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Performance of metal-free carbonaceous catalysts in the removal of paracetamol by catalytic wet peroxide oxidation

SANTOS SILVA A.[1,*], HENRIQUE A.[1], STELDINGER H.[2], DIAZ DE TUESTA J. L.[1], GLÄSEL J.[2], SILVA J. A. C.[1], ETZOLD B. J. M. [2], and GOMES H. T.[1]

[1]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253, Bragança, Portugal

[2]Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, 64287 Darmstadt, Germany

*corresponding author:
e-mail: adriano.santossilva@ipb.pt

Abstract. The performance of metal-free carbonaceous catalysts was evaluated in the removal of paracetamol, chosen as model pharmaceutical micropollutant, by catalytic wet peroxide oxidation (CWPO). The carbon materials were prepared from pentaerythritol tetraacrylate and divinylbenzene copolymer with bis(2-ethylhexyl) phthalate as porogen followed by subsequent carbonization at 900 ºC under N_2 atmosphere. The synthesized material was grinded to powder and separated into different samples, according to its granulometry. The sample with particle sizes between 53 and 106 µm (catalyst Mon11) was further functionalized with nitric acid 5 M at 120 °C for 3 h (catalyst Mon11F) to increase the hydrophilicity of the original material. Both catalysts revealed high activity in CWPO, completely removing the pharmaceutical compound within 6 and 24 h of reaction at 80 ºC, when Mon11 and Mon11F were used, respectively. Total organic carbon (TOC) conversion achieved values of 86.8 and 75.8% with Mon11 and Mon11F, respectively. Adsorption tests at the same operating conditions resulted in removals of paracetamol after 24 h around 29% for Mon11 and 11% for Mon11F, confirming the predominance of catalytic removal of the pollutant in the CWPO runs.

Keywords: CWPO, metal-free catalysts, functionalization, paracetamol

1. Introduction

The sustainable usage of water resources and its conservation is a worldwide concern identified as one of the 17 goals of the UN 2030 agenda for sustainable development (Aminot et al., 2019). The proper removal and neutralization of organic pollutants present in wastewaters are among the most significant environmental challenges that the world is facing (Malaika, 2020). Among the contaminants present in wastewaters, pharmaceutically active compounds (PhACs), synthetic and natural hormones, food additives, and personal care products represents increasing concern. These compounds are being constantly discharged into the environment through different sources, resulting in adverse effects on ecosystems and humans (Rizzo et al., 2019). This group of chemicals, generally detected in wastewater streams and aquatic ecosystems at trace concentrations, are also referred as contaminants of emerging concern (CECs). Such compounds cannot be eliminated by conventional secondary treatments (*e.g.*, trickling filter and oxidation ponds) or tertiary treatments (such as filtration) implemented in wastewater treatment plants. Its widespread occurrence in vital aquatic compartments, such as groundwater, soils, and even drinking water, represents a growing environmental issue (Serrano et al., 2019).

In the past few years, different processes reported the removal of CECs from municipal wastewaters (Bahmani et al., 2020; Figueiredo et al., 2020; Huang et al., 2020). Many of these techniques, such as adsorption, membrane filtration and flotation, present some drawbacks as transference of the pollutants to another phase or the production of a concentrated pollutant stream, requiring additional treatment (He et al., 2019). In contrast, advanced oxidation processes (AOPs) are technologies in which highly oxidizing hydroxyl radicals ($HO^{\bullet}$) are produced to degrade and mineralize organic water pollutants, using relatively simple operation units (Castañeda-Juárez et al., 2020; Van et al., 2020). Among AOPs, catalytic wet peroxide oxidation (CWPO) deserves attention for applying heterogeneous catalysts that overcomes the limitations of the homogeneous nature of the Fenton process (*i.e.*, formation of iron sludge at the end of reaction). The typical catalyst employed in CWPO is composed by two phases: the support and the active phase. The support is generally a material with high surface area, porosity and good electrical properties, and the active phase a transition metal (Pan et al., 2020). Although the experiments reported in literature at the laboratory-scale present promising results for the removal of pollutants by CWPO, the metal leaching issue hinders the acceptance of the technology in industry (Galeano et al., 2014). Besides the water contamination with the metal, caused by iron leaching, the catalyst's efficiency is also directly affected. A good alternative to overcome such problem is the use of metal-free catalysts, which presents several advantages compared with metal-based catalysts (*e.g.*, absence of iron leaching and good thermal stability) (Espinosa et al., 2015). Among metal-free catalysts, carbonaceous materials have attracted considerable interest for catalytic applications. Their eco-friendly nature, whole-carbon structure with molecular symmetries and 3D hybrids display, are the main reasons for the increasing studies with these materials (Navalon et al., 2017; Zhang et al., 2020). Thus, in this work, the application of metal-free carbon-based catalysts in the removal of paracetamol by catalytic wet peroxide oxidation was exploited. The raw material was tested, evaluating the changes in the performance of the catalyst after functionalization with nitric acid in the removal of paracetamol.

