

C. A. Orge^{1,2}, **C. Lopes**^{1,2}, **M. F. R. Pereira**^{1,2}, **O. S. G. P. Soares**^{1,2}, (1) *Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.* (2) *ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.* carlaorge@fe.up.pt



Halogenated organic compounds are important and versatile molecules with many applications in synthetic organic chemistry and industrial chemical processes [1]. Due to their widely used and very stable nature, their persistence in the environment and bioaccumulation is a problem. Catalytic hydrodehalogenation (CatHDH) represents a viable alternative for transforming toxic hazardous material into less toxic products that can be more easily degraded by (advanced) oxidation techniques, such as catalytic ozonation (CatOZO), or even possess commercial importance. In this work, the degradation of 4-fluorophenol was evaluated by CatHDH and CatOZO. For that purpose, several catalysts were tested. Ozonation reactions allowed higher 4-CF removals than CatHDH, achieving a complete degradation even in the absence of a catalyst. The best mineralization levels of solutions were also attained by O₃-based processes. The cleavage of the strong C-F bond was also confirmed.

Introduction

Halogenated compounds, including poly- and perfluoroalkyl substances (PFAS), present harmful effects on humans which require the development of efficient processes to destroy them in regard to environmental protection. Nowadays, numerous techniques are employed for handling contamination caused by these pollutants, in particular, adsorption, membrane technologies, biological degradation, photocatalytic degradation, and electrochemical oxidation [2]. However, these processes presented limitations since most of them generate secondary concentrated waste streams or saturated adsorbents that require regeneration.

Catalytic hydrodehalogenation (HDH) emerges as an economic and environmental solution since it allows the transformation of these hazardous materials into reusable hydrocarbons or into aromatic compounds and/or carboxylic acids that can be mineralized by the application of one advanced oxidation process (AOPs), such as catalytic ozonation. Fluorophenol (4-FP) is a fluorinated organic compound with valuable contributions in many industries, but it is a carcinogen compound according to the RTECS (Registry of Toxic Effects of Chemical Substances) standard [3]. These compounds are characterized by their high chemical stability, resulting in a slow degradation rate in natural environments. Furthermore, the high toxicity and persistence of these compounds primarily result from the presence of elemental chlorine [4]. Due to their extensive utilization as herbicides, insecticides, fungicides, solvents, hydraulic and heat-transfer fluids, plasticizers, cleaning agents, fumigants, aerosol propellants, gasoline additives, degreasers, and intermediates in chemical synthesis [5], these

substances are introduced into the environment in significant amounts. Therefore, the development of efficient remediation techniques is of the utmost importance for removing these contaminants from water.

The main goal of the present work is to study the removal of 4-FP by CatHDH and/or CatOZO in the presence of different catalysts. In the case of CatHDH, metal (Pd) supported materials were prepared, and during CatOZO reactions, commercial catalysts, such as carbon nanotubes and titanium dioxide, were used. The efficiency of the processes was assessed by the capacity for pollutant removal, cleavage of F-C bond and level of mineralization.

Material and Methods

In the case of CatOZO, the catalysts used were commercial materials, such as multi-walled carbon nanotubes (CNT) and titanium dioxide (TiO₂). In the case of CatHDH, different metal supported materials were tested. The prepared catalysts were obtained by impregnating 5% (wt.%) metal (Pd) on different supports by the incipient wetness impregnation methodology. The synthesised materials were texturally characterized through N₂ adsorption isotherms, determined at -196 °C in a Quantachrome NOVA 4200e multistation.

All the experiments were carried out in a semi-batch reactor (ca. 1 L) equipped with stirring. In the case of HDH experiments, a hydrogen flow rate of 100 cm³ min⁻¹ (STP) was used. In the case of ozonation reactions, O₃ was produced from pure oxygen in a BMT 802X O₃ generator under a constant flow rate (150 cm³ min⁻¹). Its concentration (50 g m⁻³ STP) in the gas phase was monitored with a BMT 964 O₃ analyser. The reactions were analysed by high-performance liquid chromatography (HPLC) using a

Hitachi Elite Lachrom apparatus equipped with a diode array detector to quantify 4-fluorophenol and released intermediates. The stationary phase was the YMC Hydrosphere C18 column (250 mm × 4.6 mm i.d.), working at room temperature. The fluoride ions concentration was quantified using ionic chromatography (IC) in a Metrohm 881 Compact IC Pro apparatus, equipped with a Metrosep A Supp 7 anionic exchange column (250 m x 4.0 mm). The total organic carbon (TOC) was measured using a Shimadzu TOC-L Total Organic Carbon Analyzer.

Results and Discussion

The specific surface areas (S_{BET}) were obtained from the N_2 adsorption isotherms at $-196\text{ }^\circ\text{C}$ of the prepared catalysts and the results are summarized in Table 1. As expected, catalysts containing CNT presented higher S_{BET} than the TiO_2 based samples.

