



D 2025



CARBON NANOTUBES DERIVED FROM PLASTIC WASTE FOR ONE-POT DESULFURIZATION AND DENITROGENATION OF LIQUID FUELS

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DOCTORAL THESIS PRESENTED TO THE
FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO
FOR THE DEGREE OF DOCTOR IN CHEMICAL AND BIOLOGICAL ENGINEERING

Carbon Nanotubes Derived from Plastic Waste for One-Pot Desulfurization and Denitrogenation of Liquid Fuels

PhD Thesis

In

Chemical and Biological Engineering

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April 2025

Ao meu marido, Adriano.

Acknowledgments

I gratefully acknowledge the financial support provided by *Fundação para a Ciência e a Tecnologia* (FCT) and the European Social Fund (FSE) for the Ph.D. scholarship with the reference SFRH/BD/143224/2019 (10.54499/SFRH/BD/143224/2019).

This work was financially supported by project "*PLASTIC_TO_FUEL&MAT – Upcycling Waste Plastics into Fuel and Carbon Nanomaterials*" (PTDC/EQU-EQU/31439/2017) and by national funds through the 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); LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); and PTDC/CTA-AMB/3489/2021 - RECY-SMARTE (DOI: 10.54499/PTDC/CTA-AMB/3489/2021). This work was also financially supported by *Sociedade Ponto Verde* through the project "*Estudo técnico-económico para a valorização de resíduos de embalagens plásticas em nanotubos de carbono*".

To my supervisor, Prof. Dr. Helder Gomes, a special thanks for his support, encouragement, trust, and all the growth I experienced within his research group. Part of the experience gained throughout this project is tied to the wonderful person that you are, and to the flexibility and faith you have put in my work, and the plethora of activities and opportunities I was able to participate in. I would also like to thank my co-supervisors, Prof. Dr. Adrián M. T. Silva, and Prof. Dr. Joaquim L. Faria, for accepting to supervise me during my PhD, for their support, and for their teachings. I feel very grateful and proud to have had you as my co-supervisors.

I would also like to acknowledge Dr. José Luiz Diaz de Tuesta (Universidad Rey Juan Carlos), who actively collaborated with the work and taught me so much about materials, synthesis, oxidation reactions, but also about ethics, friendship, and respect. I also appreciate the help with some characterization analysis that I was able to carry out in your facilities.

I also appreciate the support and opportunity to work for a brief period with prof. Ana I. Pereira, Prof. Maria Fátima Pacheco and Rebeca Kalbermatter (Research Centre in Digitalization and Intelligent Robotics - IPB) under a scholarship in science management provided by STEP project. It was an enriching experience that contributed greatly to my scientific path, and I am thankful for having shared this period with you.

I would also like to acknowledge the contribution of several colleagues and staff at both IPB and FEUP who were essential in the development of this work. At IPB, I'd like to acknowledge the help of Maria

João Afonso, Paula Plasencia, Prof. Margarida Arrobas and Dr. David Cabral and my work colleagues who helped me throughout my Ph.D. thesis in different capacities and moments: Gabriel de Freitas, Jessica Lopes, Flávia Kobayashi Santos, Larissa Piccinin, Arnaldo Dias, Maria Clara Batista, Ana Julia Briganti, Paulo Zadra, Arthur Baldo, Isabella Freitas, Ana Paula Ferreira, Dr. Sérgio Vilas Boas, Amir Bzainia, Dr. Tatiana La Banca, Dr. Adriano Henrique, and so many others who have come and stayed at Bragança, I am thankful for your help. At FEUP, I'd like to acknowledge the help and guidance provided by Dr. Marta Pedrosa, Dr. Rui Sérgio Ribeiro, Luís Matos, Dr. André Torres-Pinto, Dr. Raquel Rocha, Dr. Bruno Machado, Dr. Natalia Rey-Raap, José Barbosa, and many others who I had the opportunity of meeting. I also would like to mention the contribution provided by people from external entities where some characterization techniques were carried out: Dr. Ana Malheiro (International Iberian Nanotechnology Laboratory) for helping me with Transmission Electronic Microscopy images and Prof. Pedro Tavares (Universidade de Trás-os-Montes e Alto Douro) for X-Ray Diffraction analysis.

I would also like to express my gratitude to other colleagues who somehow collaborated with my path as a scientist: Paulo Praça and Luis Teixeira (Resíduos do Nordeste), Prof. Juliana M.T. Pietrobelli, Prof. Giane G. Lenzi, Prof. Renata Souza, Prof. Pricila Marin, Prof. Admilson Vieira, Prof. Ana M. Ferrari and Prof. Fernando Alves da Silva (Universidade Tecnológica Federal do Paraná—UTFPR), Prof. Raquel V. Mambrini (Centro Federal de Educação Tecnológica de Minas Gerais), Prof. Philippe Serp (Université de Toulouse), Dr. Manuel Bañobre-López, Dr. Ihsan Çaha, and Dr. Francis Leonard Deepak (International Iberian Nanotechnology Laboratory), Prof. Marzhan S. Kalmakhanova, Aizhan M. Serikbayeva and Prof. Rabiga M. Kudaibergenova (M. Kh. Dulaty Taraz University), Prof. Juan Garcia (Complutense University of Madrid), Madeleine Rauhauser and Dr. Daniel Snow (Water Sciences Laboratory), and Prof. Paulo Brito, Prof. Ana Maria Queiróz, and Prof. António Ribeiro (Instituto Politécnico de Bragança).

To my family (Nauria, Odacir and Camila) who listened so much during difficult times but never stopped believing in my abilities and always celebrated with me the moments of joy, I am thankful. And my friends, Laisa Torsani, Ana Caroline Stromberg, Giulia Tramontin, Alexia Vieira, Renata Drummond, Carline Schardong, Hadla El Didi, Armando Dauer, Dr. Erik Van Tilburg Bernardes, Dr. Inês Sena, Dr. João Mendes, Thadeu Brito, Felipe Teixeira, I am grateful for the support and friendship you provided.

Lastly, to my husband, Adriano dos Santos Silva, who is my family and my best friend. You have been a fundamental part of my personal and professional life over these past years, sharing moments of doubt and disappointment, and helping me rise and continue. Without your support and strength, and without your hand to hold mine, it would not have been possible to reach this moment. This thesis is also your achievement.

Abstract

This thesis explores the synthesis of carbon nanotubes (CNTs) from plastic solid waste via chemical vapor deposition (CVD) using iron and nickel-iron catalysts. Both simulated polymeric materials and real plastic solid waste were evaluated as carbon sources. CNT yields ranged from 5% to 30%, depending on the catalyst, carbon source and CVD conditions. The resulting CNTs were comprehensively characterized to assess their morphology, textural properties, and surface chemistry. The carbon source and catalyst significantly influenced key material characteristics, including outer diameter (17–33 nm), graphitization degree (D/G ratio = 0.49–3.46), surface area (144–242 m² g⁻¹), total pore volume (342–894 mm³ g⁻¹), oxygen content (0.2–9.2 wt.%), acidic and basic groups (137–1897 μmol g⁻¹ and 25–684 μmol g⁻¹, respectively), and contact angle (51–138°). These findings provide valuable insights into the sustainable production of CNTs from plastic waste, contributing to waste valorization and nanomaterial development.

The synthesized CNTs were applied as catalysts for the selective oxidation of nitrogen- and sulfur-containing model compounds under a biphasic system. In oxidative denitrogenation (ODN), using quinoline (QN) as a model compound, QN removal ranged from 30% to 100%, depending on the catalyst and reaction conditions. Under optimized conditions (H_2O_2/N molar ratio = 23, $C_{cat} = 2.5$ g L⁻¹, $T = 70$ °C, and aqueous phase pH of 3.0) 89% of QN was removed within 1 h. Kinetic modeling of the biphasic system revealed mass transfer as the rate-limiting step, highlighting the importance of designing catalysts that enhance interphase transfer. For oxidative desulfurization (ODS), using dibenzothiophene (DBT) as model compound, DBT removal varied between 25% and 91%, depending on the catalyst and extractant phase (water or acetonitrile). The highest desulfurization efficiency (91% in 4 h) was achieved with acetonitrile as the extractant, while water-oil system yielded 77% DBT removal after 8 h under identical conditions (H_2O_2/S molar ratio = 15, $C_{cat} = 2.5$ g L⁻¹, $T = 70$ °C). These results underscore the potential of CNT-based catalysts for fuel purification, with a strong influence of mass transfer phenomena and extractant selection on process efficiency.

This work demonstrates the feasibility of upcycling plastic solid waste into high-performance catalysts, contributing to the advancement of technologies for producing low-sulfur and low-nitrogen fuels. The findings highlight the potential of integrating waste valorization with sustainable catalysis, offering a promising pathway toward cleaner energy solutions.

Keywords: Carbon nanotubes; Oxidative desulfurization; Oxidative denitrogenation; Plastic solid waste;

Resumo

Esta tese explora a síntese de nanotubos de carbono (CNTs) a partir de resíduos sólidos plásticos por deposição química em fase de vapor (CVD), utilizando catalisadores de ferro e níquel-ferro. Foram avaliados tanto materiais poliméricos simulados quanto resíduos plásticos reais como fontes de carbono. O rendimento em CNTs variaram entre 5% e 30%, dependendo do catalisador, da fonte de carbono e das condições de CVD. Os CNTs resultantes foram caracterizados de forma abrangente para avaliar sua morfologia, propriedades texturais e química de superfície. A escolha da fonte de carbono e do catalisador influenciou significativamente as principais características do material, incluindo diâmetro externo (17–33 nm), grau de grafitação (relação D/G = 0,49–3,46), área superficial (144–242 m² g⁻¹), volume total de poros (342–894 mm³ g⁻¹), teor de oxigênio (0,2–9,2% em peso), grupos ácidos e básicos (137–1897 μmol g⁻¹ e 25–684 μmol g⁻¹, respectivamente) e ângulo de contato (51–138°). Esses resultados fornecem informações valiosas sobre a produção sustentável de CNTs a partir de resíduos plásticos, contribuindo para a valorização de resíduos e para o desenvolvimento de nanomateriais.

Os CNTs sintetizados foram usados como catalisadores para a oxidação seletiva de compostos modelo contendo nitrogênio e enxofre em um sistema bifásico. Na denitrogenação oxidativa (ODN), usando quinolina (QN) como composto modelo, a remoção de QN variou entre 30% e 100%, dependendo do catalisador e das condições reacionais. Em condições otimizadas (razão molar $H_2O_2/N = 23$, $C_{cat} = 2,5$ g L⁻¹, $T = 70$ °C e pH da fase aquosa de 3,0), 89% da QN foi removida em 1 h. A modelagem cinética do sistema bifásico revelou a transferência de massa como a etapa limitante da reação, destacando a importância de projetar catalisadores que aprimorem a transferência interfacial. Na dessulfurização oxidativa (ODS), usando dibenzotiofeno (DBT) como composto modelo, a remoção de DBT variou entre 25% e 91%, dependendo do catalisador e da fase extratora (água ou acetonitrila). A maior eficiência de dessulfurização (91% em 4 h) foi alcançada com acetonitrila como agente extratante, enquanto o sistema água-óleo resultou em 77% de remoção de DBT após 8 h sob as mesmas condições (razão molar $H_2O_2/S = 15$, $C_{cat} = 2,5$ g L⁻¹, $T = 70$ °C). Esses resultados ressaltam o potencial dos catalisadores à base de CNTs para a purificação de combustíveis, com forte influência dos fenômenos de transferência de massa e da escolha do agente extratante na eficiência do processo.

Este trabalho demonstra a viabilidade da conversão de resíduos plásticos sólidos em catalisadores de alto desempenho, contribuindo para o avanço de tecnologias voltadas à produção de combustíveis com baixo teor de enxofre e nitrogênio. Os resultados ressaltam o potencial da integração entre valorização de resíduos e catálise sustentável, oferecendo um caminho promissor para soluções energéticas limpas.

Palavras-chave: Nanotubos de carbono; Dessulfurização oxidativa; Denitrogenação oxidativa; Resíduos plásticos sólidos.

Résumé

Cette thèse explore la synthèse de nanotubes de carbone (CNTs) à partir de déchets plastiques solides par dépôt chimique en phase vapeur (CVD), en utilisant des catalyseurs à base de fer et de nickel-fer. Des matériaux polymériques simulés et déchets plastiques ont été évalués comme sources de carbone. Le rendement en CNTs a varié entre 5 % et 30 %, en fonction du catalyseur, de la source de carbone et des conditions de CVD. Les CNTs obtenus ont été largement caractérisés afin d'évaluer leur morphologie, leurs propriétés texturales et leur chimie de surface. Le choix de la source de carbone et du catalyseur a significativement influencé les principales caractéristiques du matériau, notamment le diamètre externe (17–33 nm), le degré de graphitisation (rapport D/G = 0,49–3,46), la surface spécifique (144–242 m² g⁻¹), le volume total des pores (342–894 mm³ g⁻¹), la teneur en oxygène (0,2–9,2 % en poids), les groupes acides et basiques (137–1897 μmol g⁻¹ et 25–684 μmol g⁻¹, respectivement) et l'angle de contact (51–138°). Ces résultats fournissent des informations précieuses sur la production durable de CNTs à partir de déchets plastiques, contribuant à la valorisation des déchets et au développement de nanomatériaux.

Les CNTs synthétisés ont été utilisés comme catalyseurs pour l'oxydation sélective de composés modèles contenant de l'azote et du soufre dans un système biphasique. Dans le cadre de la dénitrogénéation oxydative (ODN), utilisant la quinoléine (QN) comme composé modèle, l'élimination de la QN a varié entre 30 % et 100 %, selon le catalyseur et les conditions réactionnelles. Dans des conditions optimisées (rapport molaire $H_2O_2/N = 23$, $C_{cat} = 2,5$ g L⁻¹, $T = 70$ °C et pH de la phase aqueuse de 3,0), 89 % de la QN a été éliminée en 1 h. La modélisation cinétique du système biphasique a révélé que le transfert de masse constituait l'étape limitante de la réaction, soulignant l'importance de concevoir des catalyseurs améliorant le transfert interfacial. Dans la désulfuration oxydative (ODS), utilisant le dibenzothiophène (DBT) comme composé modèle, l'élimination du DBT a varié entre 25 % et 91 %, selon le catalyseur et la phase extractante (eau ou acétonitrile). La plus grande efficacité de désulfuration (91 % en 4 h) a été obtenue avec l'acétonitrile comme agent extractant, tandis que le système eau-carburant a permis d'éliminer 77 % du DBT après 8 h dans des conditions identiques (rapport molaire $H_2O_2/S = 15$, $C_{cat} = 2,5$ g L⁻¹, $T = 70$ °C). Ces résultats soulignent le potentiel des catalyseurs à base de CNTs pour la purification des carburants, avec une forte influence de transfert de masse et du choix de l'agent extractant sur l'efficacité du processus.

Ce travail démontre la faisabilité de la conversion des déchets plastiques solides en catalyseurs haute performance, contribuant au développement de technologies de production de carburants à faible teneur en soufre et en azote. Les résultats mettent en évidence le potentiel de l'intégration entre la valorisation des déchets et la catalyse durable, ouvrant une voie prometteuse vers des solutions énergétiques propres.

Mots-clés : Nanotubes de carbone ; Désulfuration oxydative ; Dénitrogénéation oxydative ; Déchets plastiques solides.

Table of Content

CHAPTER 1 - INTRODUCTION	17
1.1 Motivation and Relevance	19
1.2 Thesis objectives.....	20
1.3 Thesis organization	20
1.4 References	22
CHAPTER 2 - STATE OF THE ART.....	23
2.1 Introduction	27
2.1.1 Sulfur and Nitrogen in Crude Oils: Content and Type of Compounds.....	28
2.1.2 Health, Environmental and Technological Effects of Sulfur- and Nitrogen-Containing Compounds.....	30
2.1.3 Legislation	32
2.2 Processes for Removal of Sulfur and Nitrogen from Fuels	33
2.2.1 Hydrodesulfurization (HDS) and Hydrodenitrogenation (HDN).....	33
2.2.2 Alternative Routes to Remove Sulfur and Nitrogen.....	35
2.3 Carbon Materials in ODS	38
2.3.1 Carbon Supports and Hybrid Catalysts.....	39
2.3.2 Carbon Catalysts on Their Own.....	44
2.3.3 Amphiphilic Carbons.....	47
2.4 Carbon Materials in ODN.....	49
2.5 Final Considerations and Perspectives on Carbon Materials in ODS and ODN.....	62
2.6 Synthesis of Carbon Nanotubes	65
2.6.1 Carbon Nanotubes from Plastic Solid Waste	67
2.7 Final considerations on the synthesis of CNTs from PSW	69
2.8 References	70
CHAPTER 3 – METHODOLOGIES.....	83
3.1 Reagents and Materials	87
3.2 Synthesis of Catalysts for Chemical Vapor Deposition	88
3.3 Synthesis of Carbon Nanotubes	88
3.3.1 Purification of carbon nanotubes.....	90
3.3.2 Changing the surface chemistry	90

3.4	Materials Characterization.....	91
3.5	Reaction Runs.....	92
3.5.1	Nitrogenated compounds.....	92
3.5.2	Sulfonated compounds	94
3.6	Analytical Techniques.....	95
3.6.1	Nitrogenated compounds.....	95
3.6.2	Sulfonated compounds	97
3.7	References	100
CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF MATERIALS.....		101
4.1	Catalysts for Chemical Vapor Deposition.....	105
4.2	Carbon Nanotubes.....	108
4.2.1	Yield of carbon materials	108
4.2.2	Morphology and elemental composition of CNT samples	109
4.2.3	Raman spectra.....	114
4.2.4	Thermogravimetric analysis	115
4.2.5	Textural properties	117
4.2.6	Surface chemistry.....	119
4.3	Conclusions	122
4.4	References	123
CHAPTER 5. REMOVAL OF QUINOLINE USING FE-BASED CARBON NANOTUBES.....		127
5.1	Catalytic Wet Peroxide Oxidation of Quinoline.....	131
5.2	Selective biphasic oxidation: an oxidative denitrogenation (ODN) case study.....	134
5.2.1	Extraction and adsorption as blank runs.....	134
5.2.2	Oxidative denitrogenation (ODN) of QN	135
5.2.3	Kinetic modeling and mechanism.....	138
5.2.4	ODN of PYR and QN with sample POL-P@Fe	142
5.2.5	Catalyst reuse.....	143
5.3	Conclusions	144
5.4	References	145
CHAPTER 6 – OXIDATIVE DENITROGENATION USING NiFe-BASED CARBON NANOTUBES.....		147
6.1	Screening of materials.....	151

6.1.1 Kinetic modeling	153
6.2 Optimization of reaction conditions	156
6.2.1 Effect of hydrogen peroxide concentration.....	156
6.2.2 Effect of catalyst concentration.....	158
6.2.3 Effect of the temperature	159
6.2.4 Effect of the pH of aqueous phase.....	163
6.2.5 Effect of initial concentration of QN.....	164
6.3 Comparison with literature	165
6.4 Conclusions	166
6.5 References	168
CHAPTER 7 - OXIDATIVE DESULFURIZATION WITH NiFe-BASED CATALYSTS.....	171
7.1 Effect of acid washing.....	175
7.2 Effect of polymer source	178
7.3 Effect of extractant and co-catalyst.....	179
7.4 Reaction products.....	180
7.5 Comparison with literature	187
7.6 Conclusions	188
7.7 References	190
CHAPTER 8 - GENERAL CONCLUSIONS.....	193
8.1 Conclusions	195
8.2 Future Work.....	196

List of Figures

Chapter 2

- Figure 2.1.** Evolution of (a) total energy supply and (b) final consumption in the transport sector (only energy use) in EU 28. Source: Eurostat [1]. 28
- Figure 2.2.** Examples of S-containing compounds found in petroleum. Mercaptans: propane-1-thiol **1**, phenylmethanethiol **2**. Sulfides: diethylsulfane **3**, ethyl phenyl sulfide **4**. Disulfides: (methylidisulfanyl)methane **5**, methyl phenyl disulfide **6**. Thiophenes: thiophene (Th) **7**, 4,6-dimethyldibenzothiophene (4,6-DMDBT) **8**, dibenzothiophene (DBT) **9**, and benzothiophene (BT) **10**. 29
- Figure 2.3.** Examples of N-containing compounds found in petroleum. Pyridines group: pyridine **1**, quinoline (QN) **2**, azapyrene **3**. Pyrroles group: pyrrole **4**, indole **5**, and carbazole **6**. 29
- Figure 2.4.** Simplified flowchart of a petroleum refinery and its main boiling fractions. Adapted from Romanow-Garcia and Hoffman (2003) [9]. 30
- Figure 2.5.** Evolution of the limit of sulfur content in (a) gasoline and (b) diesel, according to the implementation date. * Refers to metropolitan areas. Source: Miller and Façanha (2014) [22], TransportPolicy.net [23,24,25,26], United States Environmental Protection Agency [20], Australian Government [27], Euro V [28], Miller, and Jin (2019) [29]. 32
- Figure 2.6.** Papers published on HDS, HDN, ODS, and ODN over the years (source: SCOPUS with the keywords “hydrodesulfurization”, “hydrodenitrogenation”, “oxidative desulfurization”, and “oxidative denitrogenation”, respectively, dated August 2021). 33
- Figure 2.7.** Order of reactivity of different S-containing compounds. Adapted from Rajendran et al. (2020) [34]. 34
- Figure 2.8.** Oxidation of thiophene (Th) **1** to a sulfoxide (thiophene 1-oxide **2**) and a sulfone (thiophene 1,1-dioxide **3**). 35
- Figure 2.9.** Percentage of published papers regarding the application of (i) hybrid materials containing carbonaceous structures, (ii) carbon-based materials as catalysts on their own, and (iii) systems applying amphiphilic catalysts containing carbon in their structure. 39
- Figure 2.10.** Oxidation mechanism of sulfur compounds (exemplified with DBT) on carbon catalysts (SS = Surface Site, draws prepared with Freeware ChemsSketch; White, Red, Yellow, and Gray atoms as hydrogen, oxygen, sulfur, and carbon, respectively). 45
- Figure 2.11.** Presumed role of amphiphilic materials in biphasic oxidation under an emulsified system. Adapted from Oliveira et al. (2014) [145], Oliveira et al. (2015) [144], and Teixeira et al. (2013) [146]. 48
- Figure 2.12.** The number of papers related to the synthesis of carbon nanotubes. Search carried out at Web of Science on December 23rd, 2024, using the keywords: “carbon nanotub*”, “chemical vapor deposition” OR “chemical vapor deposition”, “waste”, “plastic solid waste”, “plastic waste”. 65

Chapter 3

- Figure 3.1.** Vertical oven used for growth of carbon nanotubes. 89

Chapter 4

Figure 4.1. (a) XRD and (b) FTIR of the metal catalysts used in CVD.....	105
Figure 4.2. XRD reference cards of α - and γ -alumina, hematite, magnetite, nickel ferrite and nickel oxide from the COD database.	106
Figure 4.3. Nitrogen adsorption-desorption isotherms of (a) Al_2O_3 , (b) $\text{Fe}/\text{Al}_2\text{O}_3$ and (c) $\text{NiFe}/\text{Al}_2\text{O}_3$	107
Figure 4.4. Pore size distribution for Al_2O_3 , $\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{NiFe}/\text{Al}_2\text{O}_3$	107
Figure 4.5. (a) Yield of the materials after CVD and (b) mass loss after acid washing.	109
Figure 4.6. TEM images of $\text{Fe}/\text{Al}_2\text{O}_3$ -derived CNTs. (a-c) LDPE-600-P@Fe, (d-f) LDPE-800-P@Fe, (g-i) HDPE-P@Fe, (j-l) PP-P@Fe, and (m-o) POL-P@Fe.	110
Figure 4.7. TEM images of (a-c) POL-P@NiFe, (d-f) POL-OX@NiFe, (g-i) PS-OX@NiFe, and (j-l) MIX-OX@NiFe.....	111
Figure 4.8. TEM images of (a-c) $\text{POL}_{\text{PSW}}\text{-P@NiFe}$ and (d-f) $\text{POL}_{\text{PSW}}\text{-OX@NiFe}$	112
Figure 4.9. Raman spectra of the materials. (a) Fe-derived samples, (b) NiFe-derived samples and (c) samples synthesized using real PSW.	115
Figure 4.10. Correlation between PS addition in the feedstock and D/G ratio of oxidized NiFe-derived samples.....	115
Figure 4.11. (a, c, e) TGA analysis and (b, d, f) DTG of (a, b) Fe-derived CNTs, (c, d) NiFe-derived CNTs, and (e,f) CNTs using real PSW as feedstock.	116
Figure 4.12. N_2 adsorption-desorption isotherms at -196°C of (a) LDPE-600-P@Fe, (b) LDPE-800-P@Fe, (c) HDPE-P@Fe, (d) PP-P@Fe, (e) POL-P@Fe, (f) POL@NiFe, (g) POL-P@NiFe, (h) POL-OX@NiFe. (i) PS-OX@NiFe, (j) MIX-OX@NiFe, (k) POL-400@NiFe, (l) $\text{POL}_{\text{PSW}}\text{@NiFe}$, (m) $\text{POL}_{\text{PSW}}\text{-P@NiFe}$, and (n) $\text{POL}_{\text{PSW}}\text{-OX@NiFe}$	118
Figure 4.13. Correlation between CNT diameter and total volume of pores for NiFe-derived CNTs.	119
Figure 4.14. FTIR analysis of the samples. (a) Fe-derived CNTs, (b) NiFe-derived CNTs, and (c) CNTs obtained using real PSW.....	120

Chapter 5

Figure 5.1. Normalized concentration of (a) QN and (b) H_2O_2 during CWPO runs in the presence of the catalysts. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ\text{C}$, and $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$	131
Figure 5.2. Formation and degradation of intermediate compounds detected by HPLC during the non-catalytic wet peroxide oxidation of QN. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$, $T = 80^\circ\text{C}$	132
Figure 5.3. Removal of TOC after 24 h of reaction in the presence of the catalysts. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ\text{C}$, and $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$	133
Figure 5.4. (a) pH after CWPO in the presence of the catalysts (Red line indicates initial pH); and (b) abatement of ARM after CWPO in the presence of the catalysts. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ\text{C}$	134
Figure 5.5. QN removed from oil phase (a) by pure extraction effect (without catalysts), considering varying initial concentrations of QN; and (b) by pure adsorption (solid filling) and combined adsorption-extraction (patterned filling) in the presence of CNTs and CVD substrate after 8 h of contact time	

(Conditions: $[QN]_0 = 250\text{--}1000 \text{ mg L}^{-1}$, O/W volume ratio = 80:20 (where applicable), $pH_0 = 3.0$, $T = 80 \text{ }^\circ\text{C}$; and for adsorption runs: $[QN]_0 = 1000 \text{ mg L}^{-1}$, $C_{adsorbent} = 2.5 \text{ g L}^{-1}$).	135
Figure 5.6. (a) Normalized number of mols of QN in the oily phase, (b) normalized concentration of H_2O_2 during ODN, (c) normalized number of mols of QN in the water phase, and (d) normalized conversion of total amount of QN during ODN in the presence of the catalysts tested in this work. Conditions: O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$. Dashed lines are from the kinetic model described in section 5.2.3.	136
Figure 5.7. TOC conversion in the presence of the materials tested in this work. (O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]_0 = 1000 \text{ mg L}^{-1}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$, 24 h of reaction).	138
Figure 5.8. Parity plot.	140
Figure 5.9. Correlation between O/C ratio and $k'_{H_2O_2}$.	140
Figure 5.10. Schematics of the proposed route for ODN.	141
Figure 5.11. Removal of QN or PYR from the oily phase during ODN in the presence of CNT-C and POL-P@Fe after 60 min of reaction considering the components individually ($ODN_{individual}$) and in a mixture (ODN_{mixed}). (O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$ or $[PYR]^{oil}_0 = 610 \text{ mg L}^{-1}$ (in runs with mixed fuel: $[QN]^{oil}_0 = 500 \text{ mg L}^{-1}$ and $[PYR]^{oil}_0 = 305 \text{ mg L}^{-1}$), $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$, 1 h).	143
Figure 5.12. Removal of QN from the fuel phase in the presence of POL-P@Fe after 60 min of reaction for fresh catalyst and reutilization runs. Conditions: O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$ (equivalent to $[N]^{oil}_0 = 108 \text{ mg L}^{-1}$), $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$.	143