2. Methods

2.1. Synthesis of carbon materials and conditioning of the samples

The synthesis procedure follows the same method used and described elsewhere (Steldinger et al., 2019). Briefly, a photoresin was obtained by mixing monomers (pentaerythritol tetraacrylate and divinylbenzene) with phthalate (porogen agent), a photoinitiator, dye, and radical inhibitor. The photoresin was then prepared by photopolymerization. The final printed catalyst had its dye extracted from the structure by Soxhlet extraction with acetone and went through pyrolysis at 900 °C for 15 min. Finally, the purified resin was grinded to powder and separated according to its particle size into different samples (<53 μm, 53<D<106 μm, 106<D<160 μm and >160 μm).

2.2. Acid functionalization

The sample with particle sizes between 53 and 106 μm (Mon11) was further functionalized with nitric acid. For the functionalization, 1 g of sample was held at boiling point (ca. 120 °C) for 3 h in nitric acid solution with a concentration of 5 M. Lastly, the material was recovered and washed several times until rising waters reach pH 7 and dried in air oven overnight (Mon11F).

2.3 CWPO and adsorption of paracetamol

A paracetamol (PCM) concentration of 100 ppm was used in the experimental runs, and the concentration of H_2O_2 was set at the stoichiometric amount of hydrogen peroxide needed for the complete oxidation of PCM. The pollutant solution with pH adjusted to 3.5 was placed in a reactor submerged in an oil bath with heating at 80 °C. The oxidant was poured inside the reactor and the catalyst was added at a concentration of 2.5 $g{\cdot}L^{-1}$. That moment was considered the beginning of the reaction. Samples were withdrawn from the reaction media at 0, 15, 30, 60, 120, 240, 360, 480 and 1440 min. Non-catalytic run and adsorption tests were performed following the same steps, in the absence of catalyst and hydrogen peroxide, respectively. The analysis of the samples considered the determination of concentration of paracetamol, total organic carbon (TOC) and H_2O_2 concentration against time by HPLC, TOC analysis and spectrophotometry, respectively, following the methods described in a previous work (Silva et al., 2019). The efficiency of H_2O_2 consumption was estimated taking into account the conversions of TOC and hydrogen peroxide after 8 h of reaction, according to Equation (1).

$$\eta_{H_2O_2}(\%) = \frac{X_{TOC\ t=8\ h}}{X_{H_2O_2\ t=8\ h}} \times 100 \qquad (1)$$

3. Results

The results obtained in the CWPO of PCM with the catalysts Mon11 and Mon11F, for the concentration of paracetamol, hydrogen peroxide and TOC upon reaction time, are represented in Figure 1.

