Application of carbon-based catalysts derived from compost on catalytic wet peroxide oxidation of leachate waters from mechanical and biological treatment plant units for municipal solid waste

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Abstract. This work aims at the valorization of compost from mechanical and biological treatment (MBT) units of municipal solid waste by their transformation into carbon-based catalysts for further application in the treatment of MBT leachate waters (chemical oxygen demand (COD) = 60.0 g L^{-1}, total organic carbon (TOC) = 26.7 g L^{-1}, five-day biochemical oxygen demand (BOD_5) = 23.3 g L^{-1} and aromaticity = 10.2 g L^{-1}). The catalyst was prepared in this work by hydrothermal carbonization at 230 ºC from compost obtained in a MBT unit. The treatment of the leachate waters was conducted by combining a pre-treatment with a cationic ion exchange resin followed by catalytic wet peroxide oxidation (CWPO). The CWPO step was operated for 24 h using 7.2 g L^{-1} of catalyst, 85.7 g L^{-1} of H_2O_2 poured inside the reactor in 5 stepwise additions, at 80 ºC and pH = 3. The combined treatment by cationic resin and CWPO led to obtain removals of 68.2, 65.4, 96.8 and 93.1 % for COD, TOC, BOD_5 and aromaticity, respectively, after 24 h of reaction. In conclusion, it was found that compost is a suitable precursor to produce active catalysts for the CWPO of leachate waters.

Keywords: valorization; carbon-based catalysts; leachate wastewaters; advanced oxidation processes; wastewater treatment**.**

1. Introduction

According to a report published by the Eurostat in 2019, municipal solid waste (MSW) corresponds to 10% of the total waste generated worldwide and, in 2019, each European citizen generated 502 kg of MSW. Furthermore, the generation of MSW is expected to reach around 3.4 billion tonnes by 2050 (Eurostat, 2021).

If MSW is not properly managed, it can cause irreversible damage to the environment (Eurostat, 2021; Wei et al., 2017). The main approaches for MSW management are recycling, landfilling, composting, mechanical and biological treatment plants (MBT), and incineration. Landfilling is the most harmful approach, as no pre-treatment is usually performed, causing health-related risks, and resulting in the discard of profitable resources. Therefore, different actions have been taken in order to develop methods to deal with MSW. This is reflected in the gradually increasing fraction of recycled and composted MSW in the EU, rising 176% between 1995 and 2019, from 14 million tonnes (33 kg per capita) to 39 million tonnes (87 kg per capita) in 2019 (Eurostat, 2021). MBTs are also a sustainable approach to manage MSW. In a MBT plant, the organic fraction of the MSW is anaerobically digested, leading to three outputs: biogas, leachate waters and a solid, later subjected to composting. Biogas is used as an energy source. The compost can be sold as a fertilizer, but its production largely surpasses its demand. Thus, under this context, and considering the directives of "end-of-waste" criteria (Di Lonardo et al., 2012), there is a need for alternatives to valorize compost, in the light of the concept of circular economy, decreasing landfill disposal.

One valorization strategy is to use compost as a precursor for the production of carbon-based materials (Deng et al., 2016). Carbonaceous materials are of great interest, as they have several applications, such as in CO_2 capture (M. M. Titirici et al., 2015), energy storage (Deng et al., 2016) and as catalysts for wastewater treatment (Deng et al., 2016; M. M. Titirici et al., 2015). Carbon materials are produced from carbon-rich precursors by diverse carbonization methods, such as pyrolysis and hydrothermal carbonization (HTC). HTC is considered an

eco-friendly option to produce carbonaceous materials. It requires a carbon feedstock, water and a confined reactor that operates under mild temperatures (ca. 300 ◦C) (M. M. Titirici et al., 2015).

Leachate waters generated in MBT plants pose a hazardous treat to the environment. The leachate has a very complex matrix, composed of inorganic (e.g. metallic ions) and organic fractions, resulting in high TOC, COD, BOD_5 and ions, such as chlorides, carbonates, or sulphates (Luo et al., 2020). The complexity and high pollutant load hinder the leachate management by conventional treatments, demanding the development of new technologies (Oturan & Aaron, 2014).

In this context, CWPO is an eco-friendly and low-cost technology that has shown promising results in wastewater treatment (Márquez et al., 2018). CWPO uses powerful oxidants, such as hydroxyl and hydroperoxyl radicals, resultant from the selective decomposition of H_2O_2, to oxidize the organic pollutants present in wastewaters, under mild operational conditions (T = 25 - 130 ºC, P = 1 - 5 atm), through the action of an heterogeneous catalyst (Márquez et al., 2018; Ribeiro et al., 2016).

To enhance the performance of the treatment for complex matrices, such as leachates from MBT, it is an interesting strategy to couple a pre-treatment process with CWPO (Oturan & Aaron, 2014; Renou et al., 2008). Ion exchange resins are appropriate alternatives to remove ammonia and metal ions (Zamri et al., 2017).

