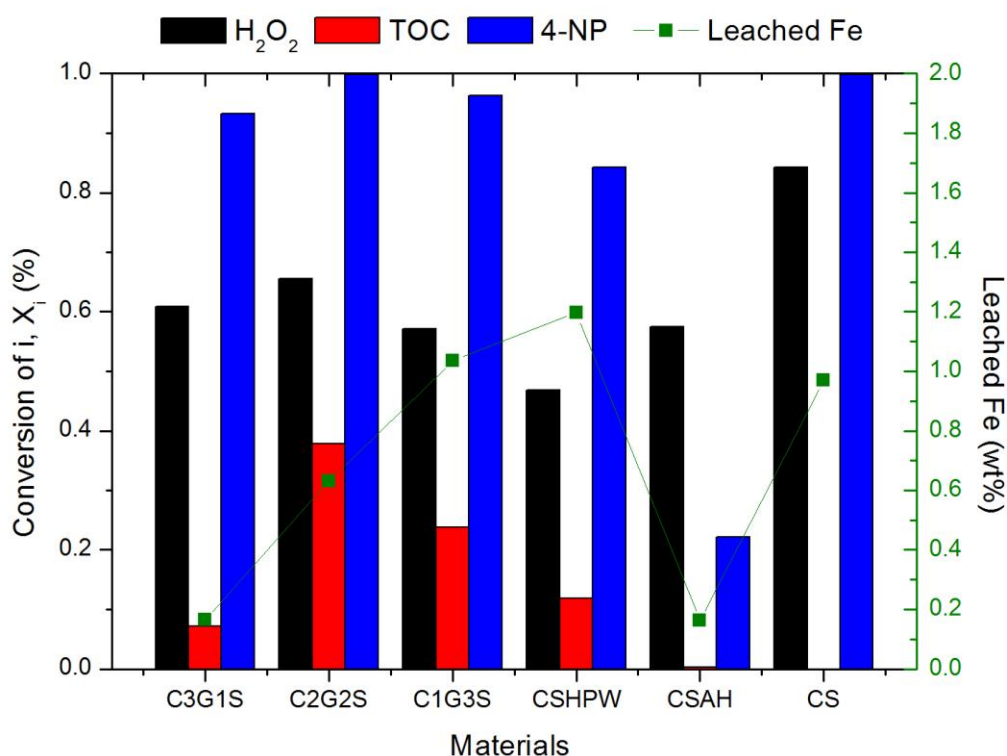


Figure 11. Relation between conversion and leaching of iron after 1440 min of reaction

The relation between iron and the conversion values obtained is visible. It is observed in Figure 11 that the higher quantities of iron leached is obtained with the materials with greater mass ratio of glycerol. A possible is that in the preparation of those materials, the iron stayed with carbon molecules. However, in the CWPO reaction, iron was leached, acting as a homogeneous catalyst and resulting in high conversion. The material CS, not synthesized from glycerol, the high conversion with the quantity of iron may be due to the carbon molecules present in compost and the

directly contact of compost with sulphur acid in reaction. This possibly made the material with more activated surface and higher specific surface area.

Other works<sup>84</sup> also show a relationship between leached iron and conversion (higher leaching in materials with more conversion), in line with the results of this work. However, the higher decomposition of H<sub>2</sub>O<sub>2</sub> studied in work with carbon nanotubes<sup>84</sup> was ascribed to the presence of an iron leached amount around 2 mg L<sup>-1</sup>. In this work, the quantity of iron leached is lower.

Another work, that studied the method to determined metals in solutions<sup>89</sup> shows that o-phenanthroline can form complexes with some metals, as Zn (II), Cu (II), Co (II), among others. The determination of iron leached in this work was done using o-phenanthroline as indicator. Thus, the high quantity of iron leached detect may also be explained by this interference.

#### 4.4 STUDY OF THE OPERATING CONDITIONS IN CWPO

The material CS presented high conversion, so it was selected to study the influence of other operation conditions. In this sense, CWPO was performed in conditions of  $C_{4-NP} = 1 \text{ g L}^{-1}$ ,  $C_{H_2O_2} = 3.56 \text{ g L}^{-1}$ ,  $C_{cat} = 0.5 \text{ g L}^{-1}$ . In Figure 12 is represented the behavior of the materials at temperatures of 50 °C and 80 °C. In this sense, at 80 °C the oxidation of 4-nitrophenol is higher, as well as the decomposition of H<sub>2</sub>O<sub>2</sub> and TOC. This is explained by the influence of temperature in the kinetic of reaction. Furthermore, in the reaction done at 80 °C the quantity of iron analyzed was 30 % higher than in reaction at 50 °C.

