Valorization of sewage sludge on the development of metal-based hydrochar for catalytic ozonation of emerging contaminants

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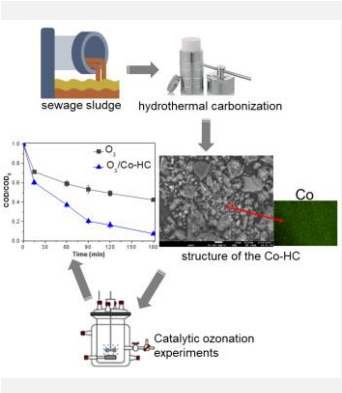

In this study, low-cost and environmentally friendly hydrochar modified with transition metals was produced for the removal of the drug primidone (PRM) through catalytic ozonation. The raw material was sewage sludge from the municipal wastewater treatment plant in Gavà-Viladecans (Barcelona, Spain). Firstly, the effect of modifying the hydrochar with the metals Co^{2+}, Fe^{3+}, Zn^{2+} and Al^{3+} on the efficiency of the catalytic ozonation of PRM was evaluated. Notably, hydrochar modified with cobalt (HC-Co) exhibited the highest rate of PRM removal and mineralization. In the second stage, the effect of hydrothermal temperature on the synthesis of HC-Co and catalyst dose was studied, achieving total COD removal using HC-Co-130 (synthesized at a temperature of 130ºC) and establishing a catalyst dose 0.025 g L^{-1}. This work contributes to the sustainable conversion of sewage sludge waste into a value-added material, potentially addressing environmental challenges.

Introduction

As is known, the availability, quality and quantity of water for basic human needs are threatened due to several factors, including population growth, increased demand for food, improved living standards, industrial expansion, and currently mainly due to the effects associated with climate change [1]. In this context, water quality management plays a crucial role in ensuring the safety of both natural and reused water for human consumption. To achieve this, the effectiveness of advanced oxidation processes (AOPs) is known, and among them, catalytic ozonation stands as a promising technology [2]. Responding to these challenges, the objective of this study is the synthesis of hydrochar with the incorporation of metals from the hydrothermal carbonization of sewage sludge for its application in the catalytic ozonation for emerging contaminants removal. This catalyst synthesis highlights the advantage of valorizing sewage sludge, which comes from wastewater treatments and can reduce waste volumes, transforming sludge into valuable products [3].

Material and Methods

Metal/sewage sludge hydrochar (M-HCs, where M = Co^{2+}, Fe^{3+}, Al^{3+} or Zn^{2+}) were prepared by the hydrothermal procedure using a stainless steel autoclave reactor containing a 100 mL teflon flask form. First, the sewage sludge residues were washed with ultrapure water to remove impurities and then the residue was immersed in a NaOH solution (1 mol L^{-1}) under continuous stirring for 2 h [4], followed by successive washing with ultrapure water. Subsequently, 25 g of the pretreated sludge wet residue (containing 80% moisture) was added to 25 mL of the metal solution (for 5% wt.) and stirred continuously at room temperature for 12 h. After the impregnation process, all obtained products were transferred to a hydrothermal reactor at 150°C for 4 h. The prepared catalysts were washed several times with ultrapure water, centrifuged and dried at 80°C for 12 h.

Hydrothermally carbonized Co-HC catalysts were also prepared at 130, 150, 170 and 200 °C, and were denoted as Co-HC-130, Co-HC-150, etc.

Catalytic ozonation experiments at natural pH were conducted in a semi-continuous reactor (600 mL) under controlled temperature (20 ºC) and magnetic stirring (600 rpm). A laboratory ozone generator (Sander, Germany) was used to transform pure oxygen to ozone, with a gas flow rate and the inlet ozone concentration maintained at 0.5 L min^{-1} and 15 mg L^{-1}, respectively, and continuously monitored by two BMT 964 ozone gas analyzers at inlet and outlet.

The catalytic degradation experiments were first conducted with 0.05 g L^{-1} of the catalysts and 0.1 mmol L^{-1} of the drug PRM, used as model pollutant, prepared in ultrapure water at natural pH (~ 5). Furthermore, using the optimal metal-based catalyst, the effect of hydrothermal temperature (130-200 ºC) and catalyst dose were evaluated (0.025 to 0.1 g L^{-1}).