This work aims to valorize matured compost from MBT plant to synthesize carbonaceous catalysts. The synthesized catalysts are then applied for the CWPO of highly concentrated leachate wastewaters derived from the same MBT plant that originate the compost. To improve the removal of COD and TOC, an ion exchange resin pre-treatment was applied before CWPO.

2. Methodology

2.1. Reagents and materials

The compost and leachate used in this work were collected from a MTB plant for MSW located in Northern Portugal. H_2SO_4 (98 wt.%) was obtained from Labkem. H_2O_2 (30% w/v) and NaOH (98.73%) were supplied by Fisher Chemical. Titanium (IV) oxysulfate ($TiOSO_4$, 15 wt.% in dilute sulfuric acid, H_2SO_4 99.99%) and Lewatit TP-207 resin were supplied from Sigma Aldrich. $AgNO_3$ (for analysis, ACS, ISO), $HgSO_4$ (99 wt.%), and $K_2Cr_2O_7$ (99.5 wt.%) were supplied from Panreac. Distilled water was used throughout the research.

2.2. Catalyst preparation and characterization

First, the compost was washed with water (100 g L^{-1}) under strong stirring to homogenize the precursor and to remove suspended solids. The suspension was filtered, the solid dried overnight at 60 ºC and sieved to obtain particle sizes from 53 to 106 μm, resulting in the starting material for the HTC process, as described elsewhere (Diaz de Tuesta et al., 2020; M. Titirici et al., 2011). Briefly, 3 g of compost was mixed with 30 mL of distilled water and placed in a 125 mL removable Teflon vessel inserted in a stainless-steel body. The reaction vessel was placed in an oven at 230 ºC for 2 h. The solids were vacuum filtrated, washed with abundant water, and dried in an oven overnight at 100 ºC, leading to catalyst HTC-230.

The catalyst was characterized by elemental analysis (C, H, N and S) using a Carlo Erba EA 1108 Elemental Analyzer. Ash content was determined using a muffle at 450 °C until reaching constant mass.

2.3. Leachate characterization and analytical methods used in CWPO

The leachate was characterized to determine its TOC (Shimadzu TOC-L), COD (by a UV-VIS colorimetric method, using $K_2Cr_2O_7$, at a wavelength of 600 nm, adapted from Ribeiro *et al.* (2017)) and BOD_5 (standardized respirometric OxiTop method (WTW, Weilheim, Germany)). Aromaticity was determined by a UV-VIS methodology at wavelength of 254 nm, adapted from Ribeiro *et al*. (2017). H_2O_2 concentration was determined by a UV-VIS colorimetric method using $TiOSO_4$ at a wavelength of 405 nm, adapted from Ribeiro *et al*. (2017). H_2O_2 consumption efficiency ($\eta_{H_2O_2}$) was determined using COD and H_2O_2 conversions after 24 h of reaction, according to Eq. (1).

$$\eta_{H_2O_2} = \frac{X_{COD}}{X_{H_2O_2}} \quad (1)$$

2.4. CWPO experiments

The CWPO runs were carried out in a 500 mL glass round-bottom flask continuously stirred, equipped with a condenser. First, the leachate with a pH of 3 (adjusted with H_2SO_4 1 M) was added to the flask. Then, it was submerged in a heated oil bath with temperature control. Upon reaching the desired temperature of 80 ºC, the first fraction of H_2O_2 was added. Then, the catalyst was loaded at a concentration of 7.2 g L^{-1}, considering this time t = 0. The H_2O_2 needed to fully oxidize the COD content (85.71 g L^{-1}) was added in 5 stepwise additions of equal volume (at 0, 1, 2, 3 and 4 h of reaction). The samples for analysis were collected at 0, 15, 30, 60, 120, 180, 240, 360, 480 and 1440 minutes of reaction. Samples at 0, 1, 2, 3 and 4 h were collected after H_2O_2 addition. The reaction was monitored by analyzing H_2O_2 concentration, COD and TOC. At the end of the reaction, aromaticity and BOD_5 were determined.

2.4. Cationic resin pre-treatment coupled with CWPO

150 mL of the leachate with a pH previously adjusted to 9.5 was mixed with 3.0 g of the cationic ion exchange resin (Lewatit TP-207) in an Erlenmeyer and stirred (240 rpm) for 48 h. Subsequently, the leachate was vacuum filtrated with a paper filter. The pH of the resulting leachate was adjusted to 3 and CWPO was conducted following the conditions described in section 2.4.

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the values of carbon, hydrogen, sulfur, nitrogen, and ashes of the mature compost and of HTC-230 material.

Table 1. Catalyst Characterization

Characteristics	Compost	HTC-230
C/H	9.3	11.0
C (%)	17.2	19.3
H (%)	1.1	1.8
S (%)	0.6	1.2
N (%)	1.5	1.7
Ash (%)	55.5	32.6
N.I. (%) *	18.6	45.0

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

HTC-230 showed a higher value of C/H ratio (11.0) when compared to compost (9.3), proving that the carbonization was accomplished (Roman et al., 2021).