Chapter 6

Figure 6.1. Screening of materials. (a) Removal of QN from the fuel phase, (b) decomposition of hydrogen peroxide in the aqueous phase, (c) QN in the water phase, and (d) overall QN abatement. (Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 123 \text{ g L}^{-1}$ (H_2O_2/N molar ratio = 230), O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0). Dashed lines represent the kinetic model described in section 5.2.3.	151
Figure 6.2. Adsorption capacity. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $T = 80 \text{ }^\circ\text{C}$, $C_{adsorbent} = 2.5 \text{ g L}^{-1}$. Solid lines are only intended to guide the eyes.	152
Figure 6.3. TOC removal and efficiency of hydrogen peroxide consumption. (Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 123 \text{ g L}^{-1}$ (H_2O_2/N molar ratio = 230), O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0).	153
Figure 6.4. Parity plot.	154
Figure 6.5. Correlation between $k'_{QN,ox}$ and (a) oxygen content and (b) basic groups.	155
Figure 6.6. ODN of QN with varying hydrogen peroxide concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 1.2\text{--}123 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. Solid lines are only intended to guide the eyes.	157
Figure 6.7. (a) TOC removal and efficiency of hydrogen peroxide consumption and (b) correlation between TOC removal and hydrogen peroxide concentration. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 1.2\text{--}123 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0.	158

- Figure 6.8.** ODN of QN with varying catalyst concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80^\circ\text{C}$, $C_{cat} = 0.25\text{--}5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. Solid lines are only intended to guide the eyes. 159
- Figure 6.9.** TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80^\circ\text{C}$, $C_{cat} = 0.25\text{--}5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. 159
- Figure 6.10.** ODN of QN with varying temperatures. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 50\text{--}80^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. Dashed lines represent the kinetic modeling described in section 5.2.3. 160
- Figure 6.11.** TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 50\text{--}80^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. 161
- Figure 6.12.** Parity plot. 162
- Figure 6.13.** Arrhenius plot. The coefficient for $k'_{\text{QN,ox}}$ at 80°C was not used for the linear regression. 162
- Figure 6.14.** ODN of QN with varying pH. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 1.0–11.0. Solid lines are only intended to guide the eye. 163
- Figure 6.15.** TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 1.0–11.0. 164
- Figure 6.16.** ODN of QN with varying initial QN concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[\text{QN}]_0 = 100\text{--}5000 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0, $t = 60\text{--}120 \text{ min}$ of reaction. 165

Chapter 7

- Figure 7.1.** (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, water as extractant phase, O/W volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$ ($\text{H}_2\text{O}_2/S$ molar ratio of 15), $T = 70^\circ\text{C}$, 0.1 vol.% of 1M H_2SO_4 (equivalent to a pH_0 of 3.0). 175
- Figure 7.2.** Extraction of DBT in the presence of the distinct extractant and co-catalysts. Conditions: $[\text{DBT}] = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $T = 70^\circ\text{C}$, O/E volume ratio 80:20, addition of 0.1 vol.% of sulfuric or formic acid (1 M). 175
- Figure 7.3.** Correlation between (a) conversion of hydrogen peroxide at 120 and 240 min *versus* amount of acidic groups, removal of DBT *versus* (b) amount of basic groups and (c) oxygen content for POL-derived CNTs at 60, 120, 240 and 480 min. 176
- Figure 7.4.** (a) Adsorption of DBT (Conditions: $[\text{DBT}] = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $T = 70^\circ\text{C}$, $C_{adsorbent} = 2.5 \text{ g L}^{-1}$, 2 h of contact time) and (b) correlation between oxygen content and DBT adsorption for polyolefin-derived CNTs. 176

Figure 7.5. (a) DBT and (b) DBT 5-oxide and DBT 5,5-dioxide extracted from the catalyst phase at the end of the reaction.....	177
Figure 7.6. Efficiency of H_2O_2 use.....	177
Figure 7.7. (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, water as extractant phase, O/W volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{water} .% of 1M H_2SO_4 (equivalent to a pH_0 of 3.0).	179
Figure 7.8. Correlations between the (a) conversion of hydrogen peroxide at 120 and 480 min and the total volume of pores and DBT removal at 60 and 120 min (b) versus contact angle and (c) D/G ratio.	179
Figure 7.9. (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction using POL-OX@NiFe as a catalyst while varying the extractant and co-catalysts. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, O/E volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{extractant} .% of 1M H_2SO_4 or FA.	179
Figure 7.10. (a) DBT in the extractant phase and formation of (b) DBT 5-oxide and (c) DBT 5,5-dioxide using POL-OX@NiFe as a catalyst while varying the extractant and co-catalysts. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), O/E volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{extractant} .% of 1 M H_2SO_4 or FA.	181
Figure 7.11. Distribution of quantified S-compounds.....	181
Figure 7.12. (a) DBT in the oil, (b) DBT, (c) DBT 5-oxide and (d) DBT 5,5-dioxide in the extractant phase (ACN) using POL-OX@NiFe as a catalyst in the presence of a radical scavenger. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), O/E volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{extractant} .% of 1M FA or H_2SO_4 , $H_2O_2/EtOH$ volume ratio of 2.	182
Figure 7.13. DBT in the oil phase and DBT and its oxidized intermediates in the extractant phase using POL-OX@NiFe as a catalyst (a) in the absence of H_2O_2 and (b) with delayed addition of FA. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (where applicable), O/E volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{extractant} .% of 1M FA.	183
Figure 7.14. TOC of the aqueous phase of the reaction carried out with POL-OX@NiFe. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$, O/W volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70 \text{ }^\circ\text{C}$, 0.1 vol _{extractant} .% of 1M H_2SO_4 ...	184
Figure 7.15. (a) Gas chromatogram of oil phase by the end of reaction with different CNTs and extractants and (b) close-up for POL-OX@NiFe using water as extractant.	184
Figure 7.16. Gas chromatogram for the water phase using POL-OX@NiFe as catalyst.	185
Figure 7.17. (a) Mass spectra of the compound retained at 31 min and (b) mass spectra of biphenyl obtained from the NIST database (correspondence: 95%).....	185
Figure 7.18. Possible reaction pathway in biphasic systems: (a) oil-ACN and (b) oil-water.	186
Figure 7.19. MS spectra and fragmentation pattern of compound retained at (a) 47.2 min (m/z of the molecular ion of 253), (b) 36.5 min (m/z molecular ion of 281), (c) compound retained at 55.2 min (m/z molecular ion of 197), (d) compound retained at 64.9 min (m/z molecular ion of 135).	187

List of Tables

Chapter 2

Table 2.1 Sulfur and nitrogen content for crude oil in different regions.	29
Table 2.2. Process conditions for different fractions of petroleum for HDS.	34
Table 2.3. Examples of carbon-based materials and respective carbon precursors, synthesis routes and characteristics studied for ODS and ODN purposes.	38
Table 2.4. ODS using mainly H ₂ O ₂ with carbon hybrid materials in a two-step system.....	50
Table 2.5. ODS using H ₂ O ₂ as oxidant with hybrid materials based in carbon nanotubes (CNTs), graphene oxide (GO), and reduced GO (rGO) in an L-L biphasic media.	52
Table 2.6. ODS using H ₂ O ₂ as oxidant with hybrid materials based on activated carbon (AC) in L-L biphasic media.	52
Table 2.7. ODS using mainly H ₂ O ₂ with hybrid materials based on other carbon forms in L-L biphasic media.	54
Table 2.8. ODS using mainly H ₂ O ₂ with hybrid materials based on graphitic carbon nitride (g-C ₃ N ₄) in L-L biphasic media.	55
Table 2.9. Other ODS systems with carbon-based hybrid materials.	56
Table 2.10. ODS with carbon hybrid materials in photocatalytic systems.	58
Table 2.11. ODS with carbon-based materials as catalysts on their own.	59
Table 2.12. ODS using mainly H ₂ O ₂ with hybrid materials based on graphitic carbon nitride (g-C ₃ N ₄) in L-L biphasic media.	60
Table 2.13. ODS using mainly H ₂ O ₂ with hybrid materials based on graphitic carbon nitride (g-C ₃ N ₄) in L-L biphasic media.	64
Table 2.14 Carbon content of PSW.....	67
Table 2.15 Carbon nanotubes derived from polymeric sources.	68

Chapter 3

Table 3.1 Carbon source, catalyst, temperature, and nomenclature adopted for each CNT sample. ...	90
--	----

Chapter 4

Table 4.1. Yield, textural properties and surface chemistry of CVD catalysts and support.	107
Table 4.2. Elemental composition of the CNT samples.	113
Table 4.3. Textural properties of the CNT samples.	119
Table 4.4. Water contact angles and acidic/basic groups for the materials used in this work.	121

Chapter 5

Table 5.1. Reported biphasic selective oxidation reactions using water as extractant, H ₂ O ₂ as oxidant source, and carbon nanotubes as catalysts.....	136
Table 5.2. Kinetic and statistical coefficients obtained from the fit of the kinetic model during ODN.	139

Chapter 6

Table 6.1. Kinetic and statistical coefficients obtained for each material during ODN.	155
Table 6.2. Kinetic and statistical coefficients obtained for each temperature during ODN.	161
Table 6.3. Activation energy and pre-exponential factor.	163
Table 6.4. Reports in the literature for ODN using carbon-containing materials as catalysts.	166

Chapter 7

Table 7.1. ODS using carbon materials as catalysts, H ₂ O ₂ as oxidant and water or ACN as extractant.	188
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Acronyms and Abbreviations

1Me-IND	1-methyl-indole
2Me-IND	2-methyl-indole
3Me-IND	3-methyl-indole
4,6-DMDBT	4,6-dimethyldibenzothiophene
4-MDBT	4-methyldibenzothiophene
AC	Activated carbon
ACN	Acetonitrile
ADS	Adsorptive desulfurization
AOP	Advanced oxidation process
ARM	Aromatic compounds
BDS	Biodesulfurization
BET	Brunauer-Emmett-Teller
BT	Benzothiophene
CA	Carbon aerogel
Cat	Catalyst
CBZ	Carbazole
CF	Carbon fibers
CHP	Cumene hydroperoxide
CNT	Carbon nanotubes
CNT-C	Commercial CNT
COD	Crystallography open database
CQD	Carbon quantum dots
CS	Carbon spheres
CVD	Chemical vapor deposition
CWPO	Catalytic wet peroxide oxidation
D/G	Ratio between the areas of D and G peaks in Raman
D-band	Band in Raman related to disordered materials
DBT	Dibenzothiophene
DBT 5,5-dioxide	Dibenzothiophene sulfone
DBT 5-oxide	Dibenzothiophene sulfoxide
DES	Deep eutectic solvents
DMF	Dimethylformamide
DTG	First-order derivative of the thermogravimetric analysis
Ea	Activation energy
ECODS	Extractive-catalytic oxidative desulfurization
EDS	Extractive desulfurization
EtOH	Ethanol
EU	European Union
FA	Formic acid
FT-IR	Fourier transform infrared
G-band	Band in Raman related to graphitic materials
g-C ₃ N ₄	Carbon nitride
GC-FID	Gas chromatography coupled with a flame ionization detector
GC-MS	Gas chromatography coupled with a mass detector

GNF	Graphitized carbon nanofiber
GO	Graphene oxide
H_2O_2/N	Hydrogen peroxide-to-nitrogen molar ratio
H_2O_2/S	Oxidant-to-sulfur molar ratio
HDN	Hydrodenitrogenation
HDPE	High-density polyethylene
HDS	Hydrodesulfurization
HPLC	High-performance liquid chromatography
HPW	Phosphotungstic acid
IL	Ionic liquids
IND	Indole
iQUI	Isoquinoline
LCO	Light cycle oil
LDPE	Low-density polyethylene
logP	Logarithm of the coefficient of partition
MC	Mesoporous carbon
MeOH	Methanol
N.C.	Non-catalytic
NOLC	N-doped onion-like carbon
NO _x	Nitrogen oxides
<i>O/E</i>	Oil-to-extractant volume ratio
<i>O/W</i>	Oil-to-water volume ratio
ODN	Oxidative denitrogenation
ODS	Oxidative desulfurization
PE	Polyethylene
PhCH ₂ CN	Benzyl cyanide
PhCN	Benzonitrile
PIC	Pickering interfacial catalysis
PM	Particulate matter
PM ₁₀	Particulate matter with aerodynamic diameter inferior to 10 μ m
POL	Polyolefins
POM	Polyoxometalate
POW	Partition coefficient between oil and water
PP	Polypropylene
PRL	Pyrrole
PS	Polystyrene
PSW	Plastic solid waste
PYR	Pyridine
QN	Quinoline
rGO	Reduced graphene oxide
SSE _{model}	Residual error of the models
TBHP	tert-butyl hydroperoxide
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
Th	Thiophene
TiO ₂	Titanium dioxide
TOC	Total organic carbon

UAODS	Ultrasound-assisted oxidative desulfurization
US	United States of America
UV-Vis	Ultraviolet-visible spectroscopy
WEEE	Waste electronic and electric equipment
XRD	X-Ray Diffraction

CHAPTER 1 - INTRODUCTION

1.1 Motivation and Relevance

Generation of plastic solid waste (PSW) has emerged as one of the most pressing environmental issues of the 21st century. With global production exceeding 400 million tons annually [1], the management of PSW remains a critical challenge. In 2024, PSW generation is projected to reach 220 million tonnes, with nearly 70 million tons likely to end up in nature [2] due to inadequate waste management systems [3]. Polyolefins, which account for most of the PSW [1], are particularly challenging due to their widespread use in single-use items, such as packaging or disposable medical devices [4]. A report published in 2020 [2] simulated the amount of microplastics reaching terrestrial and aquatic environments by 2040. It concluded that both traditional and innovative solutions would be required to limit this amount of microplastics. Transforming plastic solid waste into high-value materials such as carbon nanotubes (CNTs) offers a sustainable and innovative alternative, reducing the amount of plastics reaching landfills. It also reduces the dependency on fossil-derived precursors for synthesizing advanced materials such as CNTs, reducing the carbon dioxide emissions from CNTs produced, for instance, from methane [5]. By integrating waste valorization into circular economy, this Ph.D. thesis aims to redefine the role of PSW from a pollutant to a valuable resource.

In parallel with the PSW crisis, the transportation and energy sectors face increasing pressure to produce ultra-clean fuels. Sulfur- and nitrogen-containing compounds in petroleum-derived fuels are major contributors to air pollution, leading to hazardous emissions such as sulfur and nitrogen oxides. These pollutants are associated with severe health impacts, including respiratory and cardiovascular diseases [6-9], as well as environmental problems [10, 11] such as acid rain and soil acidification. Despite advancements in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), these conventional processes struggle to meet strict international regulations on sulfur and nitrogen content without compromising fuel quality [12]. Furthermore, these technologies are energy-intensive, requiring high temperatures ($T = 260 - 425\text{ }^{\circ}\text{C}$) and pressures ($P = 5 - 170\text{ bar}$), and are inefficient at removing refractory S- and N-containing compounds [12]. Emerging oxidative processes, such as oxidative desulfurization (ODS) and oxidative denitrogenation (ODN), have shown promise as effective alternatives [13, 14] or complementary processes to HDN/HDS. By operating under milder conditions ($T < 150\text{ }^{\circ}\text{C}$ and $P = 1\text{-}2\text{ bar}$) and targeting refractory sulfur and nitrogen compounds, these processes align with modern sustainability goals. Using CNTs as catalysts in these processes offers significant advantages, including increased sustainability, particularly when waste-derived CNTs are used.

1.2 Thesis objectives

The main goal of this thesis is to propose a coupled solution for addressing two critical challenges: the accumulation of PSW and the production of low-sulfur-and-nitrogen fuels. The specific objectives include:

1. Demonstrate the potential for upcycling PSW into valuable materials by:
 - i. Growing CNTs by chemical vapor deposition (CVD), using polymeric materials as precursors and focusing on polyolefins and polystyrene due to their extensive application in single-use plastics.
 - ii. Comparing two distinct catalysts (iron versus nickel-iron) for the CVD reaction.
 - iii. Characterizing the physicochemical properties of the CNT samples, including morphology, elemental composition, textural properties and surface chemistry.
 - iv. Comparing the characteristics of CNTs obtained from simulated and real PSW.
2. Evaluate the synthesized CNTs in the oxidative removal of sulfur and nitrogen from fuels by:
 - i. Assessing the catalytic performance of CNTs for the selective oxidation of sulfur and nitrogen compounds, specifically dibenzothiophene and quinoline, in biphasic systems using mainly water as the extractant phase.
 - ii. Investigating the correlation between CNT properties and catalytic activity.
 - iii. Obtaining insights into the reaction by modeling the kinetics of oxidative denitrogenation (ODN).
 - iv. Proposing a reaction mechanism for the selective oxidation of dibenzothiophene.

1.3 Thesis organization

This thesis is structured into eight chapters as follows:

Chapter 1 contains the Introduction and provides the motivation, relevance, and objectives of the research, along with an overview of the thesis structure. **Chapter 2** includes the State of the Art, reviewing the current knowledge on applying carbon-derived materials in oxidative desulfurization and denitrogenation processes. It also briefly highlights the synthesis of carbon nanotubes, focusing on CNTs obtained from polymeric sources, whether virgin or waste. **Chapter 3** comprises the methodologies, materials and equipment used to develop the present work, detailing the experimental procedures for CNT synthesis, materials characterization, catalytic testing in oxidative desulfurization and denitrogenation systems and analytical techniques used in catalytic applications. The presentation and discussion of the results gathered in this work start in **Chapter 4**, with the synthesis and characterization of CNTs and CVD catalysts, emphasizing the effect of CVD catalyst composition, carbon sources and reaction conditions on the CNTs properties. The application of the CNTs in oxidative

denitrogenation is reported in Chapters 5 and 6. **Chapter 5** mostly highlights the application of CNTs grown over iron-based catalysts and proposes an expected mechanism for the oxidative denitrogenation of quinoline (QN) and the role played by the CNTs. A mathematical model that takes into account the mass transference was proposed and fitted to the data in Chapter 5. **Chapter 6** investigates the use of CNTs grown over nickel-iron catalysts for ODN of QN and explores the effect of operating conditions such as catalyst concentration, hydrogen peroxide dosage, and temperature on quinoline removal, total organic carbon abatement and use of hydrogen peroxide, comparing results with literature benchmarks. **Chapter 7** is dedicated to oxidative desulfurization with CNTs derived from nickel-iron catalysts, evaluating the removal of dibenzothiophene using CNTs synthesized from different plastic sources, analyzing the influence of surface properties and the use of water *versus* acetonitrile as an extractant. **Chapter 8** summarizes the key findings of the research, highlighting its contributions to science and sustainability, and outlines potential directions for future work.

1.4 References

- [1] PlasticsEurope, Plastics - the fast Facts 2023, 2023. Available at: <https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/>. (Accessed December 6th 2024).
- [2] W.W.Y. Lau, Y. Shiran, R.M. Bailey, E. Cook, M.R. Stuchtey, J. Koskella, C.A. Velis, L. Godfrey, J. Boucher, M.B. Murphy, R.C. Thompson, E. Jankowska, A. Castillo Castillo, T.D. Pilditch, B. Dixon, L. Koerselman, E. Kosior, E. Favoino, J. Gutberlet, S. Baulch, M.E. Atreya, D. Fischer, K.K. He, M.M. Petit, U.R. Sumaila, E. Neil, M.V. Bernhofen, K. Lawrence, J.E. Palardy, Evaluating scenarios toward zero plastic pollution, *Science* (2020) 1455-1461. <https://doi.org/10.1126/science.aba9475>.
- [3] S. Perreard, J. Boucher, M. Gallato, M.I. Gomis, P. Mazzatorta, A. Gaboury, N. Voirin, Plastic Overshoot Day – Report 2024, EA – Earth Action, Lausanne, Switzerland.
- [4] Y. Miao, Y. Zhao, G.I.N. Waterhouse, R. Shi, L.Z. Wu, T. Zhang, Photothermal recycling of waste polyolefin plastics into liquid fuels with high selectivity under solvent-free conditions, *Nature Communications* 14(1) (2023) 4242. <https://doi.org/10.1038/s41467-023-40005-6>.
- [5] J. Heo, Researchers advance carbon neutrality by producing carbon nanotubes from waste plastic, 2024. Available at <https://phys.org/news/2024-08-advance-carbon-neutrality-nanotubes-plastic.html>. (Accessed December 6th 2024).
- [6] M. Kampa, E. Castanas, Human health effects of air pollution, *Environmental Pollution* 151(2) (2008) 362-7. <https://doi.org/10.1016/j.envpol.2007.06.012>.
- [7] J. Sunyer, The association of daily sulfur dioxide air pollution levels with hospital admissions for cardiovascular diseases in Europe (The Aphea-II study), *European Heart Journal* 24(8) (2003) 752-760. [https://doi.org/10.1016/s0195-668x\(02\)00808-4](https://doi.org/10.1016/s0195-668x(02)00808-4).
- [8] E.M. Khalaf, M.J. Mohammadi, S. Sulistiyani, A.A. Ramirez-Coronel, F. Kiani, A.T. Jalil, A.F. Almulla, P. Asban, M. Farhadi, M. Derikondi, Effects of sulfur dioxide inhalation on human health: a review, *Reviews on Environmental Health* 39(2) (2024) 331-337. <https://doi.org/10.1515/reveh-2022-0237>.
- [9] K.R. Hakeem, M. Sabir, M. Ozturk, M.S. Akhtar, F.H. Ibrahim, Nitrate and Nitrogen Oxides: Sources, Health Effects and Their Remediation, *Reviews of Environmental Contamination and Toxicology* 242 (2017) 183-217. https://doi.org/10.1007/398_2016_11.
- [10] T. Boningari, P.G. Smirniotis, Impact of nitrogen oxides on the environment and human health: Mn-based materials for the NO_x abatement, *Current Opinion in Chemical Engineering* 13 (2016) 133-141. <https://doi.org/10.1016/j.coche.2016.09.004>.
- [11] Y. Qian, P. Behrens, A. Tukker, J.F.D. Rodrigues, P. Li, L. Scherer, Environmental responsibility for sulfur dioxide emissions and associated biodiversity loss across Chinese provinces, *Environmental Pollution* 245 (2019) 898-908. <https://doi.org/10.1016/j.envpol.2018.11.043>.
- [12] D.D. Pham, T.M. Nguyen, T.H. Ho, Q.V. Le, D.L.T. Nguyen, Advancing hydrodesulfurization in heavy Oil: Recent developments, challenges, and future prospects, *Fuel* 372 (2024) 132082. <https://doi.org/10.1016/j.fuel.2024.132082>.
- [13] G.H.C. Prado, Y. Rao, A. de Klerk, Nitrogen Removal from Oil: A Review, *Energy Fuels* 31(1) (2017) 14-36. <https://doi.org/10.1021/acs.energyfuels.6b02779>.
- [14] A. Rajendran, T.-y. Cui, H.-x. Fan, Z.-f. Yang, J. Feng, W.-y. Li, A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment, *Journal of Materials Chemistry A* 8(5) (2020) 2246-2285. <https://doi.org/10.1039/c9ta12555h>.

CHAPTER 2 - STATE OF THE ART

Chapter 2

State of the art

This chapter provides a comprehensive review of the current knowledge regarding the application of carbon-derived materials in oxidative desulfurization (ODS) and denitrogenation (ODN) processes. It explores the role of these materials as catalysts, adsorbents or support, emphasizing (when possible) their role in removing sulfur- and nitrogen-containing compounds from fuels. Key factors such as surface chemistry, porosity, and functionalization strategies are discussed concerning their impact on catalytic activity and selectivity. It also provides a brief review of the production of carbon nanotubes, focusing mainly on their synthesis using PSW as precursors.

This chapter is based on the peer-reviewed article:

- Fernanda F. Roman, José L. Diaz de Tuesta, Adrián M. T. Silva, Joaquim L. Faria, Helder T. Gomes. Carbon-Based Materials for Oxidative Desulfurization and Denitrogenation of Fuels: A Review. *Catalysts* 11(10) (2021) 1239. <https://doi.org/10.3390/catal11101239>

2.1 Introduction

With increasing urbanization, humankind has experienced an escalating dependence on energy. As shown in Figure 2.1, for EU-28, the total energy supply amounted to 1.58M toe (tonnes of oil equivalent) in 2019, and oil and petroleum products represented the highest contribution (32.8%), followed by natural gas (25%), renewables and biofuels (15.8%), nuclear heat (13.2%), and solid fossil fuels (11%). In particular, the contribution of oil and petroleum products in energy supplies has kept with no relevant changes (31.4–33.0%) in the last decade (Figure 2.1a), with values ranging from 510k (2014) to 569k (2010) toe. Oil and petroleum products are extensively used in our society for transportation, electricity, and construction materials. Transportation may be the sector that most relies on petroleum-based fuels, from ground transportation to planes and ships. In EU-28, the final consumption of energy in the transport sector amounted to 330.8k toe in 2019, with 209.8k toe of gas oil and diesel, 79.1k toe of motor gasoline, 17.4k toe of renewables and biodiesel, and 3.7k toe of natural gas (Figure 2.1b). In the last decade, gasoline consumption has decreased from 28.5% to 23.9% of the total energy consumed in the transportation sector, whereas gas, oil and diesel have increased from 60.7% to 63.4% (Figure 2.1b).

Some heteroatoms are inherently found in petroleum and petroleum-based fuels. The atom found in the highest concentration after carbon and hydrogen is sulfur, followed by nitrogen. Their presence is associated with a series of environmental and health-related issues due to the formation of toxic gaseous products (NO_x and SO_2) during combustion. Those issues have driven legislative bodies to regulate the content and related emissions of S- and N-based compounds, increasing restrictions. Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the technologies applied at the industrial level. However, HDS and HDN fail to achieve the required-by-law content of sulfur without compromising the relevant combustion parameters of the fuels (such as diesel and gasoline). Alternative technologies have been studied in the last few years, and among them, oxidative treatments can be highlighted, namely oxidative desulfurization (ODS) and denitrogenation (ODN). As with any catalytic process, the development and selection of catalysts are critical in ODS and ODN, and carbon-based materials have revealed exciting results in the oxidative removal of S- and N-based compounds. This review aims to discuss the state-of-the-art application of carbon-based materials for ODS and ODN purposes, emphasizing the role displayed by those materials, either in hybrid forms or as carbocatalysts.