Table 1. BET surface area of the prepared catalysts.

| Sample | S_{BET} ($\pm 5\text{ m}^2\text{ g}^{-1}$) |
|----------------------|--|
| CNT | 235 |
| TiO_2 | 54 |
| 5%Pd/CNT | 203 |
| 5%Pd/ TiO_2 | 26 |

Figure 1 shows the results of 4-FP degradation during HDH process. A blank test demonstrated that 4-FP was not reduced in the presence of only hydrogen under tested experimental conditions. The addition of 5%Pd/CNT allowed higher 4-CP removal than 5%Pd/ TiO_2 sample, confirming the importance of the support. In the case of ozonation reactions (Figure 2), a fast total 4-FP removal was attained, even in the absence of a catalyst. In terms of TOC removal (Table 2), O_3 -based reactions allowed higher mineralization levels than hydrogenation processes, as expected taking into account the 4-FP removal values. The combination of O_3 and TiO_2 achieved the best TOC removal (75% after 180 min of reaction). Analysing the results of selectivity to F⁻ presented in Table 2, it is possible to conclude that

Conclusions

CatHHDH allowed a slow 4-FP degradation under tested experimental conditions. The sample 5%Pd/CNT achieved better performance than 5%Pd/ TiO_2 , however, only 60% of the pollutant was removed after 300 min of reaction. On the other hand, all O_3 -based processes attained a complete pollutant removal, even without the presence of a catalyst in solution. The mineralization achieved during the ozonation processes is high, presenting TiO_2 sample the best result. The breakage of the C-F bond was confirmed, releasing all F⁻ possible for the solution during tested O_3 based processes.

Acknowledgments

This work is financially supported by national funds through the FCT/MCTES (PIDDAC) under the project 2022.03874.PTDC - F-CAT (DOI: 10.54499/2022.03874.PTDC) and LSRE-LCM, UIDB/ 50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/ 2020 (DOI: 10.54499/UIDP/50020/2020); and ALiCE, LA/P/0045/ 2020 (DOI: 10.54499/LA/P/0045/2020). This work is a result of Agenda "GIATEX – Intelligent Water Management in the Textile & Clothing Industry", nr. C644943052-00000050, investment project nr.17, financed by the Recovery and Resilience Plan (PRR) and by European Union - NextGeneration EU. C.A. Orge acknowledges FCT funding under DL57/2016 Transitory Norm Programme. O.S.G.P. Soares thanks FCT funding under the Scientific Employment Stimulus – Institutional Call CEECINST/00049/2018 (DOI: 10.54499/CEECINST/00049/2018/CP15 24/CT0008).

References

- [1] X. Ma, S. Liu, Y. Liu, G. Gu, C. Xia, Scientific Reports, 6 (2016) 25068.
- [2] N. Sharma, V. Kumar, V. Sugumar, M. Umesh, S. Sondhi, P. Chakraborty, K. Kaur, J. Thomas, C. Kamaraj, S.S. Maitra, Case Studies in Chemical and Environmental Engineering, 9 (2024) 100623.
- [3] X. Wang, P. Wang, Q. Wang, P. Xu, C. Yang, Y. Xin, G. Zhang, Chemical Engineering Journal, 420 (2021) 127577.
- [4] X. Ding, Z. Yao, Y. Xu, B. Liu, Q. Liu, Y. She, Journal of Catalysis, 368 (2018) 336.
- [5] P. Bhatt, M.S. Kumar, S. Mudliar, T. Chakrabarti, Critical Reviews in Environmental Science and Technology, 37 (2007) 165.

the cleavage of C-F bond happens during CatHHDH despite the slow 4-FP degradation. The breakage of C-F bond was effective during single and catalytic ozonation tests, leading to selectivities of 1.

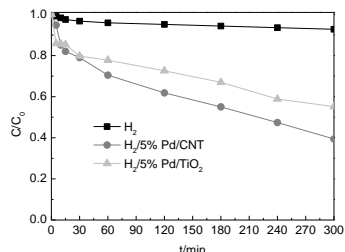


Figure 1. Normalized concentration profile of 4-FP dissolved in water during CatHHDH ($C_{4\text{-FP},0} = 0.8\text{ mM}$, $C_{\text{cat.}} = 0.5\text{ g L}^{-1}$).

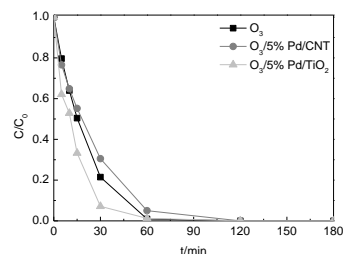


Figure 2. Normalized concentration profile of 4-FP dissolved in water during CatOZO ($C_{4\text{-FP},0} = 0.8\text{ mM}$, $C_{\text{cat.}} = 0.5\text{ g L}^{-1}$).

Table 2. Percentage of TOC removal and selectivity to F⁻ at the end of each process.

| Process | %TOC _{removal} | S _{F⁻} |
|---------------------------------|-------------------------|----------------------------|
| H_2 | 1 | 0 |
| $\text{H}_2/5\%\text{Pd/CNT}$ | 4 | 0.96 |
| $\text{H}_2/5\%\text{Pd/TiO}_2$ | 4 | 1.0 |
| O_3 | 65 | 1.0 |
| O_3/CNT | 51 | 1.0 |
| O_3/TiO_2 | 75 | 1.0 |