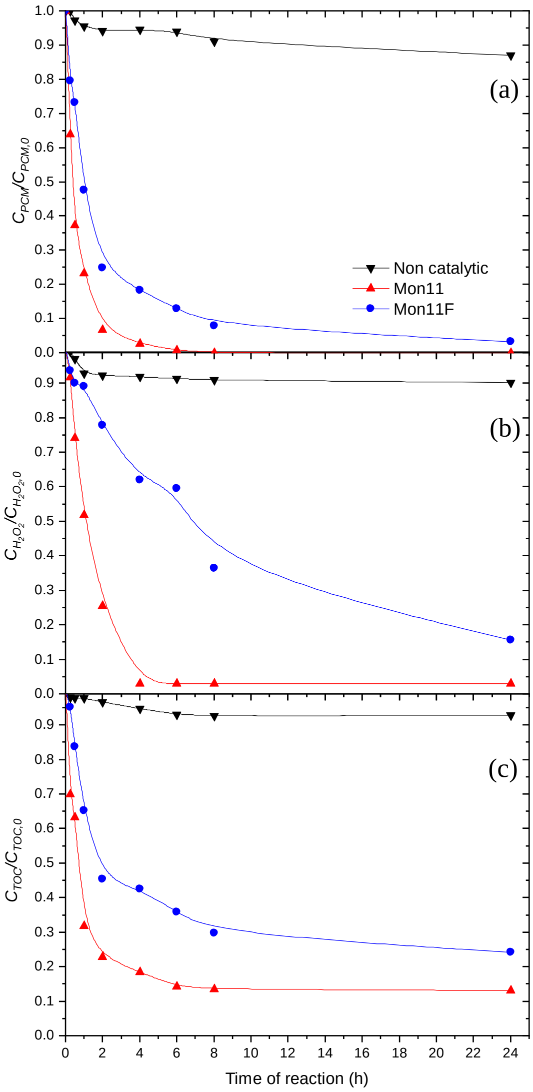

Figure 1- Normalized concentration of (a) PCM, (b) H_2O_2, and (c) TOC over reaction time (lines connecting points are only intended to show the trend of concentration profiles).

As shown in Figure 1, Mon11 and Mon11F present high catalytic activity in the CWPO of PCM, with more than 95% of pollutant removal being obtained after 24 h. In comparison, non-catalytic experiments reveal a removal of less than 10% after the same time. Mon11 was able to slightly convert more oxidant than Mon11F. While hydrogen peroxide (Figure 1.b) was fully decomposed after 4 h of reaction with Mon11, Mon11F presented a lower rate in the decomposition of the oxidant. This behavior is due to the presence of acidic groups (electron withdrawing species) on the surface of Mon11F, which hinders H_2O_2 decomposition, as reported in other works studying the influence of chemical surface properties on the mechanism of H_2O_2 decomposition (Martin-Martinez et al., 2018). Both catalysts enabled mineralization values higher than 75%, with advantage for Mon11. In all experiments done, catalytic runs overcame non-catalytic runs. The activity of both catalysts on the removal of PCM by CWPO is due to the carbon structure's donor-acceptor properties, allowing the occurrence of electron-transfer mechanisms (Liu et al., 2018). Adsorption tests were performed at the same operating conditions to evaluate its contribution in the removal of pollutant in CWPO experiences. The results are depicted in Figure 2.

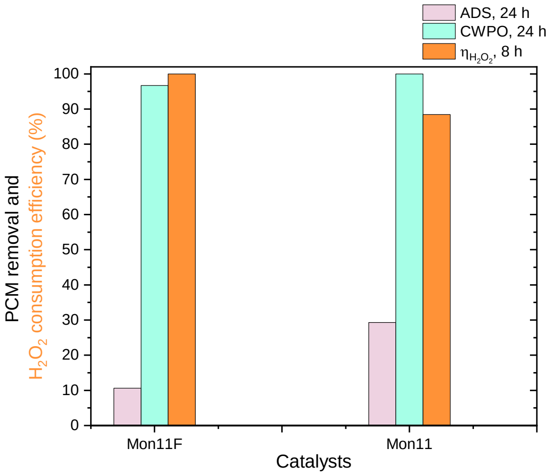

Figure 2- Efficiency of H_2O_2 consumption after 8 h and paracetamol removal after 24 h by adsorption and CWPO.

The removal of PCM by pure adsorption runs reached 29.3 and 10.6% after 24 h with Mon11 and Mon11F, respectively. The removal of PCM by adsorption with Mon11 was significantly higher than with Mon11F. The results confirm that this removal is considerably lower than the decomposition of PCM after 24 h by catalytic oxidation runs with both materials. Thus, due to the poor contribution of adsorption, the removal of PCM in CWPO occurs mainly by oxidation, being more evident with Mon11F (PCM removals of 10.6 and 96.7% after 24 h of reaction in adsorption and CWPO runs, respectively).