The results published in the literature that studied the kinetic model in CWPO using activated carbon as catalyst<sup>78</sup> show that higher temperature increases the conversions of H<sub>2</sub>O<sub>2</sub> and the oxidation of pollutant and TOC. In this sense, this work shows as well increased rates of H<sub>2</sub>O<sub>2</sub> decomposition, which leads to higher production of active radical species. The behavior of 4-NP oxidation may be explained by the formation of intermediaries, that appeared fast, which were also affected by the

temperature. The TOC results obtained in this work has a similar trend with previous work<sup>78</sup>, due to the presence of some refractory products.

It was observed that reaction with larger amount of leached iron occurred at 80 °C. A work in literature explains that the Fenton process has a strong influence of temperature<sup>90</sup>, when temperature is increased, higher conversions are obtained. Thus, the trend of this work, represented in Figure 12, shows the behavior presented. The higher conversion is possible to be observe by the normalized concentration in the oxidation of 4-NP, decomposition of H<sub>2</sub>O<sub>2</sub> and TOC at 80 °C (Figure 12).

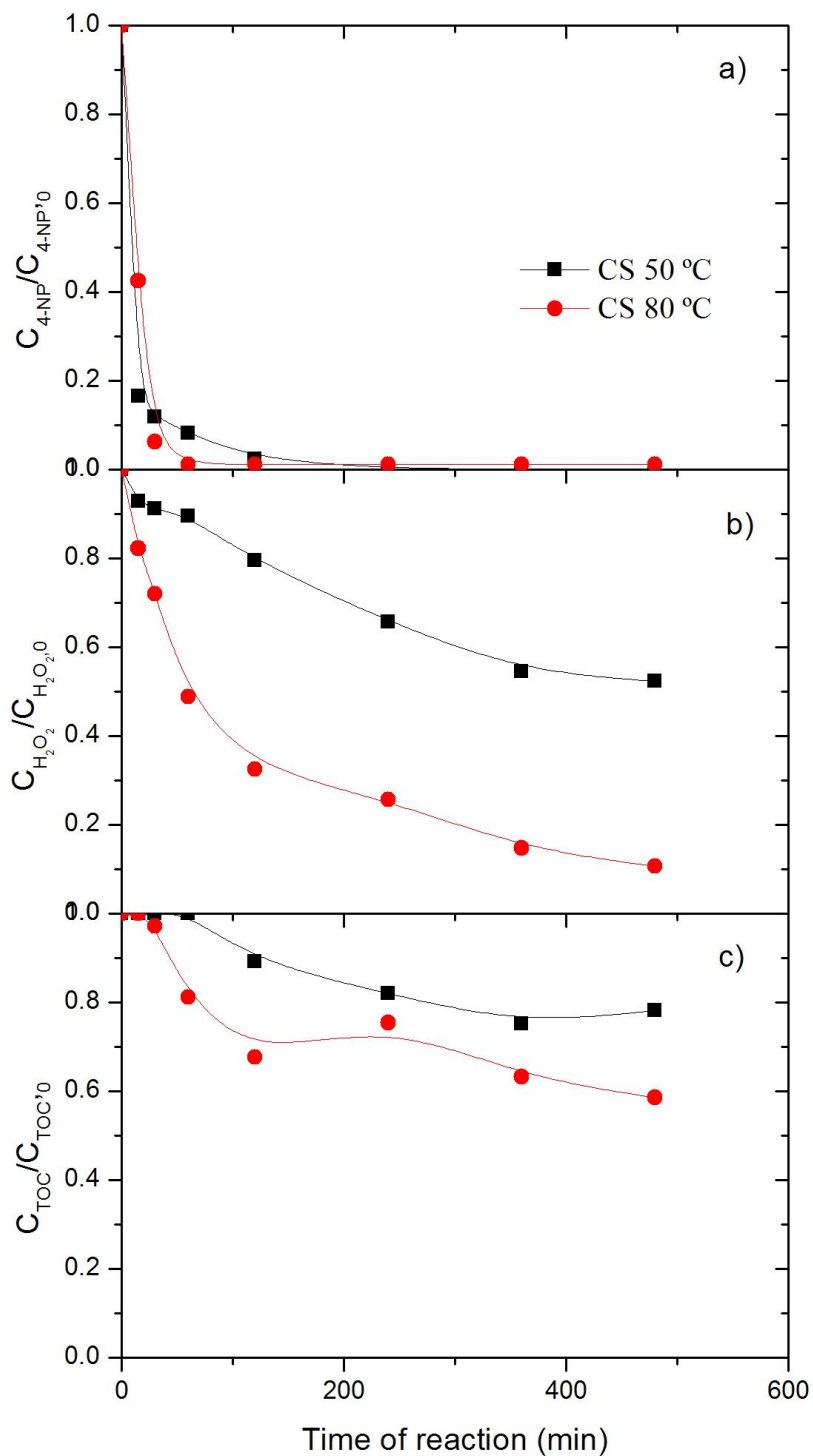
At the end of the reactions, the leached iron was determined using the method ISO 6332<sup>84</sup> with absorbance analyze made in UV/Vis to calculate concentration the iron present. Table 12 shows the values obtained.

