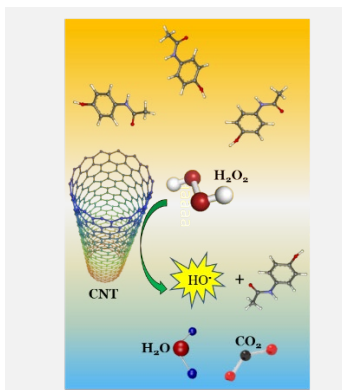


R. P. Souza¹, A. S. Silva^{2,3,4,5,6}, F. F. Roman^{2,4,5,6}, L. Leal^{2,4}, J. L. Diaz de Tuesta⁷, I. Çaha⁸, F. L. Deepak⁸, A. Pereira^{3,4}, A. M. T. Silva^{5,6}, H. T. Gomes^{2,4}. (1) Federal University of Technology – Paraná, Campus Dois Vizinhos, Boa Esperança Road, km 04, 85660-000, Dois Vizinhos, Brazil, renatapsouza@utfpr.edu.br. (2) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253, Bragança, Portugal, (3) Centro de Investigação em Digitalização e Robótica Inteligente (CeDRI), Instituto Politécnico de Bragança, 5300-253, Bragança, Portugal. (4) Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, 5300-253, Bragança, Portugal. (5) Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal. (6) Associate Laboratory in Chemical Engineering, Faculty of Engineering (ALiCE), University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal. (7) Chemical and Environmental Engineering Group, ESCET, Universidad Rey Juan Carlos, c/ Tulipán s/n 28933, Móstoles, Spain. (8) Nanostructured Materials Group, International Iberian Nanotechnology Laboratory (INL), Avenida Mestre Jose Veiga, Braga, 4715-330, Portugal.



This study presents a new method to produce carbon nanotubes (CNTs) from plastic solid waste using catalytic chemical vapor deposition (CCVD) on mixed metal substrates. The research explores CNT yield variations by adjusting nickel and cobalt ferrite compositions on alumina catalysts. The synthesized magnetic CNTs enable easy retrieval in liquid-phase applications without additional processing. Additionally, the study evaluates the synthesized CNTs as catalysts for degradation of bisphenol-A and sulfamethoxazole via catalytic wet peroxide oxidation (CWPO), emphasizing the importance of tailored catalyst design for specific applications. Overall, this research offers a sustainable and cost-effective approach for repurposing plastic solid waste to synthesize valuable carbon nanomaterials.

Introduction

The scientific community aims to develop catalysts for environmental applications, focusing on pollution control, energy storage, and conversion [1]. The use of waste materials for catalyst production aligns with the concept of circular economy, potentially adding value and reducing manufacturing costs. While biomass has been extensively explored, plastics, rich in carbon, offer untapped potential for generating carbon-based functional materials, such as carbon nanotubes (CNTs) and graphene. Unlike biomass, polymers are based on well-defined structures with narrow composition, enabling controlled morphology and content in carbonaceous materials. A novel approach to synthesize CNTs from plastic solid waste (PSW) deals with the catalytic chemical vapor deposition (CCVD) of PSW decomposition gases on magnetic metal substrates, leading to the growth of magnetic carbonaceous nanomaterials. Magnetic CNTs are promising for catalytic wet peroxide oxidation (CWPO) in wastewater treatment due to their high catalytic activity and in-situ magnetic separation capability [2]. This study evaluates various mixed metal substrates for synthesis of CNTs, revealing insights into catalytic activity on CWPO of bisphenol-A (BPA) and sulfamethoxazole (SMX). The choice of metal substrate significantly influences the material's performance in catalytic applications, highlighting the importance of substrate selection for future research.

Material and Methods

CNTs were synthesized using a modified procedure based on a well established methodology [2]. Carbonaceous materials were initially produced via CCVD with a metal phase supported on alumina. The metal substrate, prepared using a sol-gel method, involved the synthesis of mixed cobalt and nickel ferrites (15wt.%) on alumina. Different ratios of cobalt and nickel ferrite were tested to optimize growth of the CNTs. The sol-gel process included rapid hydrolysis of mixed M^{2+} (Ni and/or Co) salt in ethanol and an M^{3+} (Fe) salt in ethanediol. After heating and combining with alumina, the resulting gel was dried and calcined. CCVD was conducted in a one-chamber reactor at 850°C under a nitrogen flow for 1.5 h, preceded by a 2 h purge. CNTs were purified with a 50% H_2SO_4 solution, followed by rinsing with water and drying. Purified CNT samples were named according to the metal substrate used in the synthesis. For example, CNT@ $Co_{0.1}Ni_{0.9}/Al_2O_3$ referred to a purified CNT prepared using $Co_{0.1}Ni_{0.9}/Al_2O_3$ as the metal substrate.