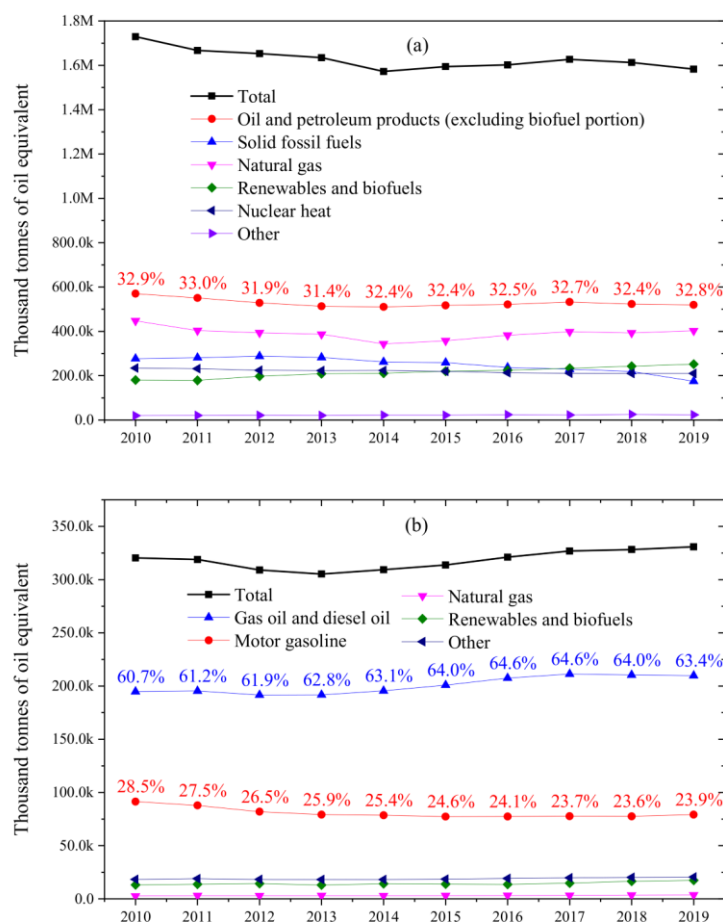


Figure 2.1. Evolution of (a) total energy supply and (b) final consumption in the transport sector (only energy use) in EU 28. Source: Eurostat [1].

2.1.1 Sulfur and Nitrogen in Crude Oils: Content and Type of Compounds

Petroleum is composed mostly of hydrocarbons, although impurities such as nitrogen, sulfur, oxygen, and metal compounds (vanadium, nickel, and iron, among others) are found [2]. Sulfur is the component that varies the most between different petroleum samples [2] and is the third most abundant element in crude oils, after carbon and hydrogen [3]. Sulfur content can vary between <0.1 to 8 wt.% [2], leading to the classifications of sweet crude oils (S content <1 wt.%) or sour oils (S content >1 wt.%) [3]. Nitrogen content can vary between <0.1 to 1.8 wt.% [2], and crudes can be classified as high-nitrogen oils (>0.25 wt.%) or nitrogen-poor oils (<0.25 wt.%) [4]. Table 2.1 displays some examples of the content of sulfur and nitrogen in different crude oil samples. There is no correlation between the content of sulfur and nitrogen. The content of those impurities depends mostly on the area of exploration [4,5].

S-containing compounds found in petroleum can be divided into four main groups: mercaptans ($R-SH$), sulfides (R_2S), disulfides ($RSSR$), and thiophenes. Some examples of these compounds can be seen in Figure 2.2. Other compounds may include H_2S and elemental sulfur, although in trace quantities [6]. N-containing compounds are classified into two major groups: basic (derived from pyridine) and non-basic or neutral (derived from pyrrole) [4]. Figure 2.3 displays some N-containing compounds commonly

found in petroleum. There is also evidence of the presence of primary amines ($R-NH_2$), porphyrin structures, or compounds that contain nitrogen and oxygen simultaneously [4].

Table 2.1 Sulfur and nitrogen content for crude oil in different regions.

Local of Exploration	Type of Oil	S Content (wt.%)	N Content (wt.%)
USA, AR, Atlanta	Petroleum (Light oil)	0.37	0.003
USA, CA, Temblor	Petroleum (Medium oil)	0.44	0.27
USA, CA, Oxnard	Petroleum (Heavy oil)	7.47	0.88
USA, MS, Eucutta	Petroleum (Heavy oil)	3.89	0.13
Iran, Agha-Jeri	Petroleum (Light oil)	1.36	0.14
Greece, Keri	Petroleum (Heavy oil)	5.76	0.17
Australia, Pumpherston	Shale oil (Medium oil)	0.56	0.52
France, Petit	Shale oil (Medium oil)	3.40	0.65
South Africa, Salermo	Shale oil (Medium oil)	0.64	0.85
Sweden, Lundstrom	Shale oil (Light oil)	0.71	0.11

Source: adapted from Ball, Whisman, and Wenger (1951) [7].

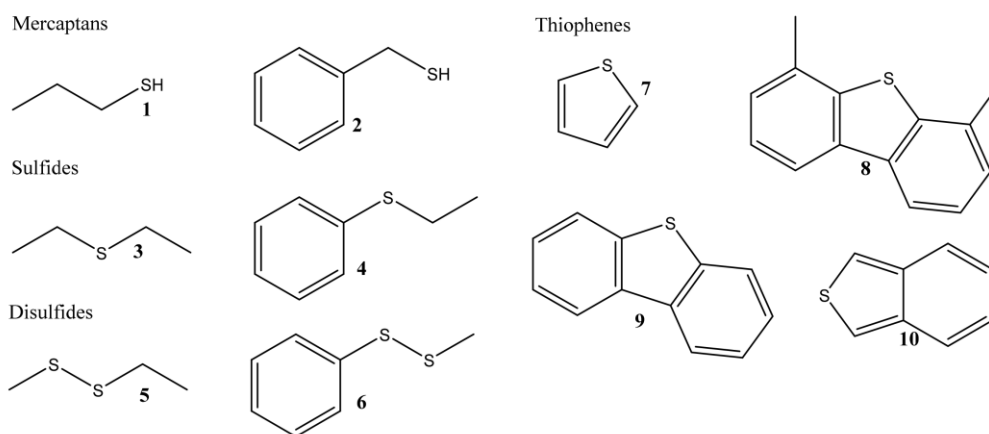


Figure 2.2. Examples of S-containing compounds found in petroleum. Mercaptans: propane-1-thiol 1, phenylmethanethiol 2. Sulfides: diethylsulfane 3, ethyl phenyl sulfide 4. Disulfides: (methyldisulfanyl)methane 5, methyl phenyl disulfide 6. Thiophenes: thiophene (Th) 7, 4,6-dimethyldibenzothiophene (4,6-DMDBT) 8, dibenzothiophene (DBT) 9, and benzothiophene (BT) 10.

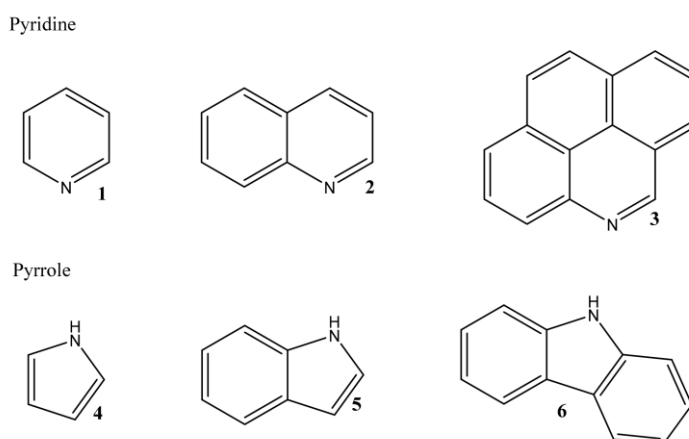


Figure 2.3. Examples of N-containing compounds found in petroleum. Pyridines group: pyridine 1, quinoline (QN) 2, azapyrene 3. Pyrroles group: pyrrole 4, indole 5, and carbazole 6.

Heavier boiling fractions contain higher amounts of sulfur compounds (main boiling fractions are displayed in Figure 2.4). In the gasoline boiling range, mercaptan, sulfide, disulfide, and thiophene groups are found. In contrast, jet fuel and diesel primarily include thiophenes and derivatives [8].

Similarly, the nitrogen content increases for heavier fractions. Most N-compounds occur in the residual boiling fractions [4].

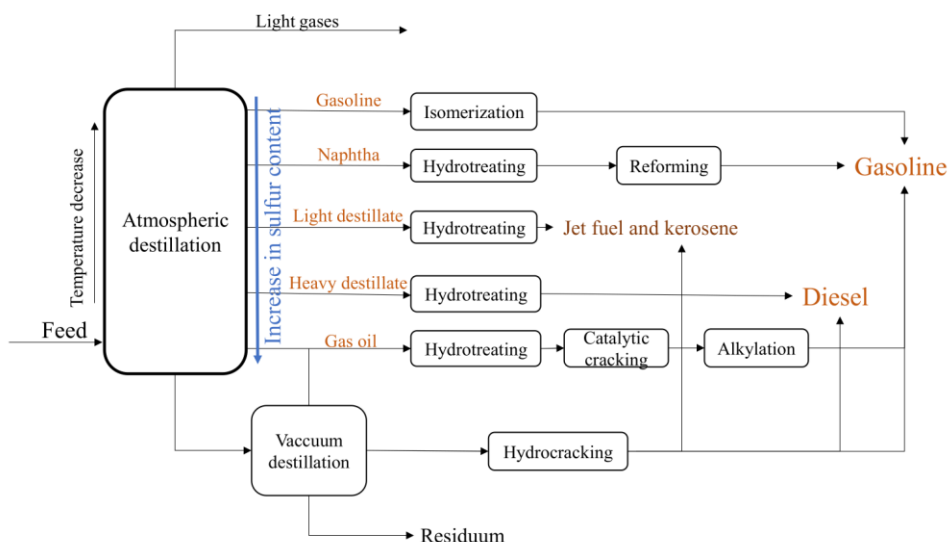


Figure 2.4. Simplified flowchart of a petroleum refinery and its main boiling fractions. Adapted from Romanow-Garcia and Hoffman (2003) [9].

2.1.2 Health, Environmental and Technological Effects of Sulfur- and Nitrogen-Containing Compounds

Upon combustion of petroleum-based fuels, hazardous gases (SO_2 and NO_x) and particulate matter (PM) are released [10]. PM can be generated directly during combustion (primary PM) or from the chemical reaction of exhaust gases, including SO_2 and NO_x (secondary PM). The exact composition of the exhaust gas depends on a series of factors, mainly fuel composition and combustion conditions. However, PM and NO_x emissions can be controlled by augmenting the cetane number and lowering the number of aromatic compounds in diesel fuels [10], besides reducing the content of N-containing compounds. Reducing the content of sulfur diminishes SO_2 and sulfur-based PM [10].

Exposure to SO_2 and NO_x is related to several health issues in humans. NO_x and SO_2 are irritants of the respiratory system and are associated with worsening existing respiratory illnesses, such as asthma, and increased susceptibility to lung infections [11]. Most of the PM emitted in diesel engines (>90%) is smaller than $1\text{ }\mu\text{m}$ in diameter [10]. PM_{10} (aerodynamic diameter $<10\text{ }\mu\text{m}$) is a nose and throat irritant causing lung damage, bronchitis, and risk of cardiac arrest, which is even associated with early death [12]. Studies have shown that long-term exposure to diesel combustion products is associated with a 20–50% increase in the likelihood of developing lung cancer due to genotoxicity [10,13]. Similarly, exposition to diesel exhausts is related to a 4-fold increase in the risk of dying of noncancerous diseases, such as cardiovascular diseases [10]. A study done in 2003 found a positive correlation between exposure to an increased daily concentration of SO_2 in the atmosphere and hospital admissions for cardiovascular diseases and ischemic heart diseases in major European cities [14]. Mortality and

morbidity rates due to SO₂ exposure result in relevant monetary costs, as estimated by Wu et al. (2020) (35.76 and 441.47 million RMB Yuan, respectively, for Beijing, China, in 2016) [15].

NO_x and SO₂ also provoke adverse environmental effects. NO_x and SO₂ from exhaust engines combine with air moisture and contribute to acid rain [10]. Acid rain is linked to the depletion of essential soil nutrients, affecting soil fertility [6]. Soil pH is also altered, destroying some microbial cultures [6]. Soil alterations threaten forest vegetation and crop production. It contributes to dissolving harmful substances (such as heavy metals) leaching into water bodies. It is also associated with lake acidification and water nitrification [16,17], impacting microorganisms' reproduction and growth. Acid rain also affects human-made structures, diminishing the lifespan of buildings, bridges, and statues, among others [7,17]. Furthermore, primary and secondary PM reduce atmospheric visibility between 8% and 25% [10].

Sulfur compounds, mainly H₂S and mercaptans, are related to a strong odor in sour petroleum [6]. Furthermore, lower aliphatic sulfides and mercaptans are highly reactive towards metals and cause corrosion, damaging storage tanks, pipelines, and equipment [6]. However, the main issue with S-containing compounds during refining is the deactivation of metal catalysts in downstream units [6]. In hydrogenation, reforming, isomerization, and alkylation processes, sulfur is adsorbed in the catalyst surface. Sulfur adsorption then hinders the adsorption of any other species. The deactivation degree depends on the extension of the active sites that were obstructed. Depending on the metal used as catalyst, irreversible poisoning can happen, and thus, the regeneration of the catalyst becomes a difficult task [6]. Additionally, sulfur chemisorbs on the catalysts used in the catalytic converter (responsible for reducing CO and NO_x emissions in passengers' vehicles) causing catalyst deactivation and reducing engine efficiency [5,18].

N-containing compounds pose issues in catalyst selection, process development and operation in oil upgrading and refining [4]. The main problems associated with nitrogen are: (i) 5-membered rings containing nitrogen compounds, such as pyrrolic compounds, are prone to free radical addition reactions, forming heavier products or gums that highly compromise storage stability [4]; (ii) the presence of basic nitrogen compounds leads to the deactivation of acid catalysts through acid-base reactions [4]; (iii) the presence of basic nitrogen compounds leads to salt precipitation (due to acid-base reactions with carboxylic acids), resulting in equipment fouling and even corrosion if water is present under high-temperature operation [4]; (iv) metal coordination is indirectly controlled by nitrogen, and nitrogen is therefore indirectly responsible for metal deposition, leading to equipment fouling [4]; (v) nitrogen competes with other compounds for active sites on catalyzed processes, such as the HDS process. Thus, the presence of nitrogen compounds hinders the removal of sulfur compounds [4]. Therefore, it is preferable to remove nitrogen compounds, especially before the refining processes.

2.1.3 Legislation

The maximum sulfur content allowed for transportation fuels (gasoline and diesel) has become stricter in the last years worldwide. Currently, the EU allows only 10 ppm of sulfur in diesel and gasoline [19]. In contrast, the US sulfur content limits for gasoline and diesel are 10 ppm [20] and 15 ppm [21], respectively. Figure 2.5 shows the evolution of the allowed content of sulfur in gasoline (Figure 2.5a) and diesel (Figure 2.5b) in the last decades. As observed, the EU was the first to regulate the content of sulfur in gasoline to 150 ppm in 2000, followed by Australia (500 ppm in 2002) > Canada (150 ppm in 2003) > US (120 ppm in 2004) > India (500 ppm in 2005) > China (500 ppm in 2006) > Japan (10 ppm in 2007) > Brazil (50 ppm in 2010) > Russia (150 ppm in 2013). However, the most restricted content of sulfur in gasoline (10 ppm) was first established by Japan in 2007, followed by Canada and EU (2009) > Russia (2016) > US and China (2017) > India (2020) and Australia (2027, to be implemented). For diesel (Figure 2.5b), Japan was also the first to limit the S-content to 10 ppm in 2007, followed by the EU and Australia (2009), Brazil (2013), Russia (2016), China (2017), and India (2020) (the US and Canada establish the value of 15 ppm). Nitrogen is not directly regulated in permitted content but indirectly by allowed NO_x emissions, gum content, storage, and thermal stability [4].

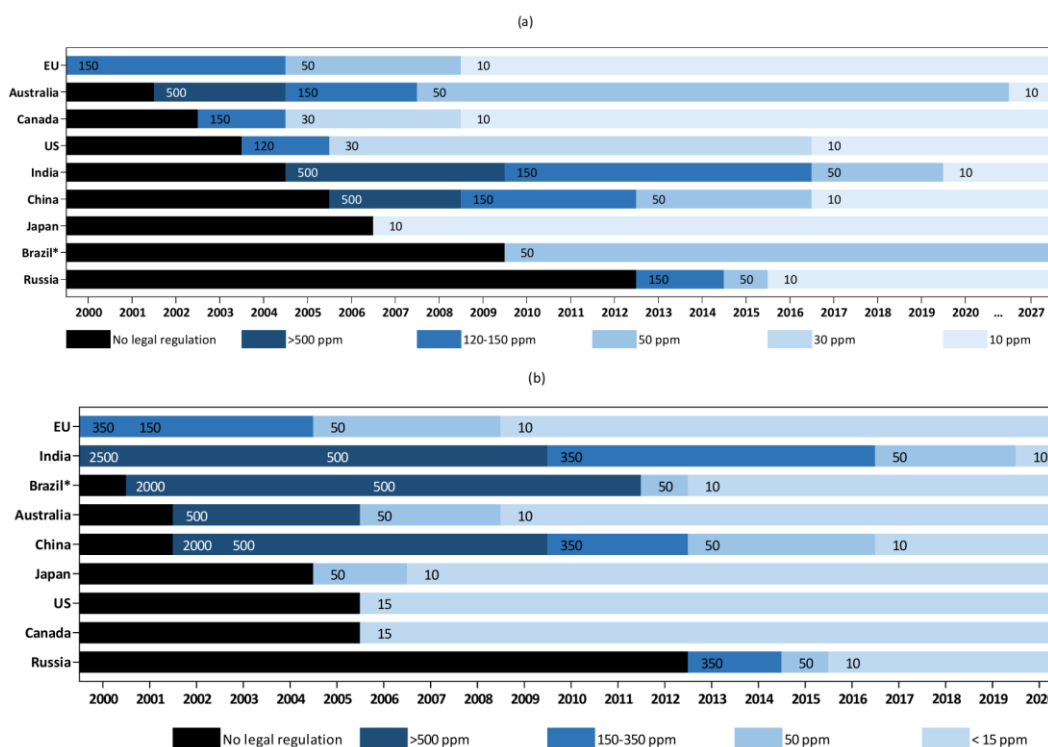


Figure 2.5. Evolution of the limit of sulfur content in (a) gasoline and (b) diesel, according to the implementation date. * Refers to metropolitan areas. Source: Miller and Façanha (2014) [22], TransportPolicy.net [23,24,25,26], United States Environmental Protection Agency [20], Australian Government [27], Euro V [28], Miller, and Jin (2019) [29].

2.2 Processes for Removal of Sulfur and Nitrogen from Fuels

Environmental issues and restrictive legislation have spiked the interest in desulfurization and denitrogenation technologies since 1951 (Figure 2.6). The most studied strategies are classified in conventional processes, as HDS and HDN, and in more novel approaches, mainly ODS and ODN.

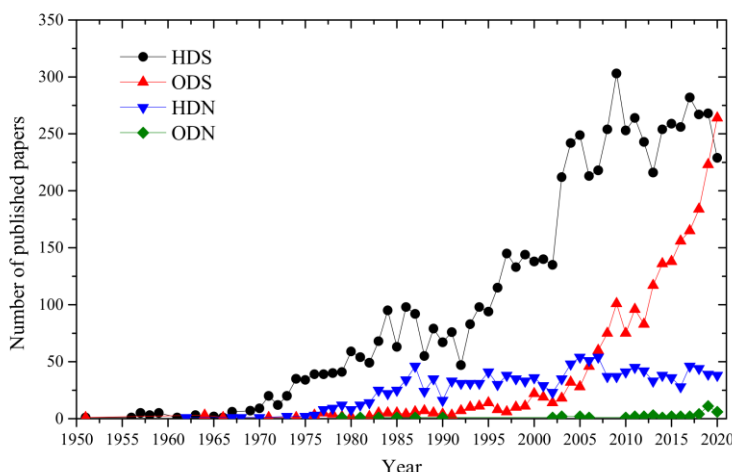


Figure 2.6. Papers published on HDS, HDN, ODS, and ODN over the years (source: SCOPUS with the keywords “hydrodesulfurization”, “hydrodenitrogenation”, “oxidative desulfurization”, and “oxidative denitrogenation”, respectively, dated August 2021).

2.2.1 Hydrodesulfurization (HDS) and Hydrodenitrogenation (HDN)

Several processes based on the reaction between hydrocarbons and hydrogen are used in the petroleum industry, such as hydrotreating, hydrocracking, and hydrogenation [30]. Hydrotreating refers to the removal of undesired species, such as sulfur, nitrogen, oxygen, and metal impurities, from petroleum fractions [30] by hydrogenolysis of C-X bonds, where X can be S, N, O, or metal. The net result is the formation of C-H bonds (hydrogenation) and H-X bonds [30]. The chemical reaction of fixing a hydrogen atom onto a hydrocarbon double bond, known as hydrogenation, using nickel catalysts, was first described in 1897. However, only in the mid-50s, the first noble metal catalyst was developed, and the HDS process commercialized [31]. Several HDS processes have been commercialized from then on, and all petroleum refineries worldwide have at least one hydrotreating unit [31].

The hydrotreatment of nitrogen-, sulfur- and oxygen-containing compounds will lead to ammonia (NH_3), hydrogen sulfide (H_2S), and water, respectively [31]. Oxygen-containing compounds are much more reactive than nitrogen- and sulfur-containing compounds towards hydrotreatment, and thus, hydrotreating is not specifically developed to remove O-compounds [32]. Most processes are designed to deal with S-compounds due to their hazardous effect on downstream processes. Removing S, N, and other impurities co-occur in refinery conditions [33]. Thus, N-containing impurities are also removed during hydrotreatment processes designed to remove sulfur [32], although nitrogen compounds are much less reactive and harder to remove than sulfur [4].

Different sulfur compounds have different rates of HDS [32]. Mercaptans, sulfides, and disulfides are highly reactive towards HDS under mild conditions. On the other hand, 5-membered ring compounds containing sulfur (thiophenes) are very little reactive towards HDS, and the reactivity decreases as the number of rings (in the range of 1–3 rings) increases [32]. However, the tendency reverses for structures containing four or more rings, and the reactivity increases as the number of rings increases [32]. The distinct behavior is that there is more than one pathway to remove sulfur from a molecule. Depending on the sulfur compound, one pathway may be more relevant than the other [32]. The order of reactivity of common organosulfur compounds towards HDS can be seen in Figure 2.7.

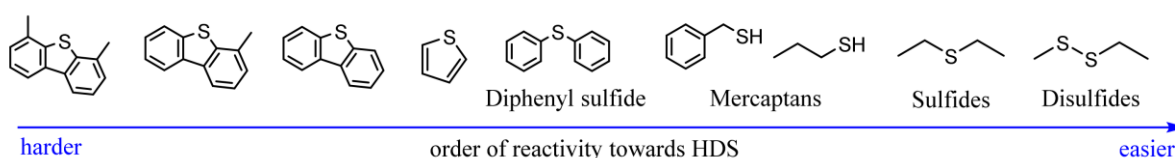


Figure 2.7. Order of reactivity of different S-containing compounds. Adapted from Rajendran et al. (2020) [34].

Analogous to thiophenes, nitrogen-containing compounds require a step of hydrogenation before the removal of N, and thus, the H_2 partial pressure is crucial [33]. Nitrogen removal for pyridinic structures is more complex than for thiophene structures. One single bond and one double bond are required to be broken [4]. In contrast, thiophenes only require two single bonds to be broken [4]. The presence of alkyl groups tends to decrease the reactivity of the S-compounds due to steric hindrance. The closer the alkyl group is to the sulfur or nitrogen atom, the stronger the effect on the reactivity [33]. Further information regarding the effect of temperature, catalysts, and other parameters in HDS and HDN processes may be found elsewhere [35].

Thus, different operating conditions may be required depending on the compounds present in the petroleum fraction. Table 2.2 shows some common hydrotreatment operational conditions for different fractions of petroleum. Heavier fractions tend to be richer in thiophene and N-containing compounds, and harsher conditions are required to remove those compounds. Increasing operational conditions affect a series of parameters in diesel and gasoline.

Table 2.2. Process conditions for different fractions of petroleum for HDS.

Feed	Temperature (°C)	Hydrogen Partial Pressure (bar)	Hydrogen Consumption (wt.%)	Catalyst life span (years)
Naphta	260–300	5–10	0.05–0.10	3–10
Kerosene	300–340	15–30	0.10–0.20	-
Gas oil	320–350	15–40	0.30–0.50	-
Residue	340–425	55–170	1.50–2.00	0.5–1

Source: adapted from Fahim et al. (2010) [30] and Speight (2011) [31].

Oxygen, benzene, aromatics and olefin contents, vapor pressure, and boiling range can be compromised during gasoline range hydrotreatment. In contrast, the compromised parameters for diesel are cetane number, density, and content on polynuclear aromatics and distillation 95% point for diesel [36]. Besides

However, the order of reactivity seems to depend significantly on the type of oxidant, catalyst, and operating conditions. Nevertheless, there is no organosulfur category that is entirely unreactive towards ODS [34].

The ODN process, in turn, has not been as extensively studied as ODS (as demonstrated in Figure 2.6). There is a broader range of possible reaction products than ODS during the oxidation of N-containing compounds due to the several bonds of N-compounds that are prone to oxidation [46]. For instance, quinoline (QN) oxidation gives reaction intermediates: 5-hydroxyquinoline and 8-hydroxyquinoline are the major products. However, trace quantities of 3-, 6- and 7-hydroxyquinoline are also observed [47]. Selectivity towards one product or the other may be tuned by controlling the reaction conditions [46].

Several oxidants have been reported in the literature for ODS and ODN, such as hydrogen peroxide, organic peracids, oxygen, and ozone, among others [6]. The oxidized compounds have an increased relative polarity compared to their parent compounds, and thus, their extraction is facilitated [5]. The oxidized compounds are more commonly removed through liquid-liquid extraction rather than through adsorption. Adequate extractants should fulfill a few criteria: they should be immiscible with the oil phase, they should be able to dissolve sulfones and sulfoxides, differences in density may exist to facilitate the separation between oil and extractant, and not impact the fuel properties, among others [34]. Some extractants found in the literature are acetonitrile (ACN), methanol (MeOH), ethanol (EtOH), diethyl ether (Et₂O), dimethylformamide (DMF), methyl cyanide, carbon tetrachloride (CCl₄), and ILs. Aqueous solutions of H₂O₂ (used as an oxidant) also are applied as extractants on their own.

As previously mentioned, both ODS and ODN are primarily conducted in a two-step process. However, to cut costs and accelerate the processes, one-pot approaches are increasingly sought. In one-pot approaches, extraction occurs concomitantly to oxidation, and hence, the extractant must be present during the oxidation step. Proper extractants are immiscible with the oil phase and, thus, one-pot approaches are commonly conducted in a biphasic medium. Biphasic systems have some advantages over traditional homogeneous systems. Biphasic systems allow conducting reactions with reactants with distinct solubility behaviors. They allow an easier separation between reactants, products, and catalysts and allow the reactions to be conducted with incompatible substances, avoiding interferences [48,49].

However, biphasic systems display some issues. The main issue is the low interfacial area between the phases, hindering reaction [48,50]. An alternative is emulsifying the biphasic medium [48], as emulsion systems significantly improve the interfacial area. Emulsifying requires the use of a surfactant or solid particles that allow the stabilization of Pickering emulsions. Pickering emulsions are an exciting template since the solid particles act as stabilizers and can also assume the role of catalysts. This approach is often referred to as Pickering Interfacial Catalysis (PIC) [50,51].

A wide range of solid particles can be used in the stabilization of Pickering emulsions, such as silica [52], magnetic particles [53], and carbon-based materials [54,55], among others. Pickering emulsions are affected by a range of conditions (pH, type of oil, ratio between the 2 phases, and concentration of particles, among others). One of the most interesting strategies to adjust emulsion formation and stability is to tune the amphiphilic character of the solid particles [56]. Amphiphilic materials display both hydrophilic and hydrophobic character and thus are wetted by more than one phase. As expected, particles wetted by more than one phase should allow easier emulsion formation and more stable emulsions [56]. Thus, amphiphilic materials should be advantageous when working under biphasic systems, especially in PIC-like approaches under emulsified systems.