**Table 12. Fe leached at the end of the CWPO experiments.**

Material	Reaction Temperature (°C)	Fe Leached (wt%)
CS	50	0,80
CS	80	1,14

In this context, the values of normalized concentration of 4-NP, H<sub>2</sub>O<sub>2</sub> and TOC present better results in CWPO reaction at 80°C as show in Figure 12. The higher percentage of iron leached present in the reaction at 80 °C may explain, with Fenton process, the higher removal values. Thus, the activity of the materials, temperature and iron have influence in reaction.





**Figure 12. a) Normalized concentration of 4-NP b) Normalized concentration of  $H_2O_2$  c) Normalized concentration of TOC (normalized by the corresponding initial concentrations) under the operating conditions:  $C_{4-NP} = 1 \text{ g L}^{-1}$ ,  $C_{H_2O_2} = 3.56 \text{ g L}^{-1}$ ,  $C_{cat} = 0.5 \text{ g L}^{-1}$ .**

## **CONCLUSIONS AND FUTURE RESEARCH**

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## **5 CONCLUSIONS AND FUTURE RESEARCH**

### **5.1 CONCLUSIONS**

Based on the objectives of this work, to find alternative strategies for the valorization of compost through the production of low-cost materials to be used as catalysts in the treatment of wastewaters, this thesis was concluded with the study of different materials produced using compost as source.

All biochar produced presented high conversion and activity in CWPO reactions and in the decomposition of  $H_2O_2$  and TOC. The material CS shows higher conversions than the other materials prepared, and this was ascribed to the leaching of iron. Thus, materials produced present activity. Glycerol was used to produce materials in order to minimize the leaching of iron, but the results show that not happened, because the carbon of glycerol react with iron and in the oxidation, leading to higher iron leaching amounts.

Results of isotherms present that this material is more catalyst than adsorbate, and not shows the presence of microporous.

To the best of my knowledge, it is possible to conclude that biochar produced from compost present activity surface and act as catalyst in oxidation of pollutant in wastewater treatment.

### **5.2 FUTURE RESEARCH**

Biochar materials have been prepared from compost to be used as catalyst in the treatment of wastewater by CWPO. In this context, all prepared biochars present catalytic activity in the CWPO of 4-NP as showed. There is interesting for future studies about the biochars from municipal solid waste (MSW), try others methods of material preparation, for example an activation of material with physical method or chemical method with basic. Thus, the material produced with these activation methods may

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result in different properties of the materials, when compared to those produced in this work. In addition, use these materials produced in CWPO reaction, but with other pollutants, as paracetamol, which is a medicine consumed by the population and present in wastewater.

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## **COMMUNICATIONS**

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## **COMUNICACIONES**

[1] Jose L. Diaz de Tuesta, Caroline M. Masso, Juliana M.T. de A. Pietrobelli, Paulo Praça, Adrián M.T. Silva, Joaquim L. Faria, Helder T. Gomes. **Catalytic activity of carbon based materials developed from compost derived from municipal solid waste.** Carbocat VIII, July 24-26<sup>th</sup>, 2018. Porto, Portugal.

[2] J.L. Diaz de Tuesta, C.M. Masso, Juliana M.T. de A. Pietrobelli, Adrián M.T. Silva, Joaquim L. Faria, Helder T. Gomes. **Strategies to minimize the leaching of iron from activated carbons prepared from compost obtained in mechanical biological treatment plants for municipal solid waste under oxidative aqueous medium.** 4<sup>th</sup> International congress water, waste and energy management, July 18-20<sup>th</sup>, 2018. Madrid, Spain

[3] Jose L. Diaz de Tuesta, Caroline M. Masso, Paulo Praça, Adrián M.T. Silva, Joaquim L. Faria, Helder T. Gomes. **Oxidação catalítica com peróxido de hidrogénio de poluentes lipofílicos usando materiais preparados por ativação de composto proveniente da digestão anaeróbia da fração orgânica de resíduos sólidos urbanos.** XXVI Congresso Ibero-Americano de Catálise, September 9-14<sup>th</sup>, 2018. Coimbra, Portugal.



