

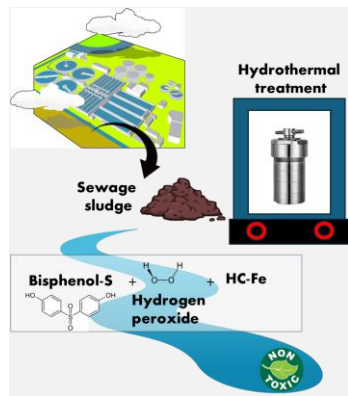
Fe-based hydrochar from sewage sludge waste for Bisphenol-S removal by Fenton oxidation.

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This work aims to develop hydrochar derived from sewage sludge as a potential catalyst for the Fenton oxidation of bisphenols in water. HC-Fe catalysts were synthesized through hydrothermal treatment with Fe³⁺ impregnation, and their efficiency in bisphenol S (BPS) removal was evaluated. The temperature synthesis on the hydrothermal treatment is a key parameter on hydrochar materials and was evaluated from 125 to 200°C. HC-Fe-125 exhibited the highest activity, achieving over 90% BPS removal in just 1 hour. The iron leached from the material was below 0.2 mg L⁻¹. Moreover, increasing the catalyst concentration to 0.5 g L⁻¹ resulted in complete BPS removal in less than 45 min. This research highlights the promise of HC-based catalysts valorising sewage sludge for efficiently removing micropollutants from water by CWPO.

Introduction

The increasing occurrence of micropollutants in water sources poses a significant concern for both aquatic ecosystems and human well-being. Among them, bisphenols, widely used additives, are specially considered due to their disrupting effects [1]. Consequently, there is a pressing need for the advancement of novel, cost-efficient, and environmentally conscious treatment methods to ensure the complete elimination of these substances in water treatment facilities. Advanced oxidation processes (AOPs) emerge as promising solutions capable of enhancing pollutant removal. Fenton-based technologies are particularly promising in terms of kinetics and operating costs compared to other AOPs. Concretely, heterogeneous Fenton, so called Catalytic Wet Peroxide Oxidation (CWPO), is particularly attractive since it allows the recovery and reusability of the catalysts employed, avoiding the formation of undesirable metal sludge [2]. For that purpose, the development of active and stable catalysts is necessary.

Our research aims to address these challenges by exploring the potential of sewage sludge, a common byproduct of wastewater treatment plants, for hydrochar synthesis as a catalyst, incorporating transition metals. This approach not only addresses water pollution concerns but also emphasizes the sustainable utilization of sewage sludge, thereby contributing to the advancement of eco-friendly water treatment technologies [3]. Thus, the primary objective of this study was to develop a hydrochar-based catalyst utilizing sewage sludge for the removal of bisphenol S (BPS), one of the most frequent bisphenol A substitutes, as target pollutant by Fenton oxidation.

Material and Methods

The catalysts were prepared by hydrothermal treatment. Briefly, 25g of sewage sludge was firstly pretreated NaOH. After, washing and centrifugating with water, the solid was introduced in a 100 mL-PTFE liner and mixed with 25mL of Fe³⁺ solution (for 5% wt.) or deionized water for 12 h to develop HC-Fe or HC, respectively. The liner was then sealed in the hydrothermal autoclave reactor and heated for 4 h at different temperatures (125, 150, 175 and 200 °C). After cooling to room temperature, the HCs were washed with deionized water and dried at 80 °C for 12 h.

Fenton experiments were conducted in a batch reactor (200 mL) under ambient conditions at initial pH of 3 and magnetic stirring (600 rpm). The initial concentration of BPS was established at 5 μM and the H₂O₂ dose was 700 μM, which corresponds to five times the stoichiometric concentration. The catalyst concentration was evaluated from 0.05 to 0.5 g L⁻¹. Adsorption and blank experiments, in the absence of H₂O₂ and catalyst, respectively, were also carried out. BPS was quantified by HPLC-UV using 50/50 acetonitrile and acid water (pH=3) as mobile phases at 258 nm. The dissolved iron was measured by the O-phenanthroline method.