Numerous catalysts have been applied for ODS and ODN purposes. However, discussing possible catalysts rather than carbon materials is not the aim of this review. Further information on other ODS catalysts may be found elsewhere [34,42,44,57]. Carbon-based materials, *i.e.*, the focus of this review, have been widely used in ODS and ODN, either by composing hybrid materials or as catalysts on their own. Carbon-based materials display several advantages in oxidative processes. Their ability to form oxidizing species (such as hydroxyl radicals) from oxidant sources (such as hydrogen peroxide) has been widely studied [58-62]. They are proven catalysts for oxidation reactions in the liquid phase, either as catalysts on their own or in hybrid forms, such as in water and wastewater remediation [63-67]. Thus, applying those materials in the oxidative removal of sulfur and nitrogen from liquid fuels is a natural extension. Carbon-based materials can be synthesized from various precursors, including waste materials [68-70], and through several synthesis procedures [68-75]. Table 2.3 summarizes the main carbon-based materials that will be discussed in the following sections, along with some common carbon sources and synthesis routes. The column with the reference will lead the reader to the appropriate literature regarding the preparation of the mentioned materials.

In the following section, papers related to ODS and ODN of liquid fuels (simulated or real matrix) using strictly carbon-based materials in hybrid forms or as catalysts on their own will be presented. Furthermore, when appropriate, a distinction between the papers that use a two-step process, a biphasic system, and a PIC-type approach will also be made.

Table 2.3. Examples of carbon-based materials and respective carbon precursors, synthesis routes and characteristics studied for ODS and ODN purposes.

Carbon-Based Material	Carbon Source	Synthesis Procedures	Characteristics	Ref.
Carbon Nanotube (CNT)	Plastic waste, coal, biomass, hydrocarbon gases.	Chemical Vapor Deposition (CVD), laser ablation, arc discharge, sonochemical, electrolysis	High Mechanical Strength (50–500 GPa), Electrical Conductivity (3000–3500 W m ⁻¹ K ⁻¹ , and Thermal Stability (>700 °C). Diameters from 0.4 to 40 nm.	[70-72]
Graphene Oxide (GO) and Reduced-GO (rGO)	Plastic waste, hydrocarbon gases.	Thermal decomposition, CVD, flash joule heating	High electrical and thermal conductivity (up to ~5000 W m ⁻¹ K ⁻¹), strongest material ever measured (Young's module~1 TPa), good stretchability, high surface area (theoretical calculations predict a value of 2630 m ² g ⁻¹ for monolayer graphene), high chemical and thermal stability.	[68,73]
	Graphite.	Electrochemical exfoliation		
Carbon Nitride (g-C ₃ N ₄)	Triazine and heptazine derivatives, cyanide, urea, melamine.	Solid-state reaction, hard-template method, chemical exfoliation, hydrothermal, thermal decomposition	Tunable optoelectronic properties and metal-free semi-conductor.	[74,75]
Activated Carbon (AC)	Biomass, C-containing wastes (e.g., plastic, food, and agricultural residues), coal, anthracite, and peat.	Pyrolysis followed by chemical or physical activation	High surface area (usually S _{BET} >500 m ² g ⁻¹), highly developed internal pore structure, presence of functional groups, especially oxygenated, wide variety of ACS, usually low cost.	[69]

2.3 Carbon Materials in ODS

The following sections will present the studies related to carbon materials in ODS systems, breaking them into three main sections: (i) hybrid materials containing carbonaceous structures, (ii) carbon-based materials as catalysts on their own, and (iii) systems applying amphiphilic catalysts containing carbon in their structure. As seen in Figure 2.9, most papers (73%) reported in the literature are related to applying carbon-based materials, forming either hybrid materials or as supports for active centers. Fewer papers deal with amphiphilic materials that contain carbon in their structure (15%) or as catalysts on their own (12%).

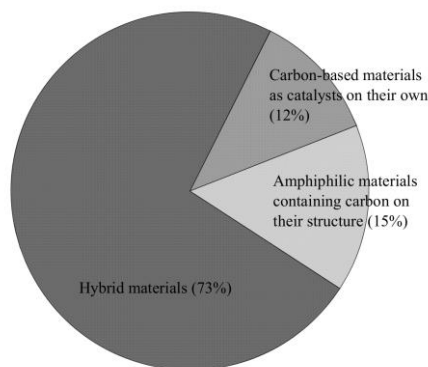


Figure 2.9. Percentage of published papers regarding the application of (i) hybrid materials containing carbonaceous structures, (ii) carbon-based materials as catalysts on their own, and (iii) systems applying amphiphilic catalysts containing carbon in their structure.

2.3.1 Carbon Supports and Hybrid Catalysts

One of the advantages of carbon materials is that they can be combined with other materials to prepare composites or hybrid catalysts. Thus, most papers related to ODS with carbon materials have applied them in hybrid forms. As discussed before, ODS can be conducted in various systems, such as two-step processes, biphasic systems, under the emulsified form, and solvent-free, among others. Hence, the different systems are separated into different sections.

2.3.1.1 Two-Step Systems

The papers related to ODS reactions using carbon hybrid materials under a two-step process are gathered in Table 2.4. As observed, several combinations of hybrid materials consisting of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, HPW), iron, palladium, molybdenum, and titanium active metal phases with g- C_3N_4 , GO and its reduced derivative (rGO), CNTs, and AC as supports/hybrids. The catalytic activities of these hybrid materials have been assessed in ODS of solutions with initial sulfur concentrations ($[\text{S}]_0$) ranging from 100 to 9400 ppm using H_2O_2 as oxidant under mild conditions (25–80 °C) and achieving sulfur removals higher than 90%. In general, most authors have not justified the role of the carbon structure in these runs [76–82], with a few exceptions.

Huang et al. (2017) [83] performed ODS of a simulated fuel using dibenzothiophene (DBT) dissolved in n-octane ($[\text{S}]_0 = 100$ ppm) using an N-doped onion-like carbon (NOLC) supported HPW. They have obtained high conversions (>90%), which were maintained for up to 10 reuse cycles. They attributed the excellent results to the excellent dispersion of the active phase (HPW) in the NOLC structure. The surface of NOLC displayed a high content of oxygenated groups, which can interact with HPW, strengthening the HPW-support interaction. In turn, the HPW dispersion is improved, boosting the reaction [75]. Rafiee, Shahbazirad, and Khodayari (2017) also found that an increased dispersion of HPW over $\text{TiO}_2/\text{g-C}_3\text{N}_4$ resulted in higher desulfurization rates of a simulated fuel (DBT ($C_0 = 500$ ppm),

BT ($C_0 = 250$ ppm) and Th ($C_0 = 250$ ppm) in EtOH/n-heptane) and for a real oil ($[S]_0 = 500$ or 1900 ppm) [84].

Abdelrahman et al. (2018) [85] also highlighted the high dispersion of Mo_{132} as one of the reasons for the high activity of a hybrid catalyst supported on GO in the ODS of DBT, benzothiophene (BT) or 4,6-dimethyldibenzothiophene (4,6-DMDBT) as model compounds dissolved in dodecane ($[S]_0 = 500$ ppm). They obtained conversions of sulfur compounds higher than 94% regardless of the model compound and were able to maintain the activity for up to 10 cycles. Besides the high dispersion of the active phase, GO was also found to increase the adsorption of sulfur compounds due to the Lewis acidic character of its defect sites. The adsorption of sulfur compounds in the catalyst structure approximates the S compound and the oxidant, thus enhancing the oxidation reaction [85].

2.3.1.2 L-L Biphasic Systems

Tables 2.5-2.8 show the studies related to the application of carbon-based hybrid materials in the ODS of a range of sulfur compounds in biphasic systems, *i.e.*, systems where oxidation and extraction occur simultaneously. Each table shows studies using different allotropes of carbon. Not all authors have studied the influence of the carbon structure in the proposed systems [86-89].

Rongxiang et al. (2017) performed ODS of a simulated fuel (DBT in n-octane) using a hybrid catalyst of WO_3 supported over g- C_3N_4 . They found that the most relevant contribution of the carbon structure is related to its high surface area, which in turn allows for a higher dispersion of the active phase [90]. The higher surface area increases the adsorption of sulfur compounds, whereas the higher dispersion impacts the desulfurization performance [90]. The high surface area of AC is also suggested by Xiao et al. (2014) as one of the reasons for the increased activity of HPW supported over AC compared to unsupported HPW in the ODS of thiophene (Th) in a mixed solvent simulating a gasoline matrix [91]. Other authors have also pointed out the high surface area and related high dispersion as relevant contributions of carbonaceous structures to the catalytic activity [92-96]. In contrast, the agglomeration of active centers was linked to a decrease in catalytic activity [97].

Hou et al. (2018) [98], on the other hand, reported that the surface area of the catalyst is not the only relevant parameter for ODS of a simulated fuel (DBT in n-octane) using a g- C_3N_4 supported MoO_2 catalyst. They also observed that the active phase concentration, or loading, is essential information. While increasing the amount of loaded MoO_2 increases the number of active sites, it significantly reduces the surface area of the catalysts, resulting in poor dispersion of the active sites. On the other hand, low loading of active centers results in a catalyst with a high surface area but a low number of active sites. Thus, finding the optimum combination between loading the active phase and maintaining a high surface area is a crucial step [98].

In 3D-carbonaceous structures, the surface area was also pointed out as a critical parameter. Ye et al. (2020) have confined MoO_x in a 3D-macroporous carbon structure and applied these hybrid materials in the ODS of a simulated fuel (BT, DBT, and 4,6-DMDBT in n-octane). One of the reasons for the high activity of the materials (conversions higher than 85% in 75 min of reaction) was attributed to the high surface area of the 3D-carbon structure, which resulted in a fast mass transfer to the active sites confined within the structure [99]. Zhu et al. (2020) also observed that the 3D structure of carbon spheres (3D-CS) is beneficial to an increased mass transfer during oxidative desulfurization [97]. Bhadra et al. (2017) also highlighted a fast mass transfer resultant from mesoporosity of the catalyst as an important contributor to the high activity of a TiO₂-C in the ODS of a simulated fuel (Th, BT, DBT or 4,6-DMDBT in n-octane, [S]₀ = 1000 ppm) [92].

Other authors have pointed out that carbon structures play an important role through adequate adsorption of sulfur compounds, which can be ascribed to an increase in DBT concentration in the vicinity of active catalytic centers [100]. Wang et al. (2010) observed that the main role of CNT in a hybrid catalyst consisting of CNT and a phosphotungstic acid was to enhance the transfer of DBT to the active center by adsorption, facilitating the oxidation of DBT [101]. Xing et al. (2017) observed that increasing the calcination temperature of a CoWO₄/g-C₃N₄ resulted in an enhanced surface area and adsorption ability towards DBT [102]. Other authors have also highlighted the adsorption capacity of carbonaceous materials, either towards DBT and other sulfur compounds [90,99,100,103] or oxidation products [104].

Yu et al. (2010) also observed that the adequate adsorption of DBT into the carbon structure was an essential contribution of the carbon-based support in an HPW/AC catalyst [105]. Their reasoning is that increased adsorption of DBT leads to a higher collision probability between DBT and active oxygen species from the decomposition of H₂O₂ that takes place in the active center (HPW). The carbon surface also influences the resonance-stabilization of these active oxygen species, boosting oxidation. Moreover, due to the hydrophobicity of AC, it can be adequately dispersed in the oily phase or placed in the interface between the oily and polar phases, acting as a phase transfer agent [105]. Kermani et al. (2018) also found that the combination of adsorption capacity towards DBT and adequate lipophilicity of AC structure was an essential feature of the composite Mo₁₃₂/AC [106].

In an ultrasound-assisted ODS (UAODS) of a simulated fuel with an HPW/AC as the catalyst, Liu et al. (2014) also identified the increased adsorption of DBT and the ability of the catalyst to act as a phase transfer agent as important features arising from the AC support [107]. However, they have also pointed out that the AC structure plays another relevant role in UAODS: the high surface area was also correlated to a higher cavitation activity in UAODS, boosting reaction rates [107,108].

Functional groups on the carbon material can impact the coordination of active species (metallic centers) [109-111]. Dini, Afsharpour, and Tabar-Heydar (2019) argued that the oxidation of DBT undergoes an

electrophilic attack of the peroxy group (LUMO) on the catalyst surface to the sulfur compound (HOMO) [110]. Thus, efficient oxidation needs to overcome the LUMO-HOMO barrier. The functional groups on the support surface (in this case, CNTs) affect the coordination of the metal-active species (Mo). This geometry boosts the electron density of peroxy groups and increases the HOMO energy level. By increasing the energy level of HOMO, the gap between HOMO-LUMO decreases, and oxidation is facilitated [110,111].

Other authors have correlated the activity of hybrid materials to an increased electron transfer between carbon structure and active phase, especially in doped carbon-based materials. Bhadra, Khan, and Jhung (2019) observed that N-doped graphitic carbon-supported Co resulted in a more effective electron transfer, which could be helpful for oxidation and reduction reactions [112]. Liao et al. (2019) observed that the strong interaction between HPW and rGO enhanced electron mobility and, consequently, the reaction rate [113].

Wang et al. (2020) [95] and Zhao et al. (2017) [96] have proposed that g-C₃N₄ was able to activate H₂O₂ and form hydroxyl radicals (HO[•]). Moreover, the carbon structure was also found to avoid the leaching of active species [113].

2.3.1.3 Other ODS Systems

Table 2.9 displays a miscellaneous of other ODS systems, whereas Table 2.10 displays photocatalytic ODS systems. Similar to what was observed earlier, the developed surface area and the structure of pores in carbon materials, leading to well-dispersed active phases, were found as a critical contribution of carbon structures [114-118]. Xun et al. (2020) [119] also highlighted the dispersion of TiO₂ over a graphite carbon (GC) as a relevant factor for the ODS of a simulated fuel (DBT, 4-methyldibenzothiophene (4-MDBT) and 4,6-DMDBT dissolved in n-octane, [S]₀ = 500 ppm). However, they also observed that the dispersion is related to the amount of active phase dispersed on the support. Upon increasing TiO₂ content over 10 wt.%, the catalytic activity of the hybrid catalyst decreased due to the agglomeration of TiO₂ particles. Thus, loading the proper amount of active phase is an important step. The synergistic effect between the support and the active centers is the main reason a catalyst displays outstanding properties in ODS systems [119]. Gao et al. (2020) [120] found that the increased surface area was also associated with a higher collision probability between sulfur compounds and the catalyst. They observed that the activity of the polyoxometalate-based IL supported over a series of carbon materials decreased accordingly to the surface area of the support (P[C₂VP] MoV/AC (170 m² g⁻¹) > P[C₂VP] MoV/CA (157 m² g⁻¹) > P[C₂VP] MoV/CNT (93 m² g⁻¹) > P[C₂VP] MoV/GO (10 m² g⁻¹)) [120]. This observation highlights the importance of a developed surface area to a well-dispersed active phase and high desulfurization rates.

Carbon-based materials were also found to accelerate the electron transfer for different active phase-support pair materials, such as $\text{MoO}_2/\text{g-C}_3\text{N}_4$ [115], $\text{FePc}(\text{NO}_2)_3\text{-CF}$ [118], V/P-doped $\text{g-C}_3\text{N}_4$ [121], $\text{VO-MoO}_2/\text{N-doped CNT}$ [122], considering different oxidants (TBHP [115,121], O_2 [118] and CHP [122]), which enhances oxidative desulfurization rate. Chen, Ren, and Yuan (2020) observed that the rate-determining step in the ODS of DBT using V supported over a P-doped $\text{g-C}_3\text{N}_4$ material is the electron transfer, and thus an enhanced electron transfer due to P doping greatly improved oxidation [121]. They also observed that P-doping $\text{g-C}_3\text{N}_4$ enhanced the electron transfer, resulting in a more efficient ODS process [121].

Some authors have reported that carbonaceous materials favor electron-hole separation [123-127] (cf. Table 2.10), thus benefiting the photocatalytic activity of those hybrid materials. Li et al. (2017) claimed that the narrower bandgap of $\text{g-C}_3\text{N}_4$ allows the application of visible light [124]. Furthermore, the well-matched band structures between the support and active phase (CeO_2) favor the ready transfer of electrons generated in the surface of the support to the surface of CeO_2 to avoid the recombination of photo-generated electrons and holes effectively. Thus, the electrons can react with hydrogen peroxide to form hydroxyl radicals. They observed that the holes might also participate in the reaction, although contributing much less than electrons, due to the weak potential of the valence band of $\text{g-C}_3\text{N}_4$ (1.79 eV) compared to the redox potential of the $\text{OH}^-/\text{HO}^\bullet$ pair (1.99 eV) [124]. Ma et al. (2017) also found that the use of carbon quantum dots (CQD) improved the efficiency of the use of visible light [125].

In general, most ODS systems require an extractant phase and a catalyst to remove the oxidized intermediates. However, in a few processes, the hybrid material can act as a catalyst to oxidize sulfur compounds and adsorbents for the oxidized products in a solvent-free approach. Jiang et al. (2017) immobilized a polyoxometalate-based IL in graphite carbon and tested this hybrid catalyst in the solvent-free ODS of a simulated fuel. A 100% removal of DBT in the model oil was observed, whereas only DBT sulfone (DBT 5,5-dioxide) was detected in the catalyst phase. The high efficiency of the process was ascribed to the hydrophilic characteristics of IL, allowing a closer contact with H_2O_2 associated with the high hydrophobic character of carbon, which allowed a closer contact with the oil phase [128]. Ma et al. (2019) reported similar results. Only DBT 5,5-dioxide was detected in the catalyst phase, and no sulfur compounds were observed in the oil phase [114].

Other reasons pointed out by the authors were the hydrophobic characteristics of GC in a polyoxometalate-based IL supported on GC, which allowed the catalyst to be better dispersed in the oil phase in the solvent-free ODS [128]. The protective environment arising from the CNT structure was also an essential feature, especially to avoid leaching of the active phase, thus increasing catalyst stability and reusability [129].

2.3.1.4 Trends on Hybrid Materials Containing Carbonaceous Structures

Carbon-based materials have proved to be an exciting platform as supports for active phases or as components in hybrid materials, leading to highly active catalysts in ODS processes. Carbon materials can be used in a wide range of different approaches and systems. Most authors agree that the main contribution of the carbon-based structure is usually related to the high surface area displayed by those types of materials, which leads to a high degree of dispersion of the active phases. Others have also pointed out that the hydrophobic nature of the carbon structure increases the interaction of the hybrid materials with the organic phase and increases the contact between the oxidant and the target S compound. A few authors also highlighted an increased electron transfer between the carbon structure and the active phase as the critical contribution of carbon structures. Specifically for photocatalytic systems, carbon-based materials have the advantage of reducing the recombination of electron-hole pairs, which dramatically boosts reaction rates. Carbon materials can act as catalysts of the process and adsorb the oxidized compounds, allowing solvent-free systems. Furthermore, carbon materials were able to avoid the leaching of active phases.

2.3.2 Carbon Catalysts on Their Own

Carbon-based materials have been reported as catalysts on their own for ODS reactions, and a summary with the main conditions and results are collected in Table 2.11. As observed, a series of carbon-based materials (AC, GO, rGO, and CNT) have been assessed in the ODS of model compounds (mainly BT, DBT, or 4,6 DMDBT). Initial sulfur concentrations ranging between 400 and 2189 ppm were studied, considering mild operating conditions (25–150 °C), allowing for removals higher than 95% from 30 min of reaction time. In general, carbon materials have displayed similar activity to those reported earlier considering hybrid or supported materials. The activity of the carbon material can be ascribed to the presence of defect sites on its surface, its developed surface area, or the presence of surface groups. Here, we propose the mechanism displayed in Figure 2.10 for the ODS of sulfur-containing compounds according to different proposals in the oxidation activity of carbon catalysts [130,131].

Gonzalez et al. (2012) compared a thermally treated AC (SX-1) and an AC treated with phosphoric acid (MW-99). MW-99 led to an increase in sulfur removal in the range of 2.8–3.3× compared to SX-1, depending on the sulfur compound. Those results were ascribed to a more developed surface area by MW-99, a lower content of basic sites and a higher concentration of acidic sites [132]. Haw et al. (2010) also found that the presence of acidic groups in AC, especially oxygenated groups, increased catalytic activity due to the electron-withdrawing characteristic of the acidic groups allied to the electron donor ability of S compounds. This interaction between acidic groups and S atoms increases the physisorption of S compounds in the AC structure [133].

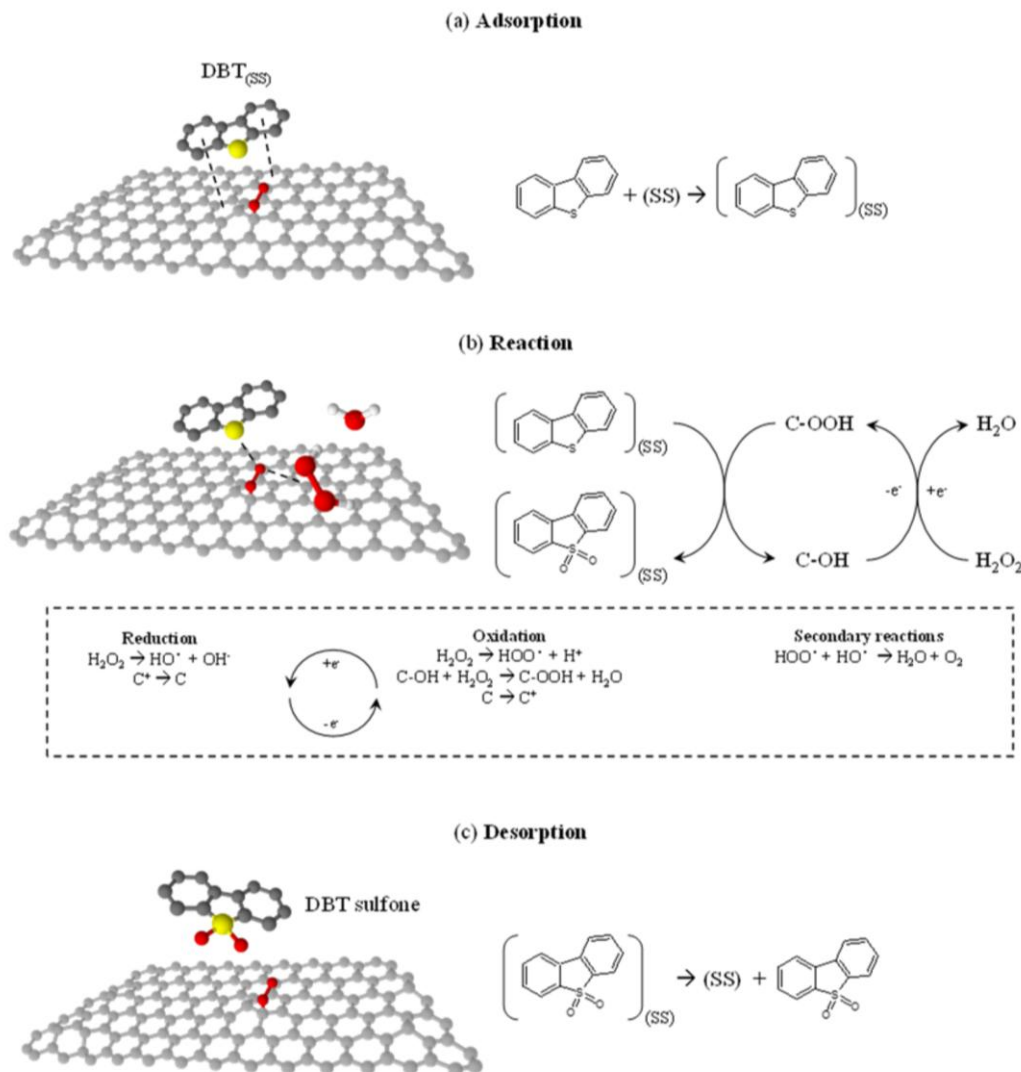


Figure 2.10. Oxidation mechanism of sulfur compounds (exemplified with DBT) on carbon catalysts (SS = Surface Site, draws prepared with Freeware Chems sketch; White, Red, Yellow, and Gray atoms as hydrogen, oxygen, sulfur, and carbon, respectively).

He et al. (2019) [131] studied the influence of doping GO with nitrogen and oxygen for the aerobic ODS of various sulfur compounds. They compared two GO samples. The first was an N-doped GO subjected to annealing at 1000 °C, leading to PG-15. The other sample was obtained by subjecting PG-15 to thermal treatment in a muffle furnace at 450 °C, leading to PG-450. PG-15 removed approximately 9.3% of DBT, which is mainly ascribed to an adsorption effect. On the other hand, PG-450 could remove 98.5% of DBT in 5 h of reaction. The activity of PG-450 was ascribed to the oxygen groups (19.9% as opposed to 3.6% for PG-15) and an increase in the content of graphitic-like N structure in the material (47.8% in PG-450 vs. 37.2% in PG-15). The main active sites for the activation of O₂ are the oxygenated groups. However, since this activation requires an electron transfer process, the existence of electron-rich oxygenated groups should facilitate this electron transfer. In N, O-doped materials, the existence of electron-rich oxygen groups is ascribed to the enhanced electron delocalization that arises from the N-doping. To demonstrate the synergistic effect of both N and O doping, a graphite material was calcined at 450 °C (Graphite-450) and tested in the ODS reactions. Graphite-450 is rich in oxygenated groups

but poor in nitrogenated groups. In 5 h, only 40% removal of sulfur compounds was observed, thus reinforcing the synergy between N and O doping [131].

The presence of oxygenated groups was also found as crucial by Gu et al. (2019) [134] in the activity of oxidized CNTs (oCNTs). To identify which oxygenated groups were more relevant, they selectively removed different oxygenated groups (carboxylic, lactone, anhydride, phenolic, or carbonyls) through thermal treatment or selectively blocked some of them. When blocking or removing carbonyl groups, the activity of oCNT decreased drastically (from 100% removal of DBT to 31%), thus pointing out the relevance of carbonyl groups. Gu et al. (2017) [135] have also found a positive correlation between carbonyl groups and catalytic activity. Other authors have reported that lactones and carboxylic groups also play an essential role [130].

On the other hand, some authors have reported that total oxygen-containing groups could not directly correlate to the catalytic activity in ODS experiments [136]. Zhang et al. (2014) have demonstrated that the change in the content of oxygen-containing groups affects the catalytic activity. However, there was no clear correlation between total content or specific groups in CNTs and desulfurization activity. Nonetheless, they did find a correlation between the increased graphitization degree of CNTs and increased catalytic activity. An increased graphitization is ascribed to a lower degree of defects. They attribute this phenomenon to a higher electron transfer due to higher electrical conductivity in highly graphitic CNTs [136]. In opposition to that, most authors seem to correlate the presence of defect sites to an increase in catalytic activity. Gu et al. (2019) observed an increase in defect sites after acid treatment (D^*/G value increased from 1.77 to 1.91 for CNTs and oCNTs, respectively), which were correlated to the increased activity of oCNTs compared to CNTs (along with the oxygenated groups discussed above) [134]. In 2017, Gu et al. [135], by saturating defect sites in rGO through the formation of C-H bonds, have observed a sharp decrease in DBT removal, thus pointing out that defect sites also play a significant role in the activity of carbocatalysts. Zeng et al. (2017) [137] also identified zigzag edges and defects in GO as relevant active centers for the catalytic process.

In contrast, Timko et al. (2016) [138] reported that basal plane defects in AC are more relevant than edge defects. They presumed that basal plane defects are oxidized to generate carboxylic or percarboxylic acids on the surface of the material. Those oxygenated groups are then responsible for promoting ODS. The sulfur compounds are also expected to adsorb into the basal planes, increasing local concentration. However, adsorption alone is not sufficient. The surface oxidation allied to an increased local concentration of the sulfur compound in the carbon basal plane is the reason pointed out by the authors that distinguish the activity displayed by distinct ACs [138].