CWPO reactions were conducted in a two-necked round bottom flask containing 100 mL of the model pollutants solution, with the pH adjusted to 3.5 using H_2SO_4 . The initial pollutants concentration was $100 \mu g mL^{-1}$ (BPA) and $10 \mu g mL^{-1}$ (SMX), simulating the approximate concentration ratio of these pollutants in real wastewater [3]. The stoichiometric amount of H_2O_2 ($581 \mu g mL^{-1}$) for the complete oxidation of the pollutants was added. The flask, placed in an oil bath at 80°C, was stirred for 5 minutes to ensure uniform heating and dispersion. Samples were taken to measure initial pollutant and

oxidant concentrations before adding the catalyst to initiate the reaction. Subsequent samples were collected at 15, 30, 60, 120, 240, 360, and 480 minutes of reaction, to monitor pollutant and H₂O₂ concentrations. Adsorption experiments followed the same procedure, excluding the addition of oxidant.

Results and Discussion

The results obtained for the removal of pollutant and decomposition of H₂O₂ are shown in Figure 1.

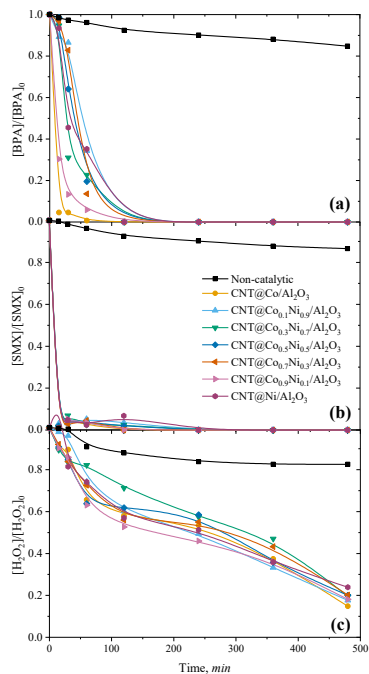


Figure 1. Degradation profile of (a) BPA, (b) SMX, and (c) H₂O₂ decomposition.

Acknowledgments

This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020) and CeDRI (UIDB/05757/2020); 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). Fernanda F. Roman acknowledges FCT and FSE, for the individual research grant (SFRH/BD/143224/2019). Adriano Santos Silva thanks FCT for financial support under the MIT Portugal Program with doctoral grant SFRH/BD/151346/2021. Jose L. Diaz de Tuesta acknowledges the financial support through 2022-T1/AMB-23946.

References

- [1] A. S. Silva, F. F. Roman, A. V. Dias, J. L. Diaz deTuesta, A. Narcizo, A. P. F. da Silva, I. Çaha, F. L. Deepak, M. Bañobre-López, A. M. C. Ferrari, H. T. Gomes. *Journal of Environmental Chemical Engineering*, 11 (2023) 110806.
- [2] J. L. Diaz de Tuesta, A. Silva, F. F. Roman, L. F. Sanches, F. A. da Silva, A. I. Pereira, A. M. T. Silva, J. L. Faria, H. T. Gomes. *Catalysis Today*, 419 (2023) 114162.
- [3] J. A. Rodríguez-Hernandez, R. G. Araújo, I. Y. López-Pacheco, D. Barceló, H. M. N. Iqbal, R. Parra-Saldívar. *Env. Sci. Adv.* 1 (2022) 680-704.

All pollutants were completely removed within 120 minutes of reaction. This result overcomes the non-catalytic removal of both pollutants, which reached 15% (BPA) and 13% (SMX) in 480 minutes. H₂O₂ decomposition in catalytic runs overcomes the non-catalytic run by at least 60%. Adsorption runs revealed less than 14% adsorption in all materials for both pollutants, confirming that CWPO is the main removal mechanism in oxidation experiments. The decomposition profile obtained for H₂O₂ presented a sharp curve between 0-120 minutes, followed by a smaller rate. After 360 minutes, the decomposition profile was accelerated again. Considering the pollutant removal in a time interval of 0-120 minutes, most likely, the pollutants partially adsorbed in the material's surface have difficult access to active sites for H₂O₂ decomposition. Once these pollutants are degraded, the sites become accessible again, and H₂O₂ decomposition is accelerated.

The different activity observed among the CNT samples is related to the remaining metals (< 5wt.%). Despite the low amount of metals in the CNT structure due to the acid washing, there is a strict correlation between the content of cobalt and catalytic activity toward H₂O₂ decomposition. The increased H₂O₂ decomposition observed for CNTs prepared with metal substrate containing more cobalt affects catalytic activity. In this case, samples with more cobalt are more efficient in the removal of both SMX and BPA.

Conclusions

All CNTs used in this work could degrade SMX and BPA simultaneously within 120 min of reaction. The results obtained reveal a prospect to apply CNTs for environmental catalysis once the materials have low metal content and the synthesis method enables the synthesis of waste-based (such as plastic solid wastes) for the synthesis.