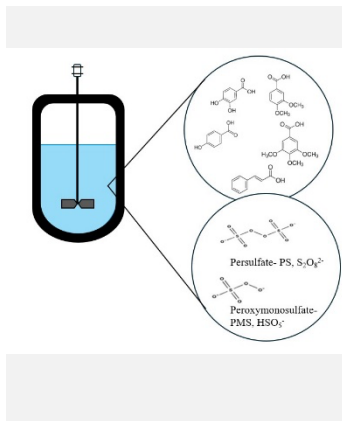


Rui C. Martins^{1*}, Telma Vaz¹, Margarida M.J.Quina¹, João Gomes¹

¹University of Coimbra, CERES, Department of Chemical Engineering, Faculty of Sciences and Technology, Rua Sílvio Lima, Polo II, 3030-790 Coimbra, Portugal; *martins@eq.uc.pt



The Mediterranean countries are the largest producers of olive oil, an industry that produces an environmentally problematic effluent, olive mill wastewater (OMW). OMW is a complex effluent characterized, among other parameters, by the presence of phenolic compounds with low biodegradability. Due to the difficult degradation of these compounds, several studies have been developed targeting the degradation of phenolic synthetic solutions. In the present study, the abatement of five phenolic compounds (Trans-cinnamic acid, 3,4-Dihydroxybenzoic, 4-Hydroxybenzoic, 3,4,5-Trimethoxybenzoic, and 3,4-Dimethoxybenzoic) was evaluated using ozonation in comparison with ozone activated persulfate (O₃-PS) and peroxymonosulfate (O₃-PMS). The processes proved to be quite efficient in the degradation of Trans-cinnamic acid. The PS load studied did not demonstrate any contribution to the degradation of phenolic acids compared to ozone alone.

Introduction

The growing demand for quality water is forcing society to change the paradigm and look for the reuse of treated wastewater whenever possible. Industrial activity consumes and produces large quantities of water, the disposal of which in public sewage treatment plants and/or bodies of water continues to be a global problem [1]. The management of olive mill wastewater (OMW) in the Mediterranean countries continues to be a challenge. These wastewaters are quite complex, due to the presence of organic compounds that are difficult to biodegrade, such as phenolic compounds. However, other parameters such as dark color, acidic pH, and high organic matter levels also contribute to its complexity [2]. Thus, in recent years, researchers have studied the applicability of advanced oxidation processes (AOPs) for treating this effluent. Due to its complexity, in the first phase, the new treatment technologies are studied using synthetic solutions with known phenolic compounds, to grasp insight about the degradation mechanism and kinetics [3]. Fenton's process, ozonation, and recently, sulfate radical-based AOPs (SR-AOPs) have been applied in the treatment of real and synthetic OMW. These processes are based on the generation of very reactive free radicals with a high capacity to degrade organic compounds. The ozonation demonstrated to be an efficient technology capable of breaking aromatic bonds of phenolic compounds that generally impair the efficiency of traditional biological processes. The breaking of aromatic bonds forms low molecular weight molecules potentially more amenable to

biotreatment. The SR-AOPs (persulfate and peroxymonosulfate) when activated can produce •OH and SO₄^{•-} radicals for organic matter removal. In recent studies, ozone (O₃) demonstrated that it is an interesting activator of persulfate (PS) and peroxymonosulfate (PMS) for the degradation of different contaminants [4].

Therefore, this work aims to evaluate the degradation of five phenolic acids (Trans-cinnamic acid, 3,4-Dihydroxybenzoic, 4-hydroxybenzoic, 3,4,5-Trimethoxybenzoic, and 3,4-Dimethoxybenzoic) in synthetic OMW comparing ozonation, PS (O₃-PS) and PMS (O₃-PMS) activated by ozone.

Material and Methods

The solution of synthetic OMW is constituted of five phenolic compounds: Trans-cinnamic acid (TCA), 3,4-Dihydroxybenzoic (3,4-DHB), 4-Hydroxybenzoic (4-HB), 3,4,5-Trimethoxybenzoic (3,4,5-TMB), and 3,4-Dimethoxybenzoic (3,4-DMB). These compounds are dissolved in ultrapure water with a concentration of 100 mgL⁻¹ each (about 800 mgO₂L⁻¹ of chemical oxygen demand-COD). The reactions were carried out in a 2 L gas/liquid stirred reactor. An ozone generator (802N, BMT) was used, producing ozone from a stream of pure oxygen. The inlet gas flow was set at 0.2 Lmin⁻¹ and the ozone inlet and outlet concentrations were monitored using two gas analyzers (BMT 963 and 964). The samples were analyzed utilizing high-performance liquid chromatography (HPLC) (Waters 2695) for determining the concentration of phenolic compounds and respectively removal. Dosages of 5mM of PS and PMS were used in the experiments.