Trends on Carbon-Based Catalysts

In general, there are fewer reports related to the application of carbon-based materials as catalysts on their own in the ODS process as compared to their application in hybrid forms. However, carbon-based materials have proved to be adequate catalysts, and there is still room to study their application for desulfurization purposes.

Overall, the presence of acidic groups on the surface of carbon-based materials was related to higher desulfurization rates due to an acid-base interaction between carbon surface and sulfur molecules. Among the acidic surface groups, oxygen-containing groups are thought to be the active centers by most studies. However, there is still a controversy related to the influence of defect sites in catalytic activity.

Carbon-based materials have some unique advantages, especially their easy manipulation and introduction of surface groups. Nevertheless, there is a lack of reports on the application of doped carbon with heteroatoms other than oxygen and nitrogen. Thus, further investigating the influence of other dopants is an opportunity to apply carbon-based materials as catalysts on their own.

2.3.3 Amphiphilic Carbons

Amphiphilic carbons are materials that simultaneously display hydrophilic and hydrophobic characteristics. Thus, amphiphilic carbons can better interact with aqueous and organic phases. The contact angle of a water drop onto a material is widely used to describe amphiphilicity. Materials with a contact angle of 0° are completely hydrophilic (high water-wettability), whereas materials with contact angles of 180° are entirely hydrophobic. Amphiphilicity is an attractive characteristic when considering a biphasic reaction, as in ODS, due to increased contact between an organic phase (fuels) and an extractant phase, which usually presents a more polar nature. Table 2.12 summarizes the reports related to the application of amphiphilic carbon-based materials for ODS reactions, main operating conditions, and results.

Abdi et al. (2017) [139] studied the removal of DBT from a simulated fuel in a biphasic system using GO/COOH as a catalyst. They have attributed the high removal rates of sulfur to the amphiphilicity of GO/COOH, which allowed for better interaction with hydrophilic H_2O_2 and hydrophobic sulfur compounds. Similarly, Liu et al. (2020) have observed that the POM catalyst alone, due to its hydrophilicity, could not properly contact DBT (which is lipophilic). Thus, much better interaction between DBT and catalyst was observed by covering the POM catalyst with a hydrophobic carbon layer, significantly increasing the reaction rate [140]. In another approach, Yu et al. (2020) immobilized lipophilic C_{12}PW on hydrophilic $\text{g-C}_3\text{N}_4$, thus increasing the use of hydrogen peroxide and the contact between DBT and active sites [141].

Li et al. (2019) found that $\text{g-C}_3\text{N}_4$ is not only responsible for improving the dispersion of the active phase (BMPO) but also for creating a heterojunction between support and BMPO, which increases the usage

rate of electrons. Furthermore, the amphiphilic character of the catalyst solves the issue of the mass transfer between oily and aqueous phases [142].

Amphiphilic materials can also be applied in PIC-like approaches that rely on emulsion formation. The higher interfacial area between the apolar and polar phases in emulsion systems should increase the reaction rates. Mambrini et al. (2017) studied the ODS of DBT in emulsion systems (cyclohexane/aqueous H_2O_2) using metallic catalysts (Fe and FeMo) modified with carbon to alter their amphiphilicity. Fe and FeMo alone could not remove any DBT; however, stable emulsions were formed when carbon coating was introduced, resulting in increased contact between organic and water phases, thus increasing reaction rates [143]. They proposed that the materials act in two ways: one, by increasing the interfacial area between phases due to the stabilization of an emulsion system, and two, through the activation of hydroxyl species in a Fenton-like system. The generated hydroxyl radicals were then able to oxidize DBT in the interface between the organic and the aqueous phases. The increased polarity and high interfacial area were also responsible for facilitating the extraction of DBTO_2 [143]. Figure 2.11 shows the presumed mechanism for emulsified systems, adapted from elsewhere [144-146]. Other authors have also reported ODS emulsion systems that rely upon amphiphilic catalysts to increase catalytic activity [147].

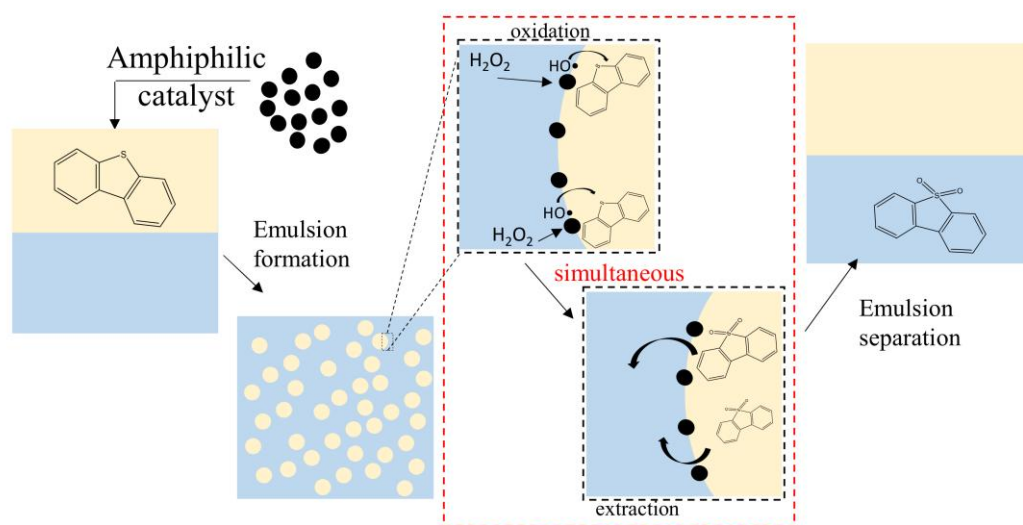


Figure 2.11. Presumed role of amphiphilic materials in biphasic oxidation under an emulsified system. Adapted from Oliveira et al. (2014) [145], Oliveira et al. (2015) [144], and Teixeira et al. (2013) [146].

Trends on the Application of Amphiphilic Materials

Amphiphilic materials have been applied in an extensive range of different ODS systems, including processes considering two-steps, biphasic systems, and PIC-like approaches. Regardless of the system, amphiphilic materials were attractive options due to their ability to interact with aqueous oxidant phases, lipophilic sulfur compounds, and organic phases simulating fuels.

2.4 Carbon Materials in ODN

Denitrogenation reactions are not as widely studied as desulfurization, and thus, there is a limited number of papers regarding denitrogenation with carbon-based materials. In general, the roles of the carbon-based materials in ODS are similar in ODN reactions. Many authors highlighted the amphiphilicity of carbon structures as beneficial in ODN reactions. Table 2.13 summarizes the papers related to ODN reactions. As observed, most works deal with ODN of QN (model component most extensively studied). ODN is mainly conducted with H_2O_2 using iron-containing carbon materials under mild conditions (25–80 °C) for reaction times up to 3 h (achieving complete oxidation of the model molecule at lower times depending on the selected catalyst and operating conditions). The selection of iron catalyst with H_2O_2 as the oxidant may be ascribed to the reactive iron- H_2O_2 pair, also known as the Fenton-reagent [148,149].

Guimarães et al. (2013) have tested magnetite covered by carbon as the catalyst for the simultaneous oxidation of DBT and QN in a biphasic system (toluene-acetonitrile, $[\text{QN}]_0 = 50$ ppm) [150]. DBT conversion was higher than QN conversion (100% instead of ~60% for QN). The presence of DBT reduced QN oxidation by about 50%. The authors have highlighted the amphiphilicity of the catalyst and its ability to remain in the interface between the two solvents as one of the critical conditions to display high catalytic activity [150].

Mambrini et al. (2017) studied the removal of QN in cyclohexane ($[\text{N}]_0 = 50$ ppm) [143] in a PIC-like system using a FeMo/C as the catalyst. Due to the amphiphilic character of the catalyst, it can interact with aqueous and oily phases, stabilizing an emulsion cyclohexane-aqueous H_2O_2 . The emulsified system increases the interfacial area and enhances the reaction rate. The high interfacial area resulted in a very fast conversion of QN: almost complete conversion in less than 10 min [143]. FeMo/C revealed a higher catalytic activity than Fe/C, which was ascribed to the higher carbon content of FeMo/C. Higher carbon content allowed a better interaction between the oily and the aqueous phase, favoring emulsion stabilization [143].

Table 2.4. ODS using mainly H₂O₂ with carbon hybrid materials in a two-step system.

Fuel*	Catalyst	Extractant	Operational Conditions	Results	Ref.
DBT in EtOH/Hexane (C_0 = 500–1200 ppm)	H ₅ PMO ₁₀ V ₂ O ₄₀ /Fe ₃ O ₄ /g-C ₃ N ₄	EtOH	V_{fuel} = 2 mL, m_{cat} = 0.03 g, $n_{H_2O_2}$ = 10 mmol, T = 80 °C.	Regardless of the initial concentration, complete desulfurization was achieved in 120–180 min. For fuel with [DBT] ₀ = 1000 ppm, the presence of <i>N</i> compounds slightly hindered the removal of DBT, reducing the overall removal to ~90–95%.	[76]
Real oil ([S] ₀ = 500 and 1900 ppm)	H ₅ PMO ₁₀ V ₂ O ₄₀ /Fe ₃ O ₄ /g-C ₃ N ₄	EtOH	V_{fuel} = 5 mL + mixed solvent EtOH: Hexane (1:1, v/v), m_{cat} = 0.03 g, $n_{H_2O_2}$ = 10 mmol, T = 80 °C.	25% and 30% removal were possible for [S] ₀ = 500 and 1900 ppm, respectively.	[76]
DBT ([S] ₀ = 1000–3000 ppm), BT ([S] ₀ = 100 ppm) or 4,6-DMDBT ([S] ₀ = 100 ppm) in n-Octane	HPW/mpg-C ₃ N ₄	MeOH	V_{fuel} = 10 mL, m_{cat} = 10–120 mg, H_2O_2/S = 2–12, T = 30–70 °C, t = 0.5–3 h.	Increasing <i>S</i> content reduces removal (90, 63, and 58% for [S] ₀ of 1000, 2000, and 3000 ppm, respectively). In 2.5 h, >99% removal was possible. Increasing the H_2O_2/S ratio from 2 to 4: a sharp increase in <i>S</i> removal. Maximum desulfurization: 100 mg of catalyst. Increasing temperature also increases <i>S</i> removal. 15 recycle runs maintaining <i>S</i> removals above 98%. Reactivity: DBT~4,6-DMDBT (100%) > BT (80%).	[78]
DBT (C_0 = 500 ppm), BT (C_0 = 250 ppm), and Th (C_0 = 250 ppm) in EtOH/n-Heptane	HPW-TiO ₂ /g-C ₃ N ₄	DMF	V_{fuel} = 5 mL, m_{cat} = 0.03 g, $n_{H_2O_2}$ = 12 mmol, T = 80 °C.	100% removal of <i>S</i> compounds in 3 h of reaction was observed. In the presence of aromatic or <i>N</i> compounds, 100% removal was also possible but with longer reaction times (4–6 h).	[84]
Real Oil ([S] ₀ = 500 or 1900 ppm)	HPW-TiO ₂ /g-C ₃ N ₄	DMF: n-heptane (1:1 v/v)	V_{fuel}/V_{DMF} = 1, m_{cat} = 0.03 g, $n_{H_2O_2}$ = 12 mmol, T = 80 °C, t = 200 min.	30% and 35% decrease in <i>S</i> content was observed ([S] ₀ of 500 and 1900 ppm, respectively).	[84]
Naphtha ([S] ₀ = 870 ppm)	Pd/CNTs	ACN	C_{cat} = 0–8.5 g mL ⁻¹ , $V_{fuel}/V_{H_2O_2}$ = 10, T = 25 °C, t = 30 min.	Increasing the catalyst dosage from 2.5 to 8.5 g mL ⁻¹ resulted in a sharp increase in <i>S</i> removal (25 to 90%).	[77]
Naphtha (C_0 = NM)	MnO _x /CNT	ACN	C_{cat} = 5 mg mL ⁻¹ , $V_{H_2O_2}$ = NM, T = 25–30 °C, t = 30 min.	EDS and ODS process, desulfurization of 9 and 83% were achieved, respectively. Under optimum conditions, 92% desulfurization was observed, maintained for 4 cycles.	[79]
Hydrotreated Gas Oil Sample ([S] ₀ = 1477 ppm)	Pd or Fe ₂ O ₃ /AC + Na ₂ CO ₃ (co-catalysts)	ACN	$V_{fuel}/V_{H_2O_2}$ = 10, m_{cat} = 3 g, T = 40 °C, t = 3 h, 5 mL of Acetic Acid	Using only H ₂ O ₂ and no co-catalyst, 10–12% desulfurization rates were achieved. By adding acetic acid and Na ₂ CO ₃ , 71 and 66% desulfurization efficiency was observed for Fe ₂ O ₃ /AC and Pd/AC, respectively.	[80]
Gas Oil ([S] ₀ = 9400 ppm)	Fe ₂ O ₃ -GO	ACN	$V_{fuel}/V_{H_2O_2}$ = 10, m_{cat} = 0.5–2.5 g, 5 mL of acetic acid, T = 40–60 °C, t = 160–240 min.	Importance of parameters: time > temperature > catalyst dosage. The optimum desulfurization (92%) was predicted at 225 min of reaction, 2.5 g of catalyst, and 60 °C.	[81]
DBT, BT, or 4,6-DMDBT in Dodecane ([S] ₀ = 500 ppm)	Mo ₁₃₂ /GO	ACN	C_{cat} = 1–10 g L ⁻¹ , H_2O_2/DBT = 2–8, T = 30–60 °C, t = 45–150 min.	Increasing time results in higher removal of <i>S</i> (48% at 45 min vs. 96% at 150 min). Increasing the H_2O_2/S ratio > 6 did not impact <i>S</i> removal. Temperature also slightly influenced (96 to 99% from 30 to 60 °C, respectively). Increasing catalyst concentration (1 to 10 g L ⁻¹) improved <i>S</i> removal. <i>S</i> removal was ~96% and 94% for 4,6-DMDBT and BT. 10 recycle runs.	[85]

* If the model fuel is described using the word 'and', it means the model fuel was a mixture of sulfur compounds. The word 'or' indicates that the sulfur compounds were used independently. Legend: NM = not mentioned. AC = activated carbon. ACN = acetonitrile. CNT = carbon nanotube. DMF = dimethylformamide. EtOH = ethanol. Et₂O = diethyl ether. g-C₃N₄ = graphitic carbon nitride. GO = graphene oxide. HPW = phosphotungstic acid (H₃PW₁₂O₄₀). MeOH = methanol. mpg-C₃N₄ = mesoporous graphitic carbon nitride. NOLC = N-doped onion-like carbon.

Table 2.4. ODS using mainly H₂O₂ with carbon hybrid materials in a two-step system (continuation).

Fuel*	Catalyst	Extractant	Operational Conditions	Results	Ref.
DBT in n-Octane ([S] ₀ = 500 ppm)	CoMo/rGO	ACN	$V_{fuel}/V_{H_2O_2} = 50:0.3$, $m_{cat} = 0.32$ g, $T = 60$ °C.	A 55–99% conversion of DBT, depending on reaction conditions. The catalyst could be reused 10 times.	[151]
Commercial Diesel ([S] ₀ = 440 ppm)	Ce/Fe-AC	DMF	$V_{fuel} = 10$ mL, $T = 45$ °C, $t = 30$ min. (Oxidant = TBHP)	Final <i>S</i> content decreased to 38 ppm.	[152]
DBT, BT, and Th in EtOH/n-Heptane (1:1 v/v) ([S] ₀ = 250–1000 ppm)	C@H ₅ PMo ₁₀ V ₂ O ₄₀	Et ₂ O	$V_{fuel} = 5$ mL, $m_{cat} = 1.4 \times 10^{-4}$ g, $V_{H_2O_2} = 8$ µL.	90, 86, and 60% removal were observed depending on [S] ₀ (250, 500, and 1000 ppm, respectively).	[82]
Light Cycle Oil (LCO) ([S] ₀ = 530 ppm)	C@H ₅ PMo ₁₀ V ₂ O ₄₀	DMF	$V_{fuel} = 5$ mL + 5 mL of Solvent EtOH: n-Heptane (1:1 v/v), $m_{cat} = 1.5 \times 10^{-4}$ g, $V_{H_2O_2} = 8.5$ µL	A 76% reduction of sulfur was observed.	[82]
DBT in n-Octane ([S] ₀ = 100 ppm)	HPW/NOLC	MeOH	$V_{fuel} = 10$ mL, $C_{cat} = 2$ –10 g L ⁻¹ , $H_2O_2/S = 2$ –10, $T = 30$ –80 °C, $t = 0.5$ –3 h.	Increasing HPW loading (5–10%): Higher <i>S</i> removal (95–100%, respectively). <i>S</i> removal reached saturation in 2 h (at $C_{cat} = 4$ g L ⁻¹). Increasing H_2O_2/S ratio (2 to 6): Sharp improvement in <i>S</i> removal; a further increase to 8 results in complete <i>S</i> removal. Increasing temperature (30 to 40 °C): a sharp increase in <i>S</i> removal. Further increasing to 60 °C allows complete <i>S</i> conversion. At 80 °C, a slight decrease in <i>S</i> removal was observed. > 90% conversion for 10 cycles.	[83]

* If the model fuel is described using the word ‘and’, it means the model fuel was a mixture of sulfur compounds. The word ‘or’ indicates that the sulfur compounds were used independently. Legend: NM = not mentioned. AC = activated carbon. ACN = acetonitrile. CNT = carbon nanotube. DMF = dimethylformamide. EtOH = ethanol. Et₂O = diethyl ether. g-C₃N₄ = graphitic carbon nitride. GO = graphene oxide. HPW = phosphotungstic acid (H₃PW₁₂O₄₀). MeOH = methanol. mpg-C₃N₄ = mesoporous graphitic carbon nitride. NOLC = N-doped onion-like carbon.

Table 2.5. ODS using H₂O₂ as oxidant with hybrid materials based in carbon nanotubes (CNTs), graphene oxide (GO), and reduced GO (rGO) in an L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
DBT, BT or 4,6-DMDBT in n-Octane ([S] ₀ = 800 µg g ⁻¹)	WO ₃ /CNT	ACN	$V_{fuel}/V_{ACN} = 5$, $m_{cat} = 0.03$ g, $H_2O_2/S = 5$, $T = 50$ °C, $t = 60$ min.	Removals of ~78, 90, and 85% were observed for BT, DBT, and 4,6-DMDBT, respectively. DBT conversion was maintained for 4 cycles, in the 5 th run decreasing to 80%. The order of reactivity was DBT > 4,6-DMDBT > 2-MBT ~ 3-MBT > 3-MTh. Conversion of all <i>S</i> compounds was higher than 99%. After the 6 th recycle run, conversion dropped to around 40–78% (depending on the compound) and stabilized around 40–70% up to the 10 th run. On the other hand, yield towards the respective sulfones varied between 38–99% depending on the <i>S</i> compound.	[86]
DBT, 4,6-DMDBT, 2-MBT, 3-MBT, 3-MTh in n-Octane ([S] ₀ = 2.8 mg mL ⁻¹)	CNT/PVP/MTO	ACN	$V_{fuel} = 2$ mL, molar ratio fuel/ACN = 3:1, $n_{cat} = 0.1$ mmol, $t = 24$ h, $T = 60$ °C, 4 equivalents of H ₂ O ₂ ,	With no extraction solvent, removal rates were low. The best desulfurization was observed at 60 °C, 7.5 mg of catalyst, H_2O_2/S ratio of 2, resulting in 99% desulfurization. Increasing <i>S</i> concentration slightly decreased conversion to 98%.	[109]
DBT in n-Octane (<i>C</i> ₀ = 100–500 ppm)	NH ₂ /COOH-CNT/MoO ₃	ACN	$V_{fuel}/V_{ACN} = 2$, $m_{cat} = 2.5$ –7.5 mg, $H_2O_2/S = 0.5$ –2, $T = 25$ –60 °C.	90% conversion of DBT for [S] ₀ = 100 or 300 ppm, which drops to 95% when [S] ₀ = 600 ppm. The maximum conversion of BT is 99%, whereas 4,6-DMDBT is 82%. Conversion depends on the initial concentration of precursors.	[110]
DBT ([S] ₀ = 100–600 ppm), BT ([S] ₀ = 300 ppm), or 4,6-DMDBT ([S] ₀ = 300 ppm) in n-Octane	WO ₃ /MoO ₃ -CNT	ACN	$V_{fuel}/V_{ACN} = 5$, $n_{cat} = 0.1$ –0.3 mmol, $V_{H_2O_2} = 0.5$ –1.5 mL, $T = 25$ –60 °C.	At room temperature, a conversion higher than 95% was obtained. After the 4 th recycle run, conversion dropped to 25% due to poisoning of active sites.	[111]
DBT in n-Hexane ([S] ₀ = 521 ppm)	W/CNT	ACN	$V_{fuel}/V_{ACN} = 2$, $C_{cat} = 5$ g L ⁻¹ , $H_2O_2/S = 17$, $T = 10$ –50 °C, $t = 90$ min.	Using CNT as support increased <i>S</i> removal from 90% to 100%, Compared to AC support. A 100% conversion of DBT was obtained, and a 100% yield towards the sulfones. Three cycles were run with only a slight decline in conversion.	[103]
DBT in n-Octane ([S] ₀ = 100–1100 ppm)	CS _{2.5} H _{0.5} PW ₁₂ O ₄₀ /CNT CS _{2.5} H _{0.5} PW ₁₂ O ₄₀ /AC	ACN	$V_{fuel}/V_{ACN} = 1$, $m_{cat} = 1$ wt.% (in relation to fuel), $H_2O_2/S = 20$, $T = 60$ °C, $t = 160$ min.	Increasing catalyst load over 0.2 g does not significantly affect desulfurization. The best H_2O_2/S ratio was 8.95% of DBT was converted in 8 h and maintained for 5 cycles.	[101]
DBT in n-Octane ([S] ₀ = 320 ppm)	HPW/rGO	MeOH	$V_{fuel}/V_{MeOH} = 1.5$, $m_{cat} = 0.1$ –0.25 g, $H_2O_2/S = 2$ –8, $T = 60$ °C.	DBT and 4,6-DMDBT removal achieved 100%, whereas BT was only 70%. In mixed fuel, overall <i>S</i> removal was 99%. Removal of <i>S</i> higher than 90% for 8 cycles.	[113]
DBT, BT, or 4,6-DMDBT ([S] ₀ = 500 ppm, each) in n-hexane and a mixed fuel of DBT, BT, and 4,6-DMDBT ([S] ₀ = 500 ppm, Total) in n-Hexane	HPW/GO	ACN	$V_{fuel}/V_{ACN} = 1$, $C_{cat} = 5$ g L ⁻¹ , $H_2O_2/S = 6$, $T = 60$ °C.	BT removal varied from 55–70%, DBT 70–100%, and 4,6-DMDBT 70–100%, depending on operational conditions. Optimal operating conditions were 50 °C, $V_{extractant}/V_{fuel}$ of 0.3 and H_2O_2/S of 6.	[153]
DBT, BT, or 4,6-DMDBT in n-Hexane ([S] ₀ = 500 mg g ⁻¹)	H ₃ PMo ₁₂ O ₄₀ -GO	ACN	$V_{ACN}/V_{fuel} = 0.1$ –1, $C_{cat} = 1$ –3 g L ⁻¹ , $H_2O_2/S = 2$ –8, $T = 25$ –60 °C.		[154]

Legend: AC = activated carbon. ACN = acetonitrile. DMF = dimethylformamide. [DVim] = cation from the IL 113divinyl-3-decyl diimidazolium bromide. PVP = poly(4-vinyl pyridine). HPW = phosphotungstic acid (H₃PW₁₂O₄₀). MeOH = methanol. MTO = Methyltrioxorhenium. POM = polyoxometalate (H₈P₂Mo₁₆V₂O₆₂·14H₂O). [Vim] = cation from the IL 1-vinyl-3-amyliimidazolium bromide

Table 2.6. ODS using H_2O_2 as oxidant with hybrid materials based on activated carbon (AC) in L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
Th in a mixed Solvent ([S] ₀ = 489 ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{fuel}/V_{H_2O_2} = 5$, $m_{cat} = 0.5$ g, 0.05 g of CTAB, Emulsified System.	In simulated fuel (n-Hexane), desulfurization is 90% (90 °C, 120 min). Mixed solvents: adding 1–15 wt.% of xylene, Th removal was 75.9–59.2%. Cyclohexane addition (1–15 wt.%), Th Removal of 62–7%. Octadiene (1–15 wt.%) decreased Th conversion to 52.6–31.4%.	[91]
Commercial Gasoline ([S] ₀ = 280 ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{fuel}/V_{H_2O_2} = 5$, $m_{cat} = 0.5$ g, 0.05 g of CTAB, Emulsified System.	Sulfur removal depended greatly on the compound. Th desulfurization was only 32%.	[91]
DBT in n-Octane ($C_0 = 2000$ ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{fuel} = 40$ mL, mass ratio cat: fuel = 1.25:100, vol. ratio H ₂ O ₂ : fuel = 1:10, $T = 60$ °C, $t = 12$ min, 70 W.	Decreasing particle size of the AC support improves desulfurization due to increased surface area. Increasing HPW loading up to 10% increases desulfurization; however, further increasing reduces AC surface area and interferes with the AC structure effect in the ultrasound-assisted process. Ultrasound power over 70 W did not improve desulfurization. DBT removal was 100%.	[108]
Th in n-Octane ($C_0 = 656$ ppm)	Pd/AC	Aqueous solution (2 g NaOH + 5 g water + 2.5 g 2-propanol)	$m_{fuel} = 14$ g, $m_{extractant} = 9.5$ g, $m_{cat} = 0.05$ g, $m_{oxidant} = 2.5$ g (2-Propanol), $T = 50$ – 70 °C.	After 20 min at 70 °C, a model fuel with sulfur content lower than 1 ppm is obtained. Obtaining fuels with ultra-low sulfur at lower temperatures is possible; however, more time is required. >99% conversion was maintained for 5 cycles.	[104]
DBT in n-Octane ($C_0 = 2000$ ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{H_2O_2}/V_{fuel} = 1:400$ – $1:10$ ($H_2O_2/S = 3$ – 123), $C_{cat} = 1.25$ wt.%, $T = 40$ – 70 °C, $t = 3$ – 30 min, 70–100 W Ultrasound, Emulsion Formation.	Upon increasing HPW loading (10 wt.%), the reaction rate increased. Increasing cat concentration improves desulfurization (up to 1.25 wt.%), whereas higher cat loading hinders propagation of US waves. Comparing the US-assisted process to a regularly mixed process, US resulted in a 30% improvement. Temperature played a significant role in increasing reaction rate. At 40 °C, 70% of DBT is oxidized in 30 min; at 70 °C, 100% is oxidized in 9 min. The proper amount of oxidant was important to fully wet the carbon surface and to permit emulsion formation. Desulfurization decreased to 90% and ~75% in the 2 nd and 3 rd runs, respectively.	[107]
DBT in n-Octane ([S] ₀ = 300 ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$m_{fuel} = 25$ g, $m_{cat} = 0.1$ g, $H_2O_2/S = 4$, $T = 80$ °C, $t = 40$ min.	HPW Loading of 10% was found as optimal. Increasing the H_2O_2/S ratio and temperature improves desulfurization. At lower temperatures, a higher amount of oxidant is necessary to achieve full desulfurization. A total of 100% removal of DBT was obtained.	[105]
DBT in n-Octane ([S] ₀ = 500–1000 ppm)	Mo ₀₁₃₂ /AC	ACN	$V_{fuel}/V_{ACN} = 1$, $m_{cat} = 0$ – 0.005 g, $H_2O_2/S = 2$ – 30 , $T = 25$ – 45 °C.	N.C.: 46% removal of DBT observed in 120 min. With 0.0025 g of catalyst: 100% removal in 30 min. Temperature reduced time required to achieve deep desulfurization to 10 min at 45 °C. Increasing the H_2O_2/S ratio (10) improved desulfurization, further increase negatively affected S removal. 100% removal was achieved for [S] ₀ of 500, 700, and 1000 ppm in 30, 60, and 120 min.	[106]

Legend: ACN = acetonitrile. HPW = phosphotungstic acid (H₃PW₁₂O₄₀).

