Application of vine-pruning-waste hydrochar for the catalytic ozonation of ibuprofen from water

J. Nieto-Sandoval[1], R. P. Cavalcante[1,2], B. Bayarri[1], L. Whelan[1], Z. Sun[1], J.A. Malvestiti[2], R.F. Dantas[2], C. Sans[1]

[1]Dept. of Chemical Engineering and Analytical Chemistry, Universitat de Barcelona, Barcelona, 08028, Spain

[2]Faculdade de Tecnologia, Universidade Estadual de Campinas, Limeira, SP, 13484-332, Brazil

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Presenting author email: zhsunsun123@alumnes.ub.edu

Viticulture is a longstanding and crucial global industry, covering millions of hectares of vineyards and generating substantial pruning waste. Traditionally, this waste has been used to enrich soil organic matter or as an energy source. However, there's a growing interest in further valorizing this by-product, driven by environmental and economic considerations, thus promoting a circular economy within the wine sector (Lorero et al., 2020). In this context, hydrothermal carbonization (HTC) emerges as a promising thermochemical process for waste valorization, garnering significant attention recently. This method involves subjecting biomass to water at temperatures usually in the range from 180°C to 240°C in a reactor under autogenous pressure, yielding a solid char, termed hydrochar (HC) (Cavali et al., 2023).

HC finds application across various environmental domains, including pollutant removal from aqueous systems since conventional processes commonly employed for water treatment do not warrant the completely removal of those compounds. Concretely, the increasingly frequent occurrence of micropollutants in water sources represents an important concern for aquatic ecosystems and human health and the development of innovative, cost-effective and environmentally-friendly treatment processes are necessary. Among them, catalytic ozonation stands out as a promising method, enhancing the efficient removal of pollutants and promoting a higher degree of mineralization than single ozonation (Issaka et al., 2022). Therefore, the development of active, reusable, and viable catalysts from the environmental, social and economic point of view is crucial. Within this framework, heterogeneous catalytic reactions using solid catalysts are the most adequate for this purpose, avoiding catalyst loss and secondary pollution in comparison to homogenous catalysts. Therefore, the employment of metals as actives phases immobilized on carbonaceous supports has showed excellent catalytic performance of micropollutants degradation. In order to avoid complex preparation methods and high fabrication costs, the development of active catalysts by HTC treatment valorizing organic waste represents a promising alternative. Thus, the aim of this work is the development hydrochar-based catalyst using vine-pruning-waste for the catalytic ozonation of the pharmaceutical ibuprofen (IBU) as target pollutant.

Vineyard pruning was obtained from the Alt Penedès region of Catalunya, northeastern Spain. First, it was cleaned with deionized water to remove dust and dirt and subsequently air-dried at room temperature. The material was manually cut and, after drying, it was milled and sieved to particle size fraction below 250 µm. Then, the catalysts were prepared by HTC treatment. Briefly, 5g of vineyard pruning was firstly pretreated NaOH for 2h. Later, after washing and centrifugating with water, the material was introduced in a 100 mL-PTFE liner and mixed with 50 mL Co^{2+} solution (for 5% wt.) or deionized water for 12 h to develop HC-Co^{2+} or HC, respectively. The liner was then sealed in the hydrothermal autoclave reactor and heated for 4 h at 200 °C. After cooling to room temperature, the HCs were washed with deionized water and dried at 80 °C for 12 h.

Regarding the ozonation experiments, they were conducted in a semi-continuous reactor (600 mL) under controlled temperature (20 ºC) and magnetic stirring (600 rpm) at natural pH, consisting of ultrapure water contaminated with 20 mg L^{-1} of IBU. A flow of ozone (15 mg L^{-1}, 0.5 L min^{-1}) was continuously fed into the reactor for 60 min and the catalyst concentration was evaluated from 0.025 to 0.1 g L^{-1}.

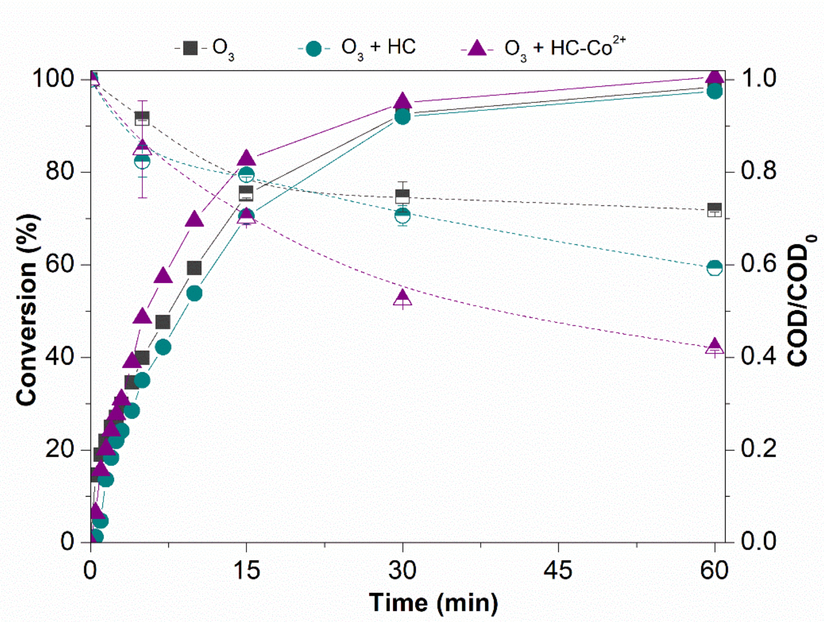

Figure 1. IBU evolution (solid lines) and COD removal (dash lines) upon ozonation reaction. ($[IBU]_0$= 20 mg L^{-1}; $[Catalyst]_0$= 0.025 g L^{-1}; O_3 flow = 7.5 mg min^{-1})

As shown in Figure 1, a single ozonation process completely degraded the drug in less than 60 min, with a 30% removal of Chemical Oxygen Demand (COD) during this timeframe. This removal remained consistent even with extended ozonation exposure. Given that Advanced Oxidation Processes (AOPs) reactions can sometimes produce intermediary substances that are more harmful than the target pollutants, achieving high levels of mineralization becomes a significant objective. The presence of HC derived from vineyard pruning resulted in similar degradation rates than single ozonation. However, in this setup, COD removal was higher, but it was observed a contribution of organic matter to recalcitrant COD in the aqueous medium from HC material.

The introduction of Co^{2+} metal into the HC material significantly enhanced the system, as shown in Figure 1. The highest degradation rates were observed using 0.025 g L^{-1} of HC-Co^{2+}, in comparison to the catalyst loads tested (ranging from 0.025 to 0.1 g L^{-1}). Moreover, up to 60 % of COD removal was achieved within 1 h reaction progressively decreasing throughout the catalytic ozonation process. In addition, it must be noted that blank experiments (performed without IBU) were carried out, showing that a catalyst load increase resulted in a linear increase in the COD contribution from the material. Hence, thorough preparation of the material is necessary to prevent an increase in COD in the reaction medium due to organic matter from the catalyst.

In conclusion, the utilization of hydrochar-based catalyst derived from vineyard pruning with the incorporation of Co^{2+} metal enhanced both pollutant degradation and mineralization grade in the catalytic ozonation application. While these materials may contribute to COD of the aqueous medium, it is important to solve this issue. All in all, this work shows the potential to valorise vineyard pruning into catalysts for water treatment.

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