PRM degradation was monitored by a high-performance liquid chromatography provided with a diode array detector and oxidation of organic matter was monitored by chemical oxygen demand (COD).

Results and Discussion

Figure 1 shows the performance of catalytic ozonation in the presence of HC with different metals for the degradation of PRM and COD removal. Single oxidation with O_3 showed 63% and 97% of

PRM removal in 5 and 15 min, respectively (Fig. 1A) and about 40% COD removal in 60 min. Similar results were observed in the presence of non-metal hydrochar, showing it did not improve PRM ozonation. In addition, in this case, the COD just decreased by 31% (lower than by single O_3). This fact could be mainly attributed to the contribution of COD resulting from the material to the aqueous medium (approximately 6.5 mg L^{-1} of COD). Morever, the adsorption effect by HC was negligible on the PRM solution (<1%).

In contrast, in the Co-HC and Zn-HC systems, the PRM degradation performance was significantly improved to 76 and 90% in 5 min and achieved 98% and 100% in 15 min, respectively. Evaluating the removal of COD, when adding Zn-HC or Fe-HC there was no increase on the removal of COD. However, when adding Al-HC and Co-HC in the O_3 reactor as catalysts, the mineralization efficiency was increased up to 50 and 71%, respectively. These results confirm that Co-HC presented the highest effective catalytic activity on both the degradation of PRM and COD removal.

The effects of hydrothermal temperature for the synthesis of the HC on the ozone activation by Co-HC for PRM degradation were also evaluated. The synthesis temperature did not significantly affect the reaction rate of PRM degradation. However, evaluating the COD removal, it was observed that an increase in the hydrothermal temperature reduces the mineralization rate. Thus, the COD removal rate varied with hydrothermal temperature reaching 67%, 71%, 61%, 57% at 60 min, respectively, for Co-HC-130, Co-HC-150, Co-HC-170, Co-HC-200. Considering factors such as cost reduction, catalyst performance and energy-saving, the hydrothermal temperature of 130 °C was chosen as ideal for the preparation of Co-HCs. Finally, the effect catalyst dose in the reaction media was also evaluated. When the catalyst dose increased from 0.025 to 0.1 g L^{-1}, the COD removal rate decreased from 82.5% to 62.1%. This occurred because using higher concentrations of catalyst leads to a greater contribution of the material to the recalcitrant COD. These observations were confirmed by blank experiments (carried out in the absence of PRM), in which it was observed that using 0.1 g L^{-1} of Co-HC, a contribution of around 6.7 mg L^{-1} of COD from of the material. On the other hand, using 0.025 g L^{-1} of Co-HC, the COD contribution from the material was around 3.6 mg L^{-1}. Moreover, total COD removal was obtained in 180 minutes, whereas with simple ozonization 58% was obtained in the same reaction time.

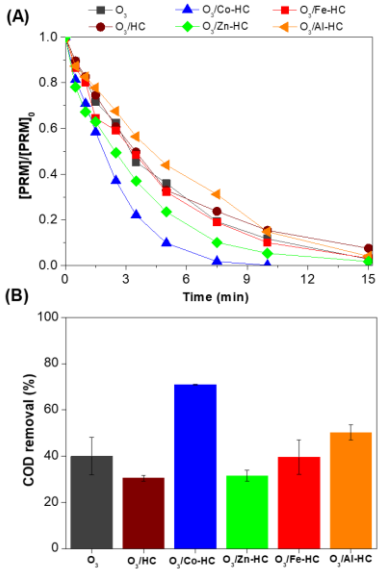

Figure 1. PRM removal (A) and COD removal (B) upon ozonation reaction. ($[PRM]_0$= 0.1 mmol L^{-1}; $[Catalyst]_0$= 0.05 g L^{-1}; O_3 flow = 7.5 mg min^{-1}).

Conclusions

The environmentally friendly catalyst, synthesized from hydrochar derived from sewage sludge with Co^{2+} metal, showed excellent performance in catalytic ozonation. The Co-RH-130 showed the highest performance, significantly improving both the degradation of the target pollutant and COD removal compared with single ozonation, even at low concentration. Although the catalysts can contribute to the total COD of the aqueous medium, their impact is negligible at low concentration. This study not only provided a facile method to synthesize catalytic composites for ozonation application, it also provided a solution that contributes to the value-added conversion of sewage sludge waste.

Acknowledgments

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