Table 2.7. ODS using mainly H₂O₂ with hybrid materials based on other carbon forms in L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
Th, BT, DBT, or 4,6-DMDBT in n-Octane ([S] ₀ = 1000 ppm)	TiO ₂ -C	ACN	$V_{fuel}/V_{ACN} = 2$, $m_{cat} = 20$ mg, $V_{H_2O_2} = 0.114$ mL ($H_2O_2/S = 15$), $T = 80$ °C.	The reactivity order is DBT (100%) > BT (60%) > Th (50%) > 4,6-DMDBT (38%). For DBT model fuel, conversion >95% was maintained for 5 runs.	[92]
Th in n-Heptane ($C_0 = 300$ ppm)	MoO ₂ /C	IL: [Hnmp]BF ₄	$V_{fuel}/V_{IL} = 20:3$, $m_{cat} = 0.1$ g, $V_{H_2O_2} = 2$ mL, $T = 70$ °C.	Upon increasing IL and H ₂ O ₂ , higher Th removal was observed. Temperature played a very relevant role: removals of >95% (70 °C), 65% (60 °C), 50% (50 °C), and <20% (40 °C) in 240 min were observed.	[88]
Th, BT or DBT in n-Octane ([S] ₀ = 1000 ppm)	W ₂ N/C	ACN	$V_{fuel}/V_{ACN} = 2$, $m_{cat} = 0.02$ g, $H_2O_2/S = 15$, $T = 30$ –80 °C.	DBT conversion maintained over 90% for 5 cycles. Removals of Th and BT were 80 and 90%, respectively.	[93]
DBT in Hexane ($C_0 = 1000$ ppm)	PET-Modified Red Mud	ACN	$V_{fuel}/V_{ACN} = 5$, $m_{cat} = 5$ –20 mg, $V_{H_2O_2} = 1$ mL, $T = 25$ °C.	Maximum removal of 80% is observed at a catalyst loading of 10 mg. Exceeding that value does not improve desulfurization.	[94]
BT, DBT or 4,6-DMDBT in Heptane ($C_0 = 0.5$ mmol)	H ₃ PMo ₁₂ O ₄₀ /C	H ₂ O	$V_{fuel}/V_{H_2O} = 1$, $n_{cat} = 0.0041$ mmol, $n_{H_2O_2} = 1.5$ mmol, $H_2O_2/S = 3$, $T = 60$ °C.	A 100% conversion of DBT in 30 min for 8 Cycles. 4,6-DMDBT required 60 min to be degraded, whereas BT Required 120 min. Increasing H_2O_2/S over 3 impacted the efficiency of H ₂ O ₂ use. Increasing reaction temperature over 60 °C negatively affected the reaction.	[100]
Pyrolysis Oil of Waste Tires ([S] ₀ = 7139 ppm)	Biochar	Aqueous 10 wt.% H ₂ O ₂ Phase	$m_{fuel} = 2$ g, $V_{extractant} = 15$ mL, $V_{H_2O_2} = 15$ mL (10 w/v), $T = 60$ –100 °C, $t = 2$ –6 h.	Desulfurization ranged from 33–64% depending on catalyst concentration and the precursor of the biochar (coffee ground or waste tire).	[155]
DBT, Th, BT, or 4,6-DMDBT in n-Octane ($C_0 = 1000$ ppm)	Co/N-doped C	ACN	$V_{fuel}/V_{ACN} = 4$, $m_{cat} = 10$ mg, $V_{H_2O_2} = 0.2$ mL, $H_2O_2/S = 15$, $T = 70$ °C, $t = 120$ min.	~93% removal of DBT for 5 cycles. BT, Th, and 4,6-DMDBT removals were 65, 50, and 50%, respectively.	[112]
DBT, 4-MDBT or 4,6-DMDB in Dodecane ([S] ₀ = 200 ppm)	HPW/3D-CS	Adsorption on 3D-CS	$V_{fuel} = 5$ mL, 1 mL of acetic acid, $m_{cat} = 0.2$ g, $H_2O_2/S = 8$, $T = 70$ °C, $t = 40$ min.	The optimal loading of HPW was found to be 7 wt.%. A total of 100% removal of DBT maintained for 3 cycles, slight decrease on the 4 th and 5 th cycles (to 93%). Desulfurization rate was very similar regardless of the model S compound. 100% desulfurization was achieved for all model oils in 2.5 h.	[97]
Th in n-Octane ([S] ₀ = 1000 ppm)	[C _n VP]MoV/CA ($n = 2, 4, 6, 8$, or 10)	DMF	$V_{fuel}/V_{DMF} = 4$, $m_{cat} = 0.04$ g, O ₂ flow rate 1 L min ⁻¹ , $T =$ room temperature.	Increasing the chain length of the catalyst ($n = 2$ –6) increases desulfurization. For $n > 6$, the steric hindrance of the material increases, and desulfurization is hindered. The maximum removal observed was 99.6%.	[89]

Legend: ACN = acetonitrile. CA = carbon aerogel. CS = carbon spheres. [C_nVP] = cation from the IL N-alkyl-4-vinylpyridinium bromide. DMF = dimethylformamide. IL = ionic liquid. MoV = heteropoly acid substituted by vanadium (H₈P₂Mo₁₆V₂O₆₂).

Table 2.8. ODS using mainly H₂O₂ with hybrid materials based on graphitic carbon nitride (g-C₃N₄) in L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
BT, DBT, or 4,6-DMDBT in n-Octane ([S] ₀ = 320 ppm)	MoO ₃ /g-C ₃ N ₄	MeOH	$V_{fuel}/V_{MeOH} = 1$, $C_{cat} = 0.013$ mg L ⁻¹ , $H_2O_2/S = 4$, $T = 60$ °C.	With the addition of specific scavengers for 'O ₂ ⁻ , h ⁺ , e ⁻ and HO [•] ', the authors have observed that HO [•] was the most important radical. Desulfurization rates were >96% removal for 6 cycles (DBT), >85% for 4,6-DMDBT and 60% for BT.	[95]
DBT, BT or Th in n-Octane ([S] ₀ = 500 µg g ⁻¹)	WO ₃ /g-C ₃ N ₄	IL: 1-Ethyl-3-Methylimidazolium Ethyl Sulfate	$V_{fuel}/V_{IL} = 5$, $m_{cat} = 0.02$ g, $V_{H_2O_2} = 0.2$ mL, $T = 70$ °C, $t = 3$ h.	WO ₃ supported over g-C ₃ N ₄ has a higher desulfurization activity than unsupported WO ₃ or supported over alumina. The order of reactivity was DBT (96%) > BT (73%) > Th (53%). The catalyst could be reused 5 times with >85% removal of DBT.	[90]
DBT, BT or Th in n-Octane ([S] ₀ = 500 µg g ⁻¹)	CoWO ₄ /g-C ₃ N ₄	IL: [EMIM][EtSO ₄]	$V_{fuel}/V_{IL} = 5$, $m_{cat} = 0.03$ g, $V_{H_2O_2} = 0.4$ mL, $T = 80$ °C, $t = 180$ min.	DBT was easily removed, achieving over 90% conversion, maintained for 5 cycles. BT and Th maximum removals were 40%.	[102]
DBT, 4,6-DMDBT or Th in n-Octane ([S] ₀ = 500 µg g ⁻¹)	MoO ₂ /g-C ₃ N ₄	IL: [BMIM][BF ₄]	$V_{fuel}/V_{IL} = 10-3.333$, $m_{cat} = 0-0.03$ g, $V_{H_2O_2} = 0-0.2$ mL, $T = 50-80$ °C.	Increasing loading of MoO ₂ to 3 wt.% resulted in higher desulfurization. A 5 wt.% loading negatively affected the S removal. Temperatures higher than 60 °C, catalyst dosage over 0.02 g, and IL volume higher than 1 mL resulted in lower desulfurization performances. Maximum removal was observed with 0.2 mL of oxidant. Maximum conversions were 95% (DBT, 120 min), 60% (4,6-DMDBT, 140 min) and 35% (Th, 140 min).	[98]
BT, DBT, or 4,6-DMDBT in n-Octane ([S] ₀ = 800 ppm)	MoO _x @3D-g-C ₃ N ₄	Methyl cyanide	$V_{fuel}/V_{Extrac.} = 5$, $m_{cat} = 0.005-0.01$ g, $m_{H_2O_2} = 0.15$ g ($H_2O_2/S = 5$), $T = 0-60$ °C, $t = 75$ min.	Maximum desulfurization was 100% for DBT, 91% for BT and 91% for 4,6-DMDBT.	[99]
DBT, BT or Th in n-Octane ([S] ₀ = 500 ppm)	WO ₃ /g-C ₃ N ₄	IL: 1-Ethyl-3-Methylimidazolium Diethylsulfate	$V_{fuel}/V_{IL} = 20$, $m_{cat} = 0.03$ g, $V_{H_2O_2} = 0.3$ mL, $T = 60$ °C, $t = 180$ min.	Increasing WO ₃ loading to 36% results in an increase in desulfurization. With 50% loading, the desulfurization was negatively affected. 90% conversion for DBT was observed (150 min) and maintained for 5 cycles. Th Removal of 60% was observed regardless of reaction time (20–180 min), and for BT a maximum of 43% was obtained in 180 min.	[96]

Legend: IL = ionic liquid. MeOH = methanol.

Table 2.9. Other ODS systems with carbon-based hybrid materials.

Fuel*	Catalyst	Oxidant	Extractant	Operational Conditions	Results	Ref.
DBT in n-Octane ([S] ₀ = 2000 ppm)	CNT@PPDA	O ₂	N.M.	$V_{fuel} = 100 \text{ mL}$, $C_{cat} = 1 \text{ g L}^{-1}$, 1.5 L min^{-1} of O ₂ , $T = 70 \text{ }^{\circ}\text{C}$.	Temperature was key, followed by catalyst mass and oxygen. DBT conversion >95% for 8 cycles.	[156]
DBT in n-Octane ([S] ₀ = 2000 ppm)	CNT@MOF-199- H ₈ P ₂ Mo ₁₆ V ₂ O ₆₂	O ₂	N.M.	$V_{fuel} = 50 \text{ mL}$, $m_{cat} = 0.1 \text{ g}$, 1.5 L min^{-1} O ₂ flow, $T = 60 \text{ }^{\circ}\text{C}$.	~100% DBT Removal in 180 min. >90% conversion maintained for 7 cycles.	[157]
DBT, 4-DMDBT or 4,6-DMDBT in n-Octane ([S] ₀ = 2000 ppm)	P[C ₂ VP] Br/AC, P[C ₂ VP] Br/CA, P[C ₂ VP] Br/CNT, P[C ₂ VP] Br/GO	O ₂	N.M.	$V_{fuel} = 50 \text{ mL}$, $15 \text{ } \mu\text{mol}$ of the active phase of catalyst, 1.5 L min^{-1} of O ₂ , $T = 70 \text{ }^{\circ}\text{C}$.	Activity followed surface area. DBT removal stayed 99.2% for 5 cycles, dropping to 95% by cycle 6 and 90% by cycle 8. 4-DMDBT and 4,6-DMDBT conversions were 95% and 80%.	[120]
DBT or 4,6-DMDBT in n-Octane ([S] ₀ = 500 ppm)	VO-MoO ₂ @N-doped CNT	CHP	N.M.	$V_{fuel} = 15 \text{ mL}$, $m_{cat} = 0.08 \text{ g}$, $CHP/S = 4$, $T = 70 \text{ }^{\circ}\text{C}$, $t = 1 \text{ h}$.	100% removal for both S compounds. For 4,6-DMDBT, 4 recycle runs with no change in conversion. From the 5 th run, a linear decrease was observed up to the 8 th run (which resulted in 80% conversion).	[122]
DBT, 4-MDBT, or 4,6-DMDBT in Dodecane ([S] ₀ = 200 ppm)	[(C ₈ H ₁₇) ₃ NCH ₃] ₃ H ₃ V ₁₀ O ₂₈ / 3D-g-C ₃ N ₄	Air (O ₂)	Adsorption by the catalyst	$V_{fuel} = 20 \text{ mL}$, $m_{cat} = 0.01 \text{ g}$, 100 mL min^{-1} air flow, $T = 120 \text{ }^{\circ}\text{C}$.	In 6 h: >95% of S removal, regardless of the S compound for 5 cycles. Adding 5 wt.% of cyclohexane and p-xylene slowed reaction: deep desulfurization in 8 h of reaction.	[117]
DBT, 4-MDBT, 4,6-DMDBT, or 3-MBT in n-Octane ([S] ₀ = 500 ppm)	WO ₃ /few-layer g-C ₃ N ₄	H ₂ O ₂	Adsorption by the catalyst	$V_{fuel} = 5 \text{ mL}$, $m_{cat} = 0.05 \text{ g}$, $H_2O_2/S = 3$, $T = 50 \text{ }^{\circ}\text{C}$, $t = 40 \text{ min}$.	100% removal for 6 runs (DBT). 100% removal in 60 min was obtained for all S compounds; however, kinetics were distinct (DBT >4-MDBT >4,6-DMDBT >3-MBT).	[114]
DBT in Decalin ($C_0 = 500 \text{ ppm}$)	MoO ₂ /g-C ₃ N ₄	TBHP	N.M.	$m_{fuel} = 10 \text{ g}$, $m_{cat} = 0.05 \text{ g}$, $m_{TBHP} = 0.1141 \text{ g}$ ($TBHP/S = 3$), $T = 80 \text{ }^{\circ}\text{C}$, $t = 2 \text{ h}$.	100% removal Of DBT. Hydroxyl radicals (HO [•]) and electrons (e ⁻) are the main active species in DBT oxidation, followed by [•] O ₂ .	[115]
DBT ([S] ₀ = 500 ppm) and 4,6-DMDBT ([S] ₀ = 250 ppm) in n-Octane	[(C ₆ H ₁₃) ₃ PC ₁₄ H ₂₉] ₃ P Mo ₁₂ O ₄₀ / g-C ₃ N ₄	H ₂ O ₂	Adsorption on g-C ₃ N ₄ .	$V_{fuel} = 5 \text{ mL}$, $m_{cat} = 0.05 \text{ g}$, $H_2O_2/S = 4$, $t = 180 \text{ min}$.	>93% of removal of DBT and >90% of 4,6-DMDBT maintained for 6 cycles.	[116]
DBT, 4,6-DMDBT or BT in n-Octane ($C_0 = 500 \text{ ppm}$)	V/P-doped g-C ₃ N ₄	TBHP	N.M.	$V_{fuel} = 30 \text{ mL}$, $m_{cat} = 0.02 \text{ g}$, $m_{TBHP} = 0.0313 \text{ g}$, $T = \text{room temperature}$ -60 °C.	100% DBT removal in 60 min. Over 80% removal was maintained for 5 cycles. BT and 4,6-DMDBT removals were 80 and 75%, respectively.	[121]
DBT in n-Hexane ([S] ₀ = 500 ppm) and BT, DBT, and 4,6-DMDBT ([S] ₀ = 125 ppm, each) in n-Octane	MoO ₂ @GNF	TBHP	N.M.	$V_{fuel} = 5 \text{ mL}$, $m_{cat} = 5 \text{ mg}$, $V_{TBHP} = 0.14 \text{ mL}$, $T = 60 \text{ }^{\circ}\text{C}$, $t = 120 \text{ min}$. Solvent-Free.	The synthesized catalyst acts as a nanosponge for the oxidized compounds; no extractant is required. Desulfurization achieved values >95% for all components resulting in a final S content of 6.5 ppm.	[129]
DBT, BT, or 4,6-DMDBT in n-Octane ([S] ₀ = 500 μg mL ⁻¹)	V ₂ O ₅ @C	CHP	N.M.	$V_{fuel} = 10 \text{ mL}$, $m_{cat} = 50 \text{ mg}$, $V_{CHP} = 0.17 \text{ mL}$, $T = 60 \text{ }^{\circ}\text{C}$, $t = 5 \text{ h}$.	BT has the lowest desulfurization (63%), followed by 4,6-DMDBT (80%) and DBT (100%). Up to 7 cycles with no obvious decrease in catalytic activity.	[158]

Legend: 3D-g-C₃N₄ = three-dimensional graphitic carbon nitride. AC = activated carbon. CA = carbon aerogel. CF = carbon fibers. CHP = cumene hydroperoxide. CNT = carbon nanotube. GC = graphitic carbon. GNF = graphitized carbon nanofiber. GO = graphene oxide. MC = mesoporous carbon. P[C₂VP] Br = Poly (N-ethyl-4-vinylpyridinium bromide). PPDA = Poly diallyldimethylammonium chloride. [PSPy] = N-(3-sulfonate propyl)-pyridinium. TBHP = tert-butyl hydroperoxide.

Table 2.9. Other ODS systems with carbon-based hybrid materials (continuation).

Fuel*	Catalyst	Oxidant	Extractant	Operational Conditions	Results	Ref.
DBT, 4-MDBT, and 4,6-DMDBT in Dodecane ($[S]_0 = 200 \text{ mg kg}^{-1}$)	MoO ₃ /MC	O ₂	Adsorption in the catalyst.	$V_{fuel} = 20 \text{ mL}$, $m_{cat} = 0.01 \text{ g}$, 100 mL min^{-1} of O ₂ , $T = 120 \text{ }^\circ\text{C}$.	All compounds were removed within 6 h of reaction. DBT displayed much faster kinetics compared to 4-MDBT and 4,6-DMDBT. Upon adding other components of diesel to the simulated fuel (Cyclohexane, Paraxylene, and 1-Octene), the desulfurization rate decreased. However, it was still possible to achieve 100% removal, requiring longer reaction times. >98% maintained for 7 cycles.	[159]
DBT in Tridecane ($C_0 = 100\text{--}2000 \text{ } \mu\text{g g}^{-1}$)	FePc (NO ₂) ₃ -CF	O ₂	N.M.	$V_{fuel} = 25 \text{ mL}$, $m_{cat} = 0.25 \text{ g}$, 0.2 MPa of O ₂ initial pressure, $T = 130 \text{ }^\circ\text{C}$.	Upon increasing initial concentration, DBT conversion decreased from 100% to 60% (100 and 2000 mg g ⁻¹ initial DBT concentration, respectively).	[118]
DBT, 4,6-DMDBT or BT in n-Octane ($[S]_0 = 250\text{--}500 \text{ ppm}$)	[PSPy] ₃ PMO ₁₂ O ₄ /GC	H ₂ O ₂	Oxidized Compounds were removed in the catalyst phase.	$V_{fuel} = 5 \text{ mL}$, $m_{cat} = 0.05 \text{ g}$, $V_{H_2O_2} = 24 \text{ } \mu\text{L}$ ($H_2O_2/S = 3$), $T = 50 \text{ }^\circ\text{C}$.	Removals were 100%, 90% and 50% for DBT, 4,6-DMDBT and BT, respectively. Results were maintained for 6 cycles.	[128]
DBT, 4-MDBT or 4,6-DMDBT in n-Octane ($[S]_0 = 500 \text{ ppm}$)	TiO ₂ /GC	H ₂ O ₂	Oxidized products extracted in the catalyst phase.	$V_{fuel} = 5 \text{ mL}$, $m_{cat} = 0.01 \text{ g}$, $V_{H_2O_2} = 32 \text{ } \mu\text{L}$ ($H_2O_2/S = 4$), $T = 50 \text{ }^\circ\text{C}$.	10% loading of TiO ₂ , 100% in 40 min for 10 cycles. Desulfurization for 4,6-DMDBT and 4-MDBT were 77% and 99%, respectively. Upon adding 5-10 wt.% of p-Xylene in the fuel, desulfurization was not greatly affected (100% and 96%, respectively). A slight decrease was observed when 5 or 10 wt.% of cyclohexane was added (85% and 75%, respectively). The radical 'O ₂ ' was found as the main active constituent in the ODS of DBT.	[119]

Legend: 3D-g-C₃N₄ = three-dimensional graphitic carbon nitride. AC = activated carbon. CA = carbon aerogel. CF = carbon fibers. CHP = cumene hydroperoxide. CNT = carbon nanotube. GC = graphitic carbon. GNF = graphitized carbon nanofiber. GO = graphene oxide. MC = mesoporous carbon. P[C₂VP] Br = Poly (N-ethyl-4-vinylpyridinium bromide). PPDA = Poly diallyldimethylammonium chloride. [PSPy] = N-(3-sulfonate propyl)-pyridinium. TBHP = tert-butyl hydroperoxide.

Table 2.10. ODS with carbon hybrid materials in photocatalytic systems.

Fuel	Catalyst	Oxidant	Extractant	Operational Conditions	Results	Ref.
DBT ([S] ₀ = 500 ppm), BT ([S] ₀ = 250 ppm), and RSH ([S] ₀ = 250 ppm) in Acetonitrile	TiO ₂ /g-C ₃ N ₄	H ₂ O ₂	1-Methyl-2-Pyrrolidone	$V_{fuel} = 20$ mL, $m_{cat} = 0.2$ g, $H_2O_2/S = 7$, $T = 30$ °C, $t = 2$ h, 250 W High-Pressure Hg Lamp. 2-Step Process.	S removal was higher in the photocatalytic system. RSH compounds were more easily removed (100%) than BT and DBT (90%).	[123]
DBT in n-Octane ([S] ₀ = 200 ppm)	CeO ₂ /Attapulgate /g-C ₃ N ₄	H ₂ O ₂	ACN	Mass ratio Cat/DBT = 1:10, $H_2O_2/DBT = 1:4$, $t = 3$ h, 300 W Xenon Lamp. 2-Step Process	100% removal of DBT. Conversion maintained above 90% for up to 8 cycles.	[124]
DBT in n-Octane ([S] ₀ = 200 ppm)	CQD/Attapulgate	H ₂ O ₂	ACN	Mass ratio Cat/Fuel = 1:1000, $t = 5$ h, 300 W Xenon Lamp. 2-Step Process	92.3% removal of DBT.	[125]
Th in n-Octane ($C_0 = 800$ µL L ⁻¹)	ZnTcPc/g-C ₃ N ₄	O ₂	CH ₂ Cl ₂	$V_{fuel} = 100$ mL, $m_{cat} = 20$ mg, Visible Light Irradiation. 2-Step Process.	85% removal of DBT in 90 min.	[126]
DBT or 4,6-DMDBT in Tetradecane ([S] ₀ = 200 ppm)	CNT/TiO ₂	NA	Adsorption with Silica.	$V_{fuel} = 100$ mL, $m_{cat} = 1$ g, High-Pressure Hg Lamp.	Desulfurization in simulated matrix: 80% for DBT and 70% for 4,6-DMDBT.	[127]
Commercial Diesel ([S] ₀ = 714 ppm)	CNT/TiO ₂	NA	Adsorption with Silica.	$V_{fuel} = 100$ mL, $m_{cat} = 1$ g, High-Pressure Hg Lamp.	S content decreased to 0 ppm after 120 min of reaction.	[127]

Legend: ACN = acetonitrile. CNT = carbon nanotube. g-C₃N₄ = graphitic carbon nitride. NA = not applicable.

Table 2.11. ODS with carbon-based materials as catalysts on their own.

Fuel	Catalyst	Oxidant	Extractant	Operational Conditions	Results	Ref.
DBT in n-Octane ([S] ₀ = 500 ppm)	oCNT	H ₂ O ₂	IL: OmimPF ₆	$V_{fuel}/V_{IL} = 5$, $m_{cat} = 5$ mg, $V_{H_2O_2} = 64$ μ L, $T = 70$ °C, $t = 60$ min.	Conversion of >95.8% for 5 cycles. Removals of 93.7% (4,6-DMDBT), 100% (DBT), 97.3% (2-MBT), 100% (3-MBT) and 100% (BT) were observed.	[134]
BT, DBT, or 4,6-DMDBT in n-Dodecane ([S] ₀ = 427 ppm)	CNT	O ₂	N.M.	$m_{fuel} = 30$ g, $m_{cat} = 0.01$ g, 150 mL min ⁻¹ of O ₂ , $T = 150$ °C, $t = 40$ min.	100% DBT removal < 30 min. 100% conversion for BT (70 min) and 4,6-DMDBT (45 min). A slight decrease was observed for 5 reuse cycles.	[136]
DBT in Dodecane ([S] ₀ = 200 ppm)	N,O-doped GO	Air (O ₂)	CCl ₄	$V_{fuel} = 20$ mL, $m_{cat} = 10$ mg, 100 mL min ⁻¹ air flow, $T = 120$ °C. 2-step process.	Removals of 99.8% (DBT), 97.5% (4,6-DMDBT) and 88.7% (4-MDBT) in 8 h of reaction were observed.	[131]
Diesel Sample ([S] ₀ = 400 ppm)	N,O-doped GO	Air (O ₂)	CCl ₄	$V_{fuel} = 20$ mL, $m_{cat} = 10$ mg, 100 mL min ⁻¹ air flow, $T = 120$ °C. 2-Step Process.	84% removal of sulfur was observed.	[131]
BT, DBT or 4,6-DMDBT in n-Decane ([S] ₀ = 500–1100 ppm)	GO	Air (O ₂)	ACN	$V_{fuel}/V_{ACN} = 2$, $m_{cat} = 0.6$ mg, 20 mL min ⁻¹ air flow, 4.5 mL FA, $T = 25$ °C, $t = 140$ min, 100 W.	A removal of >99.5% of sulfur was observed. High removal rates were maintained for 3 cycles.	[137]
DBT, BT, 3-MBT and 4,6-DMDBT in Dodecane ([S] ₀ = 400 ppm)	rGO	O ₂	N.M.	$V_{fuel} = 25$ mL, $m_{cat} = 5$ mg, 200 mL min ⁻¹ O ₂ flow, $T = 140$ °C, $t = 6$ h.	Removals of 96.1% (3-MBT), 90.5% (BT), 100% (DBT), and 97.7% (4,6-DMDBT) were observed.	[135]
Jet fuel (JP-8) ([S] ₀ = 717 ppm)	AC	H ₂ O ₂ + FA	N.M.	$V_{fuel} = 10$ mL, $m_{cat} = 0.1$ g, $V_{oxidant} = 2$ mL, $T = 25$ °C, $t = 4$ h.	Acid treatment leads to better removal performance compared to ammonia treatment. Removals in the range of 41–69% were obtained.	[138]
JP-8 ([S] ₀ = 717 ppm)	AC	H ₂ O ₂ + FA	Adsorption	$V_{fuel} = 36$ mL, $m_{cat} = 0.3$ g, $V_{oxidant} = 7$ mL, $T = 60$ °C, $t = 60$ min, Ultrasound: 20 kHz, and Amplitude of 60%.	Over 94% of sulfur was removed.	[132]
Ultra-Low-Sulfur Diesel ([S] ₀ = 9 ppm)	AC	H ₂ O ₂ + FA	Adsorption	$V_{fuel} = 36$ mL, $m_{cat} = 0.3$ g, $V_{oxidant} = 7$ mL, $T = 60$ °C, $t = 60$ min, US: 20 kHz	It was possible to obtain a fuel with less than 1 ppm of sulfur.	[132]
Commercial Diesel ([S] ₀ = 2189 ppm)	AC	H ₂ O ₂ + acetic acid	ACN	$V_{fuel} = 50$ mL, $m_{cat} = 0.5$ g, $H_2O_2/S = 3$, 0.5 g of TBPA, $T = 50$ °C, $t = 1$ h.	After 3 consecutive oxidations, 88–92% removal was observed.	[133]
4,6-DMDBT in Hexadecane ($C_0 = 200$ ppm)	AC	H ₂ O ₂	Adsorption	$V_{fuel} = 10$ mL, $m_{cat} = 25$ mg, $V_{H_2O_2} = 1$ mL, $T = 60$ °C, $t = 24$ h.	75% removal of 4,6-DMDBT for original AC. Oxidized AC, 100% removal in only 10 min.	[130]
JP-8 fuel ([S] ₀ = 1400 or 720 ppm)	AC	H ₂ O ₂	Adsorption	$V_{fuel} = 180$ mL, $V_{H_2O_2} = 35$ mL, 10 mL of formic acid, $m_{cat} = 120$ mg, $T = 60$ °C, $t = 90$ min.	Oxidation only resulted in a small <i>S</i> removal (3–20%). Combining with adsorption, results improved (75–95%).	[160]

Legend: N.M. = not mentioned. AC = activated carbon. ACN = acetonitrile. CNT = carbon nanotube. GO = graphene oxide. IL = ionic liquid. oCNT = oxidized carbon nanotube. rGO = reduced GO, TBPA = Tetrapropylammonium Bromide.