The COD was analyzed using the Standard Method 5220D [5].

Results and Discussion

Figure 1 shows the removal efficiencies of the five phenolic compounds during treatment with ozonation (Fig. 1a), O_3 -PS (Fig. 1b), and O_3 -PMS (Fig. 1c).

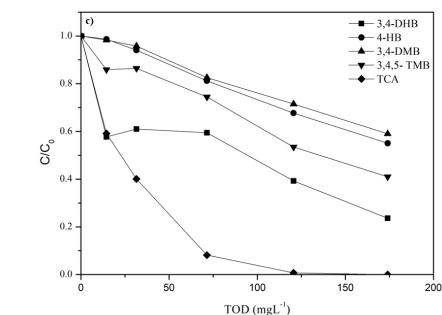
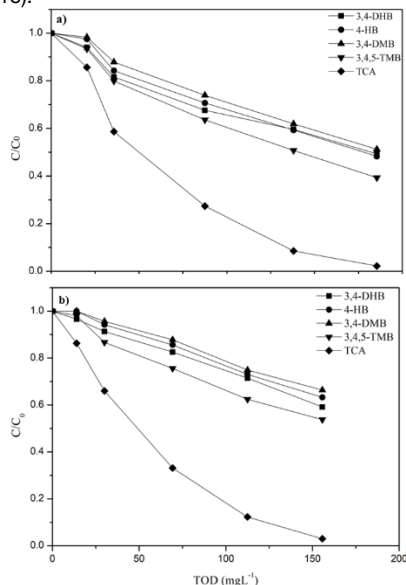


Figure 1. Degradation of five phenolic compounds by a) O_3 b) O_3 -PS and c) O_3 -PMS during 2h.

Ozonation has been demonstrated to be quite efficient in the degradation of the five phenolic acids, although it has demonstrated greater efficiency in the degradation of TCA. While PS is not activated by O_3 (Fig 1b), the same has not been true for PMS. Figure 1c shows that PMS allowed complete degradation of TCA after 2h while reducing the amount of ozone required (TOD). Removals of 76, 45, 41 and 59% were obtained for 3,4-DHB, 4-HB, 3,4-DMB and 3,4,5-TMB respectively by the O_3 -PMS system. Removals of 20 and 24% of COD were obtained in the ozonation process and O_3 -PMS, respectively.

Conclusion

Ozonation, O_3 -PS and O_3 -PMS proved to be very efficient in the degradation of the five phenolic acids under study. These phenolic compounds are commonly found in real OMW, being one of the main contributors to the toxicity of this effluent. The studied processes demonstrated greater efficiency in the degradation of TCA. However, PS was not able to be activated by ozone since no differences between ozonation and O_3 -PS were detected. O_3 -PMS system was able to improve degradation while reducing the amount of ozone required for TCA total removal.

Acknowledgments

The authors gratefully acknowledge FCT (Fundação para a Ciência e Tecnologia, Portugal) for the PhD Grant (2022.14237.BD) and the financial support (CEECIND/01207/2018). Thanks are due to FCT/MCTES for the financial support to CERES (UIDB/00102/2020).

References

- [1] Arslan-Alaton, I.; Koba-Ucun, O. Treatment of Reactive Dye Hydrolysates with UV-C-and Ozone-Activated Percarbonate and Persulfate. *International Journal of Environmental Research* **2023**, *17*, 58.
- [2] Görmez, F.; Görmez, Ö.; Yabalak, E.; Gözmen, B. Application of the central composite design to mineralization of olive mill wastewater by the electro/Fell/persulfate oxidation method. *SN Applied Sciences* **2020**, *2*, 1-11
- [3] Martins, R. C.; Rossi, A. F.; Quinta-Ferreira, R. M. Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement. *Journal of Hazardous Materials* **2010**, *180*, 716-721.
- [4] Deniere, E.; Van Langenhove, H.; Van Hulle, S. W.; Demeestere, K. Improving the ozone-activated peroxymonosulfate process for removal of trace organic contaminants in real waters through the implementation of an optimized sequential ozone dosing strategy. *Science of The Total Environment*, **2023**, *856*, 158764.
- [5] Baird, R.B.; Eaton, A.D.; Rice, E.W. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; American Public Health Association: Washington, DC, USA, **2017**.