Results and Discussion

Preliminary experiments allowed to discard the contribution to BPS removal through a non-catalytic reaction with H₂O₂. Figure 1 shows the evolution of BPS by CWPO in the presence of HC-Fe catalysts developed at different temperatures. Although higher temperature led to a magnetic character on the solids, as can be seen, the highest activity was obtained with the material treated at 125°C (HC-Fe-125), achieving more than 90% of BPS removal in 1 h reaction time. An increase in the temperature

synthesis led to lower reaction rates that could be attributed to a modification on the iron oxidation state. The adsorption effect was discarded since less than 5% of BPS removal was observed by adsorption experiments. In addition, the dissolved iron was measured in the reaction effluents obtaining values below 0.2 mg L^{-1} in all cases, showing that homogeneous contribution was negligible.

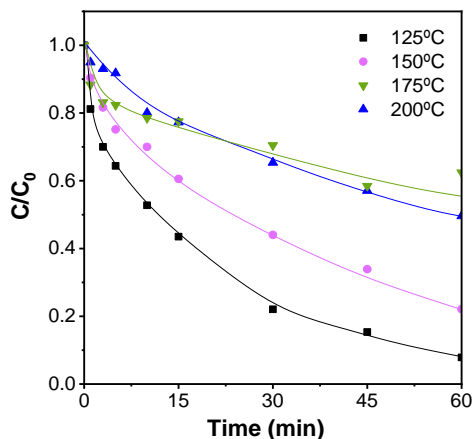


Figure 1. BPS evolution upon Fenton oxidation by HC-Fe developed at different temperatures. ($[\text{BPS}]_0=5 \mu\text{M}$; $[\text{HC-Fe}]_0=0.1 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0=700 \mu\text{M}$; $T=25^\circ\text{C}$)

Furthermore, the catalyst dose was evaluated using the catalyst HC-Fe-125. As shown in Figure 2a, higher reaction rates were obtained increasing the catalyst concentration up to 0.5 g L^{-1} , allowing to completely remove BPS in less than 45 min. The experimental data was successfully described by a pseudo-first order kinetic equation and the resulting apparent rate constant values are shown in Figure 2b. Reaction rates linearly increased with the increasing catalyst concentration.

Finally, a new experiment was carried out with the HC material, without further Fe impregnation. Since the sewage sludge used contained 5% of Fe, as

analysed by ICP-MS, BPS was also removed in the presence of HC solid although longer times were necessary.

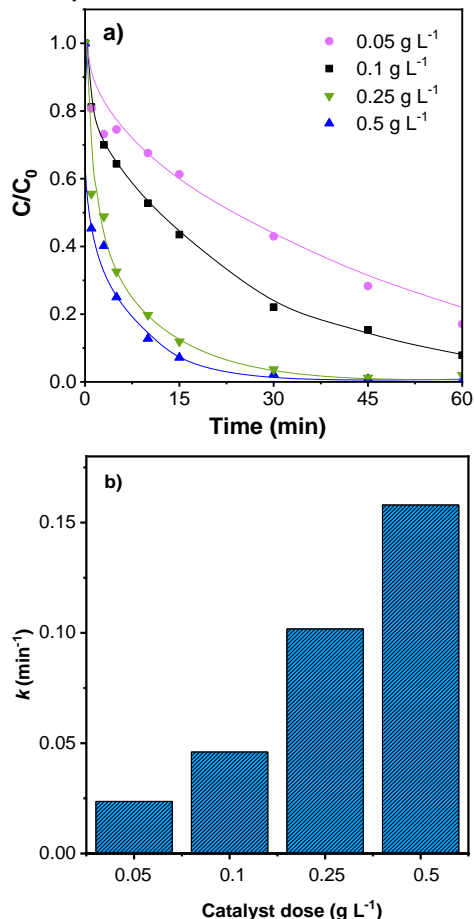


Figure 2. BPS evolution upon Fenton oxidation by HC-Fe-125 at different catalyst concentrations (a) and kinetic constants (b). ($[\text{BPS}]_0=5 \mu\text{M}$; $[\text{H}_2\text{O}_2]_0=700 \mu\text{M}$; $T=25^\circ\text{C}$)

Conclusions

All in all, this work shows the potential to valorise sewage sludge into catalysts for water treatment. The results obtained in this work have demonstrated that hydrochar-based catalyst derived from sewage sludge could be an alternative for the degradation of micropollutants such as bisphenols by Fenton oxidation.

Acknowledgments

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References

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