Table 2.12. ODS using mainly H₂O₂ with hybrid materials based on graphitic carbon nitride (g-C₃N₄) in L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
DBT in n-Dodecane (C ₀ = 100–1000 ppm)	GO/COOH	Adsorption	V _{fuel} = 25 mL, m _{cat} = 0.05 g, V _{H₂O₂} = 5 mL, T = 273–313 K, 20 kHz Ultrasound Apparatus at 120 W	95% sulfur removal was achieved for an initial concentration of DBT of 1000 ppm.	[139]
DBT, BT or 4,6-DMDBT in n-Octane ([S] ₀ = 500 ppm)	PW ₁₂ O ₄₀ –/C-Si	ACN	V _{fuel} /V _{ACN} = 1, 4 wt.% of catalyst, H ₂ O ₂ /S = 6, T = 60 °C, 5 min in US to form an emulsion, t = 1 h.	Maximum conversion of 99.86% maintained for 5 cycles.	[147]
Two Real Oil Samples ([S] ₀ = 968.72 and 2668.78 ppm)	PW ₁₂ O ₄₀ –/C-Si	ACN	V _{fuel} /V _{ACN} = 1, 4 wt.% of catalyst, H ₂ O ₂ /S = 6, T = 60 °C, 5 min in US to form an emulsion, t = 1 h.	Three consecutive cycles of ODS resulted in S content lower than 10 ppm.	[147]
DBT in Cyclohexane ([S] ₀ = 50 ppm)	Fe/C and FeMo/C	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 15 mg, V _{H₂O₂} = 1 mL, T = 25 °C, t = 120 min. Emulsion	>60% conversion of DBT for up to 3 cycles.	[143]
DBT in n-Octane ([S] ₀ = 250 ppm)	SiO ₂ @C-dots/[PW ₁₂ O ₃₈] ^{3–}	ACN	V _{fuel} /V _{ACN} = 1, m _{cat} = 0.2 g, H ₂ O ₂ /DBT = 3, T = 60 °C, t = 3 h.	100% removal of DBT in 180 min.	[161]
DBT in Cyclohexane ([S] ₀ = 50 ppm)	Si-C	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 10 mg, V _{H₂O₂} = 1 mL, t = 180 min. Emulsión	Maximum removal of 15 mgs g _{cat} ^{–1} observed.	[144]
Diesel S1800 ([S] ₀ = 1800 ppm)	Si-C	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 10 mg, V _{H₂O₂} = 1 mL, t = 180 min. Emulsion	57% removal of sulfur in Diesel S1800.	[144]
DBT in n-Octane (C ₀ = 800 ppm)	H ₃ PMo ₁₂ O ₄₀ /AmHMSiO ₂ @C	ACN	V _{fuel} /V _{ACN} = 1, n _{cat} = 0.002 mmol, n _{H₂O₂} = 0.15 mmol, T = 40 °C, t = 3 h.	>99% conversion was obtained in 180 min and maintained for 5 cycles.	[140]
DBT (C ₀ = 500 ppm), 4-MDBT (C ₀ = 200 pm), 4,6-DMDBT (C ₀ = 200 ppm) in Dodecane	g-C ₃ N ₄	Adsorption	V _{fuel} = 5 mL, m _{cat} = 0.05 g, H ₂ O ₂ /S = 4, T = 60 °C, t = 60 min, 800 rpm.	100% removal of DBT and ~80% for 4-MDBT and 4,6-DMDBT.	[141]
Th and DBT in Cyclohexane (C ₀ = 100 ppm)	CNT/red mud	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 20 mg, V _{H₂O₂} = 1 mL, Emulsion	67% removal of Th and 82% of DBT in 1 h.	[145]
DBT in Cyclohexane (C ₀ = 500 ppm)	FeMo/CNT	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 20 mg, V _{H₂O₂} = 1 mL, Emulsion	Oxidation efficiency varied between 20–100%.	[146]
DBT in n-Heptane (C ₀ = 0.1 wt.%)	[Bmin] ₃ PMo ₁₂ O ₄ o/g-C ₃ N ₄	Aqueous H ₂ O ₂ Phase	V _{fuel} = 25 mL, m _{cat} = 0.05 g, H ₂ O ₂ /S = 3, T = 40 °C, t = 120 min, 250 W Sodium Lamp.	Conversion increased from ~30% to 94.5% in 120 min with visible light. The active species was found to be HO [•] .	[142]
DBT in Toluene (C ₀ = 50 ppm)	Fe ₂ O ₃ /C	MeOH	V _{fuel} = 9.9 mL, m _{cat} = 10 mg, V _{oxidant} = 0.1 mL (H ₂ O ₂ /HCOOH (1:1 mol/mol)), T = 25 °C. 2-Step	97% conversion of DBT in 180 min of reaction, with a yield towards sulfones of ~60%.	[150]
DBT in Cyclohexane ([S] ₀ = 50 ppm)	Au/RmEtB	Aqueous H ₂ O ₂ Phase	V _{fuel} = 5 mL, m _{cat} = 20 mg, V _{H₂O₂} = 1 mL.	The highest removal rate attained with the carbon-coated catalyst due to amphiphilic characteristics (~4.5 mgs g _{cat} ^{–1}).	[162]
Th, BT and DBT in n-Heptane ([S] ₀ = 500 ppm)	C ₃ N ₂ H ₅ @H ₃ PMo ₁₂ O ₄₀ @CS	ACN	V _{fuel} = 50 mL, m _{cat} = 0.1 g, V _{oxidant} = 3 mL (H ₂ O ₂ /acetic acid), T = 30–35 °C, t = 1 h. 2-step.	>96% removal of S depending on the condition applied.	[163]
Real Gasoline ([S] ₀ = 0.498 wt.%)	C ₃ N ₂ H ₅ @H ₃ PMo ₁₂ O ₄₀ @CS	ACN	V _{fuel} = 50 mL, m _{cat} = 0.1 g, V _{oxidant} = 3 mL (H ₂ O ₂ /acetic acid), T = 30–35 °C, t = 1 h. 2-step.	> 95% removal of S while not impacting other parameters (density, salt content, water content, and distillation point).	[163]

Legend: ACN = acetonitrile. AmHMSiO₂ = amphiphilic hollow mesoporous silica. C-dots = carbon dots. CNT = carbon nanotube. g-C₃N₄ = graphitic carbon nitride. GO = graphene oxide. MeOH = methanol. RmEt = red mud residue modified by chemical vapor deposition using ethanol as a carbon source.

Oliveira et al. (2014) prepared amphiphilic catalysts through the modification of red mud by chemical vapor deposition (CVD) of ethanol [145]. The materials were tested in the PIC-like oxidation of QN in cyclohexane with H_2O_2 . Within 60 min, QN was removed entirely, and this activity was maintained for 5 cycles. They ascribed the exciting results to the amphiphilicity resulting from the carbon deposits after CVD, which allowed the stabilization of the emulsified system, increasing the contact between the organic and the aqueous phases [145]. Similar materials were synthesized by Teixeira et al. (2013) [146] and applied in the biphasic oxidation of QN in a PIC-like system. One hundred percent oxidation of QN was possible in less than 30 min of reaction. The efficiency of the reaction system was maintained for 5 cycles [146].

Souza, Pereira, and Oliveira (2012) produced amphiphilic catalysts based on onion-like carbon (OLC) over iron oxide and applied them in the biphasic oxidation of QN in toluene [164]. A 93% percent removal of QN was obtained. The activity of the material was ascribed to increased contact between the aqueous oily phases due to the presence of a hydrophobic carbon layer on the catalyst [164].

Oliveira et al. (2020) prepared N-doped CNTs over red mud and applied them in the biphasic oxidation of QN in cyclohexane ($[\text{N}]_0$ of 30 ppm) with H_2O_2 [165]. The catalysts were synthesized sequentially feeding ethylene (as carbon source) and acetonitrile (as carbon and nitrogen sources), leading to 4 samples. (i) A completely undoped (synthesized using only ethylene); (ii) a completely N-doped (synthesized using only acetonitrile); and (iii) two samples synthesized using both precursors during different times, leading to two partially N-doped samples. QN oxidation varied according to the content of nitrogenated groups on the material: higher N contents led to increased removal of QN (80% versus 44%) [165]. A study with similar materials was previously done by Purceno et al. (2015) [166]. However, the selectively N-doped CNTs acted only as emulsion stabilizers in their case, and a homogeneous catalyst (Fe^{2+}) was applied. Without the CNTs, only 10% of QN was removed. On the other hand, by adding amphiphilic CNTs, a removal of QN in the 85–100% range was observed in 15–40 min of reaction, depending on the CNT sample. The results were directly ascribed to the ability of amphiphilic CNTs to stabilize Pickering emulsions, increasing interfacial area [166].

Ammar, Kareem, and Mohammed (2020) studied exclusively the ultrasound-assisted catalytic oxidative-adsorptive denitrogenation (COADN) of pyrrole (PYR) and indole (IND) (dissolved in n-nonane, $[\text{PYR}]_0$ and $[\text{IND}]_0$ of 200 ppm) [167] using a $\text{PMo-Fe}_2\text{O}_3/\text{rGO}$ as the catalyst. Upon increasing sonication power and time, the oxidation of N compounds increased. The best results were obtained with 200 W ultrasound power for 240 min, leading to 86% and 90% conversion for PYR and IND, respectively. Compared to the silent reaction (no ultrasound), an increase in 50% and 58% removals for PYR and IND, respectively, were observed. This high conversion was maintained for up to 5 cycles [167]. The authors did not highlight the role of the carbon structure.

Raffie and Khodayari (2017) added *N* compounds to a simulated fuel containing DBT to investigate the influence of the presence of *N* compounds (IND, QN, pyridine, and pyrrole, $C_0 = 60$ ppm) in the removal of DBT using a catalyst containing $\text{PMoV/Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ [76]. All nitrogenated compounds were oxidized in very short reaction times (20 min). Although *N* compounds slowed DBT oxidation, the effect was minimal. Thus proving that desulfurization and denitrogenation can be conducted simultaneously for the proposed system [76]. A similar study was performed previously by the same group [84] using an $\text{HPW/TiO}_2/\text{GC}$ catalyst. They have also concluded that adding nitrogenated compounds slightly impacts DBT removal. However, they have not reported the conversion of those nitrogenated compounds in the system.

Bhadra et al. (2019) studied the denitrogenation of a simulated fuel containing a range of different *N* compounds (IND, 1-, 2- and 3-methyl-substituted indoles (1-Me-IND, 2-Me-IND, and 3-Me-IND, respectively), PYR, carbazole (CBZ), and QN in *n*-octane, $C_0 = 5000$ ppm) [168]. The biphasic oxidation was conducted in the presence of acetic acid and with H_2O_2 as the oxidant. For IND, upon increasing the $\text{H}_2\text{O}_2/\text{N}$ ratio and catalyst dosage up to a certain point ($\text{H}_2\text{O}_2/\text{N} = 10$ and catalyst concentration of 0.25 g L^{-1}), IND removal increased. However, further increasing any of those parameters did not have a significant impact on IND removal. The removal of the remaining *N* compounds was also investigated. In 120 min of reaction, $\sim 90\%$ of IND was removed (maintained for 4 cycles), followed closely by 2-Me-IND. Removals of 1-Me-IND and 3-Me-IND were $\sim 70\%$, whereas PYR and CBZ removals were 40% and $<20\%$, respectively. QN was not oxidized in the studied conditions. The distinction between the oxidation rates of different compounds was ascribed to the electron density around the N atom, similar to that observed with S compounds. However, the authors have highlighted that further studies are necessary to truly understand the relation between electron density in *N* compounds and reaction rate [168]. The authors did not highlight the role of the carbon structure.

2.5 Final Considerations and Perspectives on Carbon Materials in ODS and ODN

Carbon-based materials have proved to be interesting materials that can be used in ODS and ODN processes under different systems. The facility to tune their properties and combine them with other materials to form composites makes them attractive when designing effective catalysts for desulfurization and denitrogenation. Especially in biphasic systems, their developed surface areas, which impact the dispersion of active phases and an increased adsorption capacity towards S pollutants, have been pointed out as a key contribution of those materials, mainly for hybrid catalysts. Besides that, carbon materials were found to benefit ultrasonic cavitation, boosting reactions in ultrasound-assisted processes. Their usual hydrophobic nature increases the interaction with fuels and lipophilic pollutants, such as sulfur compounds, allowing them to act as phase transfer agents to extract these S compounds. Finally, they were found to accelerate electron mobility, and in photocatalytic systems, they avoid

electron-hole recombination. When considering carbon-based materials as catalysts on their own, their activity is mainly ascribed to the presence of oxygenated groups and defect sites. However, there is still some controversy on how each influences the desulfurization capacity. In amphiphilic materials, carbon-based materials were again used as catalysts on their own and in hybrid forms. Their main contribution comes from stabilizing PIC-like systems, where the material acts simultaneously as a catalyst and emulsifier.

However, a few points must be raised. (i) There are much more reports related to the application of carbon-based hybrid materials and much less related to carbonaceous structures as catalysts on their own. However, the results reported in this review point out that carbon materials have allowed similar removals to those observed with hybrid materials. Thus, there is still the opportunity to study carbon-based materials as catalysts on their own for desulfurization and denitrogenation. (ii) There is also a lack of reports testing carbon-based materials as catalysts on their own containing dopants other than oxygen. Nitrogen, phosphorus, and sulfur are all possible dopants that have been shown to increase catalytic activity in aqueous phase oxidation reactions [64,169-171]. (iii) Denitrogenation approaches are much less common, and there is still the opportunity to study denitrogenation reactions, mainly aiming at simultaneous high removals of N and S-containing compounds. (iv) There are very few works dealing with the use of catalysts prepared from renewable or waste sources. Environmental aspects related to the catalyst (metal leaching species and waste generation, among others), economic issues, or life cycle assessment (LCA) are not reported by any papers. (v) Most authors fail to explain the role of the carbonaceous structure in the process, or the advantages of using carbon-based materials, mainly when considering carbon-based composites for ODS and ODN purposes. Understanding the role of each component of the catalyst is critical to developing outstanding catalysts. (vi) The decomposition or utilization efficiency of oxidant sources, such as hydrogen peroxide, oxygen, organic peracids, or others, is rarely reported. However, understanding the rate of oxidant consumption is essential for designing more economically viable ODS and ODN processes.

Table 2.13. ODS using mainly H₂O₂ with hybrid materials based on graphitic carbon nitride (g-C₃N₄) in L-L biphasic media.

Fuel	Catalyst	Extractant	Operational Conditions	Results	Ref.
IND or PYR in n-Nonane ($C_0 = 50\text{--}800$ ppm)	H ₃ PMo ₁₂ O ₄₀ -Fe ₃ O ₄ /rGO	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 50$ mL, $C_{\text{cat}} = 0\text{--}2$ g L ⁻¹ , $H_2O_2/\text{PYR} = 0\text{--}10$, $t = 15\text{--}240$ min, US: $50\text{--}300$ W.	Increasing US power (200 W) increases denitrogenation (max. 90% in 240 min, 5 cycles). Increasing the H_2O_2/PYR molar ratio over 5 did not increase N removal.	[167]
QN in Toluene ($C_0 = 50$ ppm + 50 ppm of DBT)	Fe ₂ O ₃ /C	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 9.9$ mL, $m_{\text{cat}} = 10$ mg, $V_{\text{oxidant}} = 0.1$ mL (H_2O_2/HCOOH), $T = 25$ °C, pH 4 (natural pH).	Approximately 60% removal of QN. The presence of DBT inhibited the complete removal of QN.	[150]
QN in Cyclohexane ($[\text{N}]_0 = 50$ ppm)	Fe/C and FeMo/C	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 5$ mL, $m_{\text{cat}} = 15$ mg, $V_{H_2O_2} = 1$ mL, $T = 25$ °C, natural pH.	100% removal of QN in 120 min of reaction.	[143]
QN in Cyclohexane ($[\text{N}]_0 = 30$ ppm)	N-Doped CNT/Red Mud	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 5$ mL, $m_{\text{cat}} = 20$ mg, $V_{H_2O_2} = 1$ mL.	Maximum removal of 80% in 45 min of reaction.	[165]
DBT, IND, QN, PYR, Pyrrole in EtOH: Hexane (1:1 vol. ratio) ($C_0 = 60$ ppm + 1000 ppm of DBT)	H ₅ PMo ₁₀ V ₂ O ₄₀ /Fe ₃ O ₄ /g-C ₃ N ₄	EtOH	$V_{\text{fuel}} = 5$ mL, $m_{\text{cat}} = 0.03$ g, $n_{H_2O_2} = 10$ mmol, $T = 80$ °C.	All N-containing compounds were wholly oxidized in 20 min of reaction. Their presence did not affect to a great extent the removal of DBT.	[76]
QN in Cyclohexane ($C_0 = 500$ ppm)	WEEE impregnated in clay and hydrophobized with CTAB.	ACN	$V_{\text{fuel}}/V_{\text{ACN}} = 5$, $V_{H_2O_2} = 320$ μL, $T = 60$ °C, $t = 3$ h.	A maximum removal rate of $73.5 \text{ mg}_{\text{QN}} \text{ g}_{\text{cat}}^{-1}$	[172]
IND, 1Me-IND, 2Me-IND, 3Me-IND, PYR, QN, or CBZ in n-Octane ($C_0 = 5000$ ppm)	TiO ₂ @porous C	Acetic Acid	$V_{\text{fuel}}/V_{\text{extractant}} = 10$, $C_{\text{cat}} = 0\text{--}0.5$ g L ⁻¹ , $H_2O_2/N = 0\text{--}15$, $T = 30\text{--}50$ °C, $t = 5\text{--}120$ min, $100\text{--}1000$ rpm, $5\text{--}10$ wt.% water.	Increasing H_2O_2/N to 10 and catalyst dosage up to 0.25 g L^{-1} increases N removal. Denitrogenation varied between $15\text{--}90\%$, depending on the N compound. Similar results were maintained for 4 cycles.	[168]
QN in Cyclohexane ($C_0 = 500$ ppm)	C/red mud	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 5$ mL, $m_{\text{cat}} = 20$ mg, $V_{H_2O_2} = 1$ mL	100% removal of QN in 60 min of reaction.	[145]
QN in Cyclohexane ($C_0 = 500$ ppm)	FeCl ₂ .4H ₂ O	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 5$ mL, $C_{\text{cat}} = 5.6$ mmol L ⁻¹ and 1 wt.% CNT, $V_{H_2O_2} = 300$ μL, 300 μL of FA, 20 s sonication to form an emulsion.	Depending on the sample (<i>i.e.</i> , whether it is amphiphilic), 100% removal of QN in 15 min.	[166]
QN in Toluene ($C_0 = 25$ ppm)	Fe/OLC	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 10$ mL, $m_{\text{cat}} = 10$ mg, $CH_2O_2 = 0.05$ mol L ⁻¹ , $T = 25$ °C, pH 6.	Maximum removal observed was 93%	[164]
QN in Cyclohexane ($[\text{N}]_0 = 500$ ppm)	FeMo/CNT	Aqueous H ₂ O ₂ phase	$V_{\text{fuel}} = 5$ mL, $m_{\text{cat}} = 20$ mg, $V_{H_2O_2} = 1$ mL	100% QN oxidation in 30 min of reaction.	[146]

Legend: ACN = acetonitrile. CNT = carbon nanotube. CTAB = cetyltrimethylammonium bromide. EtOH = ethanol. g-C₃N₄ = graphitic carbon nitride. OLC = onion-like carbon. rGO = reduced graphene oxide. WEEE = waste electrical and electronic equipment.

2.6 Synthesis of Carbon Nanotubes

CNTs are one-dimensional (1D) materials that consist of graphene sheets rolled into cylindrical shapes. They can be formed by one sheet of graphene (single-walled carbon nanotubes (SWCNTs)) or by several layers (multi-walled carbon nanotubes (MWCNTs)). SWCNTs have a diameter in the 0.4 – 3 nm range, whereas MWCNTs can have diameters up to 240 nm [173]. Initially discovered in 1991 by Iijima and Ichihashi [174], CNTs have generated growing interest due to their outstanding characteristics, such as high mechanical strength (50–500 GPa), thermal conductivity (3000–3500 W m⁻¹ K⁻¹), and thermal stability (>700 °C) [70–72, 175], translated into a high number of papers (>180000) with the keyword “carbon nanotub*” in the last 10 years (Figure 2.12). They can be applied in a wide range of industries, including for environmental purposes [176], energy-related [177], internet-of-things devices [178], as reinforcers in polymer blends [179], and in biomedical applications [180]. CNTs can be prepared using various methods, such as chemical vapor deposition (CVD) (*ca.* 26% of reported papers, Figure 2.12), laser ablation, arc discharge, sonochemical, and electrolysis [173, 181]. Among those techniques, CVD is advantageous, as the conditions required are less harsh compared to laser ablation and arc discharge. Additionally, CVD yields more CNTs at a better quality and purity, being the only method allowing control over structure and growth [173].

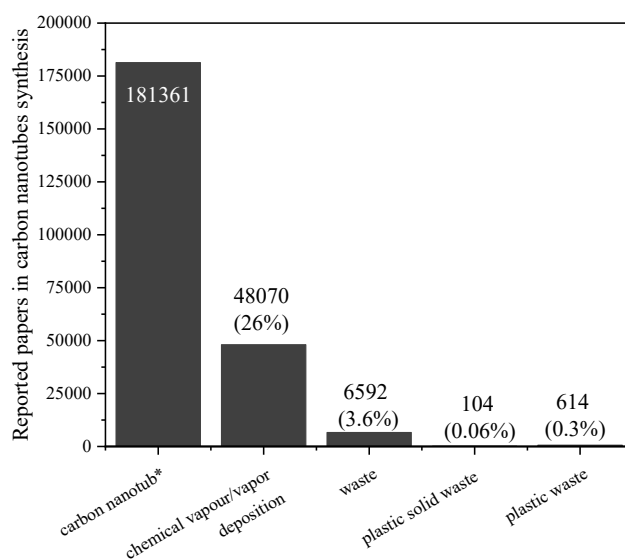


Figure 2.12. The number of papers related to the synthesis of carbon nanotubes. Search carried out at Web of Science on December 23rd, 2024, using the keywords: “carbon nanotub*”, “chemical vapor deposition” OR “chemical vapor deposition”, “waste”, “plastic solid waste”, “plastic waste”.

The CVD process relies on the cleavage of a carbon-rich gas into carbon atoms (releasing hydrogen), followed by the generation of CNTs at the surface of a catalyst [173]. Catalysts for CVD are metal particles supported on a substrate (or support). When this carbonaceous gas enters in contact with the metal particle, it decomposes into carbon and hydrogen. Hydrogen is carried away with the carrier gas, whereas carbon dissolves on the metal particle. Once the carbon solubility limit of the specific metal is reached, the carbon precipitates and crystallizes, forming CNTs [173]. Depending on the metal-substrate

interaction, two different growth methods are believed to happen [173]. (i) Tip-growth: when there is little interaction between the metal and the substrate, the carbon precipitates between the metal particle and the substrate, thus promoting the growth of the entire metal particle, and growth stops when the metal particle is entirely covered by carbon. (ii) Root or base growth: when there is a strong interaction between the metal and the substrate, the carbon precipitates without pushing up the metal particles, forcing it to precipitate on top of the metal particle [173]. Several parameters affect the morphology and properties of CNTs, such as carbon source, metal particle and support, and reactor temperature [173], among others.

The metal particle and the support also influence the synthesis of CNTs. The most common active centers are transition metals, such as Fe, Ni, Co, and Mo, and their oxides [173]. They are widely used due to their high carbon solubility and diffusion coefficient. Furthermore, those metals have high melting points, which allows for a wide range of CVD temperatures [71, 173]. Bimetallic catalysts are also extensively used. For instance, higher catalytic activity in the decomposition of hydrocarbon gases was attributed to Fe, although Fe leads to a lower degree of graphitization. On the other hand, Co increases the graphitization degree but leads to lower yields. Thus, preparing bimetallic catalysts is an attempt to overcome those issues. Bimetallic catalysts are considered better options than monometallic ones [71, 173]. Catalytic phase dispersion is also correlated with the effective synthesis of CNTs, and the dispersion rate is primarily associated with the support. Several supports can be used, such as graphite, quartz, silica, alumina, zeolites, and magnesium oxide, among others [71]. The support nature, its textural properties, and surface morphology affect both the yield and the quality of CNTs. Alumina (Al_2O_3) was found to be more effective than silica (SiO_2) due to higher metal dispersion [173]. The support also allows for avoiding the sintering and redispersion process of the metal particles during CVD, which could influence the diameter of CNTs [182]. Interactions between metal particles and support are also relevant, as these interactions would hinder metal aggregation and the formation of large clusters [71].

Temperature also has a strong effect on CNTs. CVD is usually carried out in the range between 500-1200 °C. MWCNTs are expected in the lower range (500-900 °C). Temperatures higher than 900 °C benefit the synthesis of SWCNTs [71] if carbon sources stable at higher temperatures are considered [173]. Temperature also affects the sintering of the metal particles, and thus, for a fixed metal concentration, higher temperatures can lead to the formation of CNTs with higher diameters [71]. Higher temperatures also tend to allow CNTs with higher graphitization degrees and higher yields [173], as more precursor is expected to decompose. On the other hand, higher temperatures also lead to more defective CNTs [173]. As the temperature is also expected to influence the interaction between the metal particle and support, it also influences the growth mechanism: at a lower temperature, base growth is expected, whereas, at higher temperatures, tip growth is more pronounced [71].

2.6.1 Carbon Nanotubes from Plastic Solid Waste

Carbon sources can be of any state [173], including solid-state precursors, such as coal, naphthalene, and graphite, as non-renewable examples, or from biomasses and waste materials, as renewable examples [70]. Plastic solid wastes (PSW) have recently been explored as renewable sources for CNT production [183-191]. Plastics are polymers, mainly composed of carbon and hydrogen. Their use as a carbon source offers the advantage of employing low-cost precursors and adding value to waste materials [192]. Table 2.14 displays some examples of PSW and their carbon content. The CVD of PSW consists of a two-step process, where the long chain of the polymer is initially cracked into smaller gaseous products, and then this gas deposits into the catalyst to grow CNTs. Some examples of polymers that have been used as a carbon source on CNT synthesis (either as virgin or waste) are polypropylene (PP) [185-187, 193-195], low and high-density polyethylene (LDPE and HDPE, respectively) [185, 188-190, 193-196], polyethylene terephthalate (PET) [183, 185, 194, 197] and polystyrene (PS) [183, 185, 194, 195], among others.