A decrease of 22.9% in the ashes content of HTC-230 is observed compared to compost, likely because the HTC treatment can cause the leaching of 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 oxygen. As observed, N.I. reaches values of 45.0% for HTC-230, likely due to hydroxylation and formation of surface oxygen groups on the surface of the materials.

3.2. Leachate characterization and treatment

The MBT leachate characterization is shown in Table 2.

Table 2. Leachate characterization

Parameter	Value (g L^{-1})
COD	60.0
TOC	26.7
BOD_5	23.3
Aromaticity	10.2

The leachate has high values of COD, TOC and BOD_5, and this pollutant concentration coupled with its complexity makes the leachate unsuited to conventional wastewater treatments (Márquez et al., 2018). The leachate treatment with CWPO and the treatment with the cationic resin pre-treatment coupled with CWPO are shown in Figure 1.

A blank experiment was performed (results not shown), revealing no significant removal of COD or TOC (< 5%), highlighting the influence of the catalyst on this treatment. The application of the stepwise addition of H_2O_2 (the instants of H_2O_2 addition are marked in grey lines) was used for a controlled consumption of H_2O_2 and to minimize side reactions that inefficiently consume the generated hydroxyl radicals.

H_2O_2 consumption was almost fully achieved in both treatments after 24 h and, as can be seen in Fig. 1 (a).

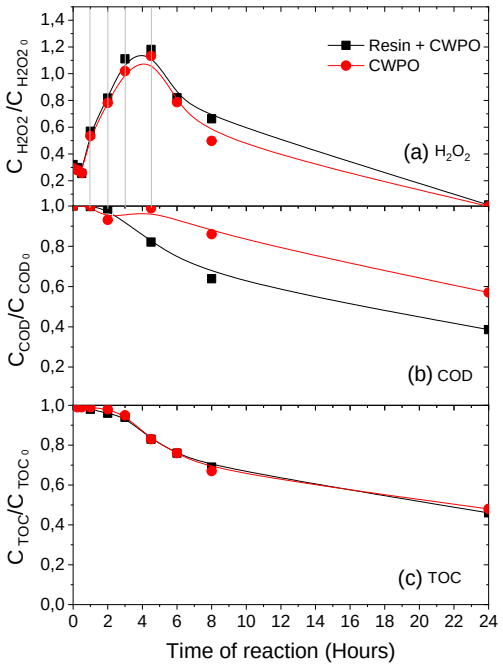

Figure 1. Concentraton evolution profile of (a) H_2O_2, (b) COD and (c) TOC obtained in the treatment of the leachate by CWPO and by sequential resin and CWPO treatment.

For the catalyst HTC-230, the use of combined resin pre-treatment and CWPO proved to enhance the treatment of the leachate, when compared with the single CWPO treatment, the COD abatement increasing from 43.5 to 62.2% for the single CWPO treatment to the combined cationic exchange and CWPO treatment process. However, the same was not observed for TOC removal, since removals between 52 and 54% were observed.

The major enhancement can be noted in the hydrogen peroxide consumption efficiency. For the CWPO treatment alone $\eta_{H_2O_2}$ was 44%, whilst by coupling the resin pre-treatment with CWPO, an efficiency of 64% was attained after 24 h of reaction. The improved efficiency can be explained by the enhancement of the COD removal. The BOD_5 and aromaticity removals are shown in Table 3.

Table 3. BOD_5 and aromaticity removal after 24 h of reaction

Parameter	CWPO	Resin+CWPO
BOD_5 (%)	92.8	99.7
Aromaticity (%)	82	95.0

The aromaticity and BOD_5 removals were also enhanced after combining resin pre-treatment and CWPO. CWPO alone led to 92.8 and 82% removal of BOD_5 and aromaticity, respectively, whereas the combined treatment resulted in 99.7 and 95%, respectively. Therefore, this increase in the BOD_5 removal combined with the enhance of COD abatement indicates that CWPO after the resin pre-treatment was able to degrade a higher fraction of organic matter. Thus, proving that for the organic matter removal, it is an efficient strategy to combine a cationic resin pre-treatment with CWPO.

4. Conclusions

As demonstrated, compost resultant from the mechanical and biological treatment of MSW can be valorized by HTC, converting it into a material with suitable catalytic properties for CWPO applications.

The leachate generated from a MBT plant, characterized by high pollutant concentration was treated by CWPO, using the catalyst prepared, considering 24 h of reaction, initial pH = 3, 85.71 g L^{-1} of H_2O_2 and catalyst concentration of 7.2 g L^{-1}. Since the leachate has a complex matrix, the pre-treatment with a cationic ion-exchange resin was tested followed by the same CWPO treatment. It was found that the organic matter removal was enhanced by combining both treatments. The combined treatment allowed to obtain removals of 62.5, 54, 82 and 99.7% for COD, TOC, aromaticity and BOD_5, respectively.

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