Considering that the running cost of a CWPO unit is mainly due to H_2O_2 consumption (Diaz de Tuesta et al., 2020), an efficient H_2O_2 consumption represents a fundamental parameter to be assessed to avoid the formation of molecular oxygen (Ribeiro et al., 2013). In this context, the efficiency of hydrogen peroxide consumption, determined as specified in Eq (1), was good for both catalysts, with advantage for Mon11F, probably because the catalyst favours the efficient use of radicals $HO^{\bullet}$, $HOO^{\bullet}$ and $O_2^{\bullet-}$ to oxidize the organic matter, instead of leading to undesirable side reactions, enabling more efficient utilization of the oxidant.

For the catalyst with higher efficiency of hydrogen peroxide consumption, Mon11F, a reutilization test of paracetamol removal by CWPO was performed. For this purpose, the catalyst was recovered in the first reaction run and dried in air oven at 60 °C. The material was then applied again in the reaction under the same operating conditions to evaluate if the catalyst remained active after the first run, meaning good stability. The results obtained for the second run are represented in Figure 3, together with the first run results.

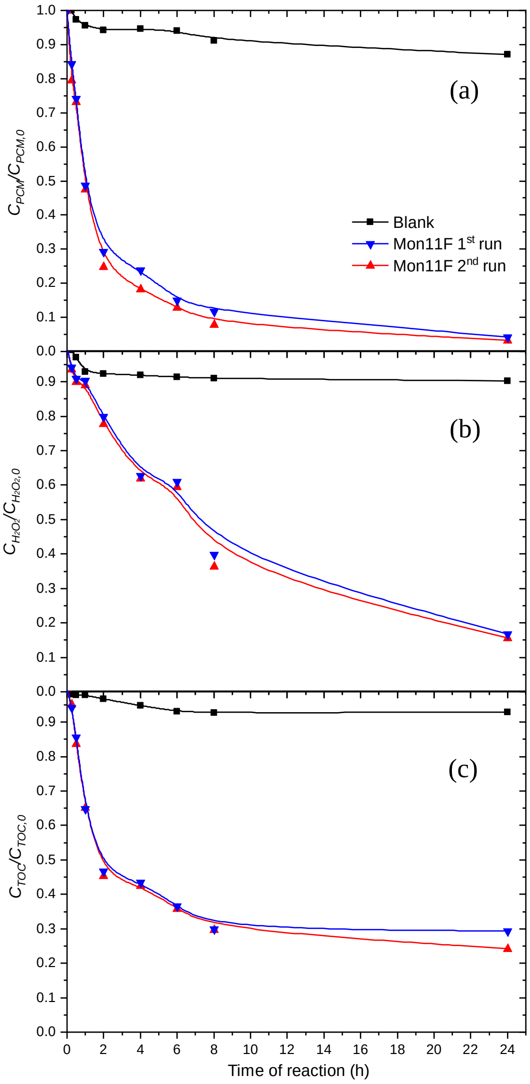

Figure 3- Normalized concentration profiles of (a) PCM, (b) H_2O_2 and (c) TOC obtained in a reutilization CWPO run (lines connecting points are only intended to show the trend of concentration profiles).

4. Conclusion

In this work, a whole-carbon catalyst was able to degrade more than 95% of the model organic pollutant after 24 h of reaction by wet peroxide oxidation. The catalysts promoted high mineralization of PCM, measured as TOC conversion, with 86.8 and 75.8% for Mon11 and Mon11F, respectively. Even with lower mineralization when compared with the parent material, Mon11F can be considered the catalyst with the best performance since the hydrogen peroxide consumption efficiency was higher than Mon11. This result can be ascribed to the presence of acidic groups on the surface of Mon11F that collaborates for a more controlled hydrogen peroxide decomposition, resulting in higher consumption efficiency of oxidant when compared to Mon11.

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