Table 2.14 Carbon content of PSW	
Polymer	Carbon content (wt.%)
PP, HDPE and LDPE	85.6
PET	62.6
PS	92.2

Source: adapted from [198]

Among the papers reported on the synthesis of carbon nanotubes (Figure 2.12), only a fraction of those focus on the synthesis of CNTs based on waste sources (<4%), and papers using the keywords ‘plastic waste’ or ‘plastic solid waste’ represent less than 0.5% of the literature. Table 2.15 displays a few works related to the synthesis of CNTs from plastic sources.

Several works explore only commercially-obtained polymers as carbon sources [185, 187, 189, 193, 194, 196], while some use purely waste sources [186, 190, 197, 199-203] and some both commercial and waste sources [188, 195]. In some cases, it is unclear whether the polymers used are waste or virgin [183, 204]. Most works have used CVD catalysts based on Ni and Fe supported over alumina, with a few works reporting other metals as catalysts (in combination with either Fe or Ni), such as Co [201], Mn [187, 188] or Mo [183, 190, 201], or alternative supports, such as CaO, MgO and zeolites [185, 195, 200-202]. The reactor set-up is usually based on a two-stage process, where pyrolysis and cracking of the polymer source happen in a chamber (at temperatures in the range 450-800 °C) and CNT growth in a separate chamber (temperature reported in the range of 600-1100 °C). Only a few works report CNT synthesis using a one-chamber reactor with simultaneous cracking and CNT growth in the same chamber [193, 196]. One-chamber reactors could be advantageous from an energy-saving perspective. The main results have indicated that the carbon yields can vary significantly (0.6-60%) depending on temperature, carbon source and catalyst used, with similar observations to the degree of graphitization (D/G ratio) reported, which has varied from 0.07 to 2.21. Diameters are typically reported in the range of 20-50 nm,

typical of MWCNTs, although some works have reported the growth of CNTs with smaller diameters (3.5-13 nm) [201]. Reported surface areas varied significantly (BET in the range 66-263 m² g⁻¹). It should be further highlighted that most works related to the synthesis of CNTs do not typically explore the application of the materials.

Table 2.15 Carbon nanotubes derived from polymeric sources.

Carbon source	Catalyst	Conditions	Yield	Others	Application	Ref
PE, PP, PS and PET (Individual; commercial)	Ni/Al ₂ O ₃	2-stage reactor; 1 g plastic; 0.5 g cat.; N ₂ : 50 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C.	20-33%;	D/G: 0.48-0.54	None	[194]
PE (not clear if waste or commercial)	Fe-Ni/Al ₂ O ₃	Microwave plasma-initiated; 0.15 g plastics; 0.3 g cat.; N ₂ : 200 mL min ⁻¹ ; 700 W; 400 °C	-	30-45 nm; D/G: 0.6-0.94	None	[204]
PP, LDPE, PS and HDPE (Mixed; commercial and waste)	Fe/MgO	2-stage reactor; plastic: Fe/MgO mass ratio = 2:1; Ar (100 sccm); Pyrolysis: 450 °C; CVD: 900 °C.	38%;	D/G: 0.07-0.2.	None	[195]
Meal box, milk cup, express package (waste)	Fe/Al ₂ O ₃	2-stage reactor; plastic: catalyst mass ratio = 2:1; N ₂ : 100 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C.	8-30%	10-100 nm; D/G: 0.8-1.75	None	[199]
Flexible plastic packaging (waste)	Fe-ZSM (pyrolysis) and Ni-Ca (CVD)	3-stage reactor; 50 g plastic; 7.5 g Fe-ZSM; 9 g Ni-Ca; N ₂ : 50 mL min ⁻¹ ; Pyrolysis: 550 °C; Cracking: 400 °C; CVD: 700 °C;	-	D/G : 1.1-1.3; BET: 144-263 m ² g ⁻¹	Supercapacitor	[200]
KF94 masks (waste)	CoMo/MgO FeMo/MgO	2-stage reactor; 250 g plastic; 0.5 g cat.; Ar: 1 L min ⁻¹ ; Pyrolysis: 800 °C; CVD: 900 °C	2-516 %;	3.5-13 nm; D/G : 0.18-1.4	Battery additives	[201]
PET plastic bottles (waste)	Ni	1-stage reactor; 10 g plastic; 1 g cat; Ar: 90 mL min ⁻¹ ; CVD: 8000 °C		30-45 nm	Food packaging	[197]
Centrifuge tubes (waste)	None; reactor wall	2-stage reactor; 1-2 g plastic; Ar: 100 sccm; Pyrolysis: 500 °C; CVD: 600-1100 °C.	0-43%;	28-35 nm; D/G: 0.5-0.9	None	[186]
LDPE, HDPE, PP (Individual and mixed; commercial)	Fe/Al ₂ O ₃	1-stage reactor; 5 g plastic; 1 g cat; N ₂ : 50 mL min ⁻¹ ; CVD: 850 °C.	41-48%	28-44 nm; BET: 66-98 m ² g ⁻¹	Water treatment	[193]
LDPE (commercial)	Ni or NiFe/Al ₂ O ₃	1-stage reactor; 5 g plastic; 1 g cat; N ₂ : 100 mL min ⁻¹ ; CVD: 800 °C.	7-20	4-63 nm; BET: 151-226 m ² g ⁻¹	Water treatment	[196]
LDPE, PP, PS, PET (Mixed; commercial)	Ni/CaO	2-stage reactor; 1.5-2 g plastic; 0.5 g cat; N ₂ : 50 mL min ⁻¹ ; Pyrolysis: 600 °C; CVD: 500-800 °C	3-33%	D/G : 0.5-1.57	None	[185]
PP (commercial)	Ni-Mn-Al	2-stage reactor; 1 g plastic; 3 g cat; N ₂ : 80 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C; steam.	46-58%	-	Polymer reinforcement	[187]
HDPE (commercial and waste)	Ni-Mn-Al	2-stage reactor; 1 g plastic; 0.5 g cat; N ₂ : 80 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C; steam.	19-48%	30 nm; D/G: 0.63-1.53	None	[188]
HDPE (commercial)	Ni-stainless steel	2-stage reactor; Plastic:cat mass ratio: 2:1-4:1; N ₂ : 80 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C; 40 min.	25-38%	10-20 nm; D/G: 1.18-1.53	None	[189]
LDPE (waste)	Ni-Mo/Al ₂ O ₃	2-stage reactor; 10 g plastic; 0.5 g cat; N ₂ : 30 mL min ⁻¹ ; Pyrolysis: 500-800 °C; CVD: 600-800 °C.	15-25%;	11-49 nm; D/G: 0.93-2.21	None	[190]
HDPE, LDPE, PP, PS and PET (Individual; not clear if waste or virgin)	Ni-Mo/Al ₂ O ₃	2-stage reactor; 10 g plastic; 0.5 g cat; N ₂ : 100 mL min ⁻¹ ; Pyrolysis: 700 °C; CVD: 650 °C.	25-60%	6-35 nm; D/G: 1.26-1.74	None	[183]
Food packaging (waste)	Ni-Fe/zeolite	Two-stage reactor; 1 g plastic; 0.5 g of catalyst; N ₂ : 100 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C, 15 min.	36-56%	12-25 nm; D/G: 0.51-0.77	None	[202]
PP, HDPE, LDPE, and PS (Individual; Waste)	Fe/Al ₂ O ₃	Two-stage reactor; 1 g plastic; 0.5 g of catalyst; N ₂ : 100 mL min ⁻¹ ; Pyrolysis: 500 °C; CVD: 800 °C, 10 min.	30-50%;	D/G: 0.52-0.66	None	[203]

2.7 Final considerations on the synthesis of CNTs from PSW

CNTs can be synthesized from various carbon sources, including non-renewable and renewable materials. The exploration of PSW as a carbon source for CNT synthesis represents a promising area of research. This approach not only addresses the growing environmental concerns associated with the accumulation of plastic waste but it also offers a cost-effective alternative to conventional non-renewable feedstocks, such as methane, for producing high-value nanomaterials.

Although the synthesis of CNTs from plastic waste is less prevalent in the literature, studies have shown considerable potential in using diverse waste plastics such as polypropylene, polyethylene, and polystyrene. The results of these studies suggest that various factors, such as catalyst type, reactor temperature, and plastic source, significantly influence the yield and quality of the CNTs produced.

While challenges remain, such as optimizing catalyst efficiency and achieving consistent production of high-quality CNTs, this approach shows significant potential for both sustainable waste management and the development of advanced materials for energy, environmental, and industrial applications. Nevertheless, it should also be noted that more research is needed to explore and validate the applications of CNTs derived from plastic waste to establish their commercial viability.

2.8 References

- [1] Eurostat. Available online: https://ec.europa.eu/eurostat/databrowser/view/nrg_bal_c/default/table?lang=en (Accessed on 13 July 2021).
- [2] Walters, C. Petroleum. In Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2020; pp. 1–44.
- [3] A. Marafi, H. Albazzaz, M.S. Rana, Hydroprocessing of heavy residual oil: Opportunities and challenges, *Catalysis Today* 329 (2019) 125–134. <https://doi.org/10.1016/j.cattod.2018.10.067>.
- [4] G.H.C. Prado, Y. Rao, A. de Klerk, Nitrogen Removal from Oil: A Review, *Energy Fuels* 31(1) (2017) 14–36. <https://doi.org/10.1021/acs.energyfuels.6b02779>.
- [5] P. Sikarwar, V. Gosu, V. Subbaramaiah, An overview of conventional and alternative technologies for the production of ultra-low-sulfur fuels, *Reviews in Chemical Engineering* 35(6) (2019) 669–705. <https://doi.org/10.1515/revce-2017-0082>.
- [6] W. Ahmad, Sulfur in Petroleum: Petroleum Desulfurization Techniques, in: T.A. Saleh (Ed.), *Applying nanotechnology to the desulfurization process in petroleum engineering*, Engineering Science Reference, Hershey, 2016, pp. 1–50.
- [7] J.S. Ball, M.L. Whisman, W.J. Wenger, Nitrogen Content of Crude Petroleum, *Industrial and Engineering Chemistry* 43(11) (1951) 2577–2581.
- [8] C. Song, X. Ma, New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization, *Applied Catalysis B: Environmental* 41(1–2) (2003) 207–238. [https://doi.org/10.1016/s0926-3373\(02\)00212-6](https://doi.org/10.1016/s0926-3373(02)00212-6).
- [9] Romanow-Garcia, S.; Hoffman, H.L. Petroleum and Its Products. In Riegel's Handbook of Industrial Chemistry, 10th ed.; Kent, J.A., Ed.; Kluwer Academic/Plenum Publishers: New York, NY, USA, 2003; pp. 506–544.
- [10] A.C. Lloyd, T.A. Cackette, Diesel engines: environmental impact and control, *Journal of the Air & Waste Management Association* 51(6) (2001) 809–47. <https://doi.org/10.1080/10473289.2001.10464315>.
- [11] M. Kampa, E. Castanas, Human health effects of air pollution, *Environmental Pollution* 151(2) (2008) 362–7. <https://doi.org/10.1016/j.envpol.2007.06.012>.
- [12] Pénard-Morand, C.; Annesi-Maesano, I. Air pollution: From sources of emissions to health effects. *Breathe* 2004, 1, 108–119.
- [13] A.J. Cohen, C.A. Pope, 3rd, Lung cancer and air pollution, *Environmental Health Perspectives* 103 Suppl 8(Suppl 8) (1995) 219–24. <https://doi.org/10.1289/ehp.95103s8219>.
- [14] J. Sunyer, The association of daily sulfur dioxide air pollution levels with hospital admissions for cardiovascular diseases in Europe (The Aphea-II study), *European Heart Journal* 24(8) (2003) 752–760. [https://doi.org/10.1016/s0195-668x\(02\)00808-4](https://doi.org/10.1016/s0195-668x(02)00808-4).
- [15] Y. Wu, R. Li, L. Cui, Y. Meng, H. Cheng, H. Fu, The high-resolution estimation of sulfur dioxide (SO₂) concentration, health effect and monetary costs in Beijing, *Chemosphere* 241 (2020) 125031. <https://doi.org/10.1016/j.chemosphere.2019.125031>.
- [16] P. Grennfelt, A. Engleryd, M. Forsius, O. Hov, H. Rodhe, E. Cowling, Acid rain and air pollution: 50 years of progress in environmental science and policy, *Ambio* 49(4) (2020) 849–864. <https://doi.org/10.1007/s13280-019-01244-4>.
- [17] D.A. Burns, J. Aherne, D.A. Gay, C.M.B. Lehmann, Acid rain and its environmental effects: Recent scientific advances, *Atmospheric Environment* 146 (2016) 1–4. <https://doi.org/10.1016/j.atmosenv.2016.10.019>.
- [18] H.S. Gandhi, M. Shelef, Effects of sulphur on noble metal automotive catalysts, *Applied Catalysis* 77 (1991) 175–187.
- [19] Council of the European Union. Official Journal of the European Union 140, Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 Amending Directive 98/70/EC as Regards the Specification of Petrol, Diesel and Gas-Oil and Introducing a Mechanism to Monitor and Reduce Greenhouse Gas Emissions and Amending Council Directive 1999/32/EC as Regards the Specification of Fuel Used by Inland

- Waterway Vessels and Repealing Directive 93/12/EEC. 2009. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32009L0030> (accessed on 23 April 2021).
- [20] Control of Air Pollution from Motor Vehicles: Tier 3 Motor Vehicle Emission and Fuel Standards (Final Rule). Environmental Protection Agency. Federal Register Vol. 79, no 81, Monday, April 28th, 2014. Available online: <https://www.govinfo.gov/content/pkg/FR-2014-04-28/pdf/2014-06954.pdf> (accessed on 23 April 2021).
- [21] EPA-420-B-16-005-Highway and Nonroad, Locomotive, and Marine (NRLM) Diesel Fuel Sulfur Standards. Office of Transportation and Air Quality, 2016. Available online: <https://nepis.epa.gov/Exec/ZyPDF.cgi?Dockey=P100O9ZH.pdf> (accessed on 24 April 2021).
- [22] Miller, J.D.; Façanha, C. The State of Clean Transport Policy: A 2014 Synthesis of Vehicle and Fuel Policy Developments. International Council on Clean Transportation. Washington: International Council on Clean Transportation, 2014. Available online: <https://theicct.org/publications/state-clean-transport-policy-2014-synthesis-vehicle-and-fuel-policy-developments> (accessed on 10 June 2021).
- [23] Japan: Fuels: Diesel and Gasoline. Available online: <https://www.transportpolicy.net/standard/japan-fuels-diesel-and-gasoline/> (Accessed on 24 April 2021).
- [24] China: Fuels: Diesel and Gasoline. Available online: <https://www.transportpolicy.net/standard/china-fuels-diesel-and-gasoline/> (Accessed on 24 April 2021).
- [25] India: Fuels: Diesel and Gasoline. Available online: <https://www.transportpolicy.net/standard/india-fuels-diesel-and-gasoline/> (Accessed on 24 April 2021).
- [26] Russia: Fuels: Diesel and Gasoline. Available online: <https://www.transportpolicy.net/standard/russia-fuels-diesel-and-gasoline-2/> (Accessed on 24 April 2021).
- [27] Fuel Quality Standards (Petrol) Determination 2019, Minister for the Environment. 2019. Available online: <https://www.legislation.gov.au/Details/F2019L00455> (Accessed on 24 April 2021).
- [28] Regulation (EC) No. 715/2007 of the European Parliament and of the Council of 20 June 2007 on Type Approval of Motor Vehicles with Respect to Emissions from Light Passenger and Commercial Vehicles (Euro 5 and Euro 6) and on Access to Vehicle Repair and Maintenance Information. Available online: <https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32007R0715> (Accessed on 24 April 2021).
- [29] Miller, J.; Jin, L. Global Progress Toward Soot-Free Diesel Vehicles in 2019. International Council on Clean Transportation, 2019. Available online: <https://theicct.org/publications/global-progress-toward-soot-free-diesel-vehicles-2019> (Accessed on 17 May 2021).
- [30] Fahim, M.A.; Alsahhaf, T.A.; Elkilani, A. Hydroconversion. In Fundamentals of Petroleum Refining; Fahim, M.A., Alsahhaf, T.A., Elkilani, A., Eds.; Elsevier: Oxford, UK, 2010; pp. 153–198. <https://doi.org/10.1016/b978-0-444-52785-1.00007-3>.
- [31] J.G. Speight, Hydrotreating and Desulfurization, The Refinery of the Future 2011, pp. 237-273. <https://doi.org/10.1016/b978-0-8155-2041-2.10008-6>.
- [32] Mochida, I.; Choi, K.-H. An Overview of Hydrodesulfurization and Hydrodenitrogenation. Journal of the Japan Petroleum Institute 47 (2004) 145–163. <https://doi.org/10.1627/jpi.47.145>
- [33] M. Bachrach, T.J. Marks, J.M. Notestein, Understanding the Hydrodenitrogenation of Heteroaromatics on a Molecular Level, ACS Catalysis 6(3) (2016) 1455-1476. <https://doi.org/10.1021/acscatal.5b02286>.
- [34] A. Rajendran, T.-y. Cui, H.-x. Fan, Z.-f. Yang, J. Feng, W.-y. Li, A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment, Journal of Materials Chemistry A 8(5) (2020) 2246-2285. <https://doi.org/10.1039/c9ta12555h>.
- [35] S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, On the hydrodesulfurization of FCC gasoline: a review, Applied Catalysis A: General 278(2) (2005) 143-172. <https://doi.org/10.1016/j.apcata.2004.10.012>.
- [36] I. Babich, Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, Fuel 82(6) (2003) 607-631. [https://doi.org/10.1016/s0016-2361\(02\)00324-1](https://doi.org/10.1016/s0016-2361(02)00324-1).
- [37] M.H. Ibrahim, M. Hayyan, M.A. Hashim, A. Hayyan, The role of ionic liquids in desulfurization of fuels: A review, Renewable and Sustainable Energy Reviews 76 (2017) 1534-1549. <https://doi.org/10.1016/j.rser.2016.11.194>.

- [38] R. Abro, A.A. Abdeltawab, S.S. Al-Deyab, G. Yu, A.B. Qazi, S. Gao, X. Chen, A review of extractive desulfurization of fuel oils using ionic liquids, *RSC Advances* 4(67) (2014) 35302-35317. <https://doi.org/10.1039/c4ra03478c>.
- [39] M.F. Majid, H.F. Mohd Zaid, C.F. Kait, K. Jumbri, L.C. Yuan, S. Rajasuriyan, Futuristic advance and perspective of deep eutectic solvent for extractive desulfurization of fuel oil: A review, *Journal of Molecular Liquids* 306 (2020) 112870. <https://doi.org/10.1016/j.molliq.2020.112870>.
- [40] E. Svinterikos, I. Zuburtikudis, M. Al-Marzouqi, Carbon Nanomaterials for the Adsorptive Desulfurization of Fuels, *Journal of Nanotechnology* 2019 (2019) 1-13. <https://doi.org/10.1155/2019/2809867>.
- [41] J.G. Speight, N.S. El-Gendy, Biocatalytic Desulfurization, *Introduction to Petroleum Biotechnology* 2018, pp. 165-227. <https://doi.org/10.1016/b978-0-12-805151-1.00006-0>.
- [42] J. Li, Z. Yang, S. Li, Q. Jin, J. Zhao, Review on oxidative desulfurization of fuel by supported heteropolyacid catalysts, *Journal of Industrial and Engineering Chemistry* 82 (2020) 1-16. <https://doi.org/10.1016/j.jiec.2019.10.020>.
- [43] M. Hossain, H. Park, H. Choi, A Comprehensive Review on Catalytic Oxidative Desulfurization of Liquid Fuel Oil, *Catalysts* 9(3) (2019) 229. <https://doi.org/10.3390/catal9030229>.
- [44] M. Haghighi, S. Gooneh-Farahani, Insights to the oxidative desulfurization process of fossil fuels over organic and inorganic heterogeneous catalysts: advantages and issues, *Environmental Science and Pollution Research* 27(32) (2020) 39923-39945. <https://doi.org/10.1007/s11356-020-10310-4>.
- [45] S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai, T. Kabe, Oxidative Desulfurization of Light Gas Oil and Vacuum Gas Oil by Oxidation and Solvent Extraction, *Energy & Fuels* 14(6) (2000) 1232-1239. <https://doi.org/10.1021/ef000096i>.
- [46] A.S. Ogunlaja, M.S. Abdul-quadir, P.E. Kleyi, E.E. Ferg, P. Watts, Z.R. Tshentu, Towards oxidative denitrogenation of fuel oils: Vanadium oxide-catalysed oxidation of quinoline and adsorptive removal of quinoline-N-oxide using 2,6-pyridine-polybenzimidazole nanofibers, *Arabian Journal of Chemistry* 12(2) (2019) 198-214. <https://doi.org/10.1016/j.arabjc.2017.05.010>.
- [47] A.R. Nicolaescu, O. Wiest, P.V. Kamat, Mechanistic pathways of the hydroxyl radical reactions of quinoline. 1. Identification, distribution, and yields of hydroxylated products, *The Journal of Physical Chemistry A* 109(12) (2005) 2822-8. <https://doi.org/10.1021/jp0450179>.
- [48] N. Weeranoppanant, Enabling tools for continuous-flow biphasic liquid-liquid reaction, *Reaction Chemistry & Engineering* 4(2) (2019) 235-243. <https://doi.org/10.1039/c8re00230d>.
- [49] N. Xue, G. Zhang, X. Zhang, H. Yang, A reinforced Pickering emulsion for cascade reactions, *ChemComm* 54(92) (2018) 13014-13017. <https://doi.org/10.1039/c8cc07644h>.
- [50] M. Pera-Titus, L. Leclercq, J.M. Clacens, F. De Campo, V. Nardello-Rataj, Pickering interfacial catalysis for biphasic systems: from emulsion design to green reactions, *Angewandte Chemie International Edition* 54(7) (2015) 2006-21. <https://doi.org/10.1002/anie.201402069>.
- [51] H. Jiang, Y. Sheng, T. Ngai, Pickering emulsions: Versatility of colloidal particles and recent applications, *Current Opinion in Colloid & Interface Science* 49 (2020) 1-15. <https://doi.org/10.1016/j.cocis.2020.04.010>.
- [52] M. Sjo, M. Rayner, M. Wahlgren, Particle-stabilized Emulsions, in: M. Rayner, P. Dejmek (Eds.), *Engineering Aspects of Food Emulsification and Homogenization*, CRC Press, Boca Raton, 2015, pp. 101-122. <https://doi.org/10.1201/b18436-6>.
- [53] Y. Chevalier, M.-A. Bolzinger, Emulsions stabilized with solid nanoparticles: Pickering emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 439 (2013) 23-34. <https://doi.org/10.1016/j.colsurfa.2013.02.054>.
- [54] N. Briggs, A.K.Y. Raman, L. Barrett, C. Brown, B. Li, D. Leavitt, C.P. Aichele, S. Crossley, Stable pickering emulsions using multi-walled carbon nanotubes of varying wettability, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 537 (2018) 227-235. <https://doi.org/10.1016/j.colsurfa.2017.10.010>.
- [55] N.M. Briggs, J.S. Weston, B. Li, D. Venkataramani, C.P. Aichele, J.H. Harwell, S.P. Crossley, Multiwalled Carbon Nanotubes at the Interface of Pickering Emulsions, *Langmuir* 31(48) (2015) 13077-84. <https://doi.org/10.1021/acs.langmuir.5b03189>.
- [56] Z. Wang, Y. Wang, Tuning Amphiphilicity of Particles for Controllable Pickering Emulsion, *Materials* 9(11) (2016) 903. <https://doi.org/10.3390/ma9110903>.

- [57] B.N. Bhadra, S.H. Jhung, Oxidative desulfurization and denitrogenation of fuels using metal-organic framework-based/-derived catalysts, *Applied Catalysis B: Environmental* 259 (2019) 118021. <https://doi.org/10.1016/j.apcatb.2019.118021>.
- [58] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, The influence of structure and surface chemistry of carbon materials on the decomposition of hydrogen peroxide, *Carbon* 62 (2013) 97-108. <https://doi.org/10.1016/j.carbon.2013.06.001>.
- [59] G. Fang, J. Gao, C. Liu, D.D. Dionysiou, Y. Wang, D. Zhou, Key role of persistent free radicals in hydrogen peroxide activation by biochar: implications to organic contaminant degradation, *Environmental Science & Technology* 48(3) (2014) 1902-10. <https://doi.org/10.1021/es4048126>.
- [60] E. Vega, H. Valdés, New evidence of the effect of the chemical structure of activated carbon on the activity to promote radical generation in an advanced oxidation process using hydrogen peroxide, *Microporous and Mesoporous Materials* 259 (2018) 1-8. <https://doi.org/10.1016/j.micromeso.2017.09.018>.
- [61] M. Martin-Martinez, S. Álvarez-Torrellas, J. García, A.M.T. Silva, J.L. Faria, H.T. Gomes, Exploring the activity of chemical-activated carbons synthesized from peach stones as metal-free catalysts for wet peroxide oxidation, *Catalysis Today* 313 (2018) 20-25. <https://doi.org/10.1016/j.cattod.2018.01.003>.
- [62] M. Martin-Martinez, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Carbon nanotubes as catalysts for wet peroxide oxidation: The effect of surface chemistry, *Catalysis Today* 357 (2020) 332-340. <https://doi.org/10.1016/j.cattod.2019.03.014>.
- [63] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review, *Applied Catalysis B: Environmental* 187 (2016) 428-460. <https://doi.org/10.1016/j.apcatb.2016.01.033>.
- [64] X. Duan, H. Sun, S. Wang, Metal-Free Carbocatalysis in Advanced Oxidation Reactions, *Accounts of Chemical Research* 51(3) (2018) 678-687. <https://doi.org/10.1021/acs.accounts.7b00535>.
- [65] P.-f. Xiao, L. An, D.-d. Wu, The use of carbon materials in persulfate-based advanced oxidation processes: A review, *New Carbon Materials* 35(6) (2020) 667-683. [https://doi.org/10.1016/s1872-5805\(20\)60521-2](https://doi.org/10.1016/s1872-5805(20)60521-2).
- [66] X. He, N. Zheng, R. Hu, Z. Hu, J.C. Yu, Hydrothermal and Pyrolytic Conversion of Biomasses into Catalysts for Advanced Oxidation Treatments, *Advanced Functional Materials* 31(7) (2020) 2006505. <https://doi.org/10.1002/adfm.202006505>.
- [67] R.P. Rocha, M.F.R. Pereira, J.L. Figueiredo, Metal-free carbon materials as catalysts for wet air oxidation, *Catalysis Today* 356 (2020) 189-196. <https://doi.org/10.1016/j.cattod.2019.04.047>.
- [68] O. Vieira, R.S. Ribeiro, J.L. Diaz de Tuesta, H.T. Gomes, A.M.T. Silva, A systematic literature review on the conversion of plastic wastes into valuable 2D graphene-based materials, *Chemical Engineering Journal* 428 (2022) 131399. <https://doi.org/10.1016/j.cej.2021.131399>.
- [69] P. González-García, Activated carbon from lignocellulosics precursors: A review of the synthesis methods, characterization techniques and applications, *Renewable and Sustainable Energy Reviews* 82 (2018) 1393-1414. <https://doi.org/10.1016/j.rser.2017.04.117>.
- [70] S. Vivekanandhan, M. Schreiber, S. Muthuramkumar, M. Misra, A.K. Mohanty, Carbon nanotubes from renewable feedstocks: A move toward sustainable nanofabrication, *Journal of Applied Polymer Science* 134(4) (2017) 44255. <https://doi.org/10.1002/app.44255>.
- [71] M. Kumar, Y. Ando, Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production, *Journal of Nanoscience & Nanotechnology* 10(6) (2010) 3739-58. <https://doi.org/10.1166/jnn.2010.2939>.
- [72] R. Das, Z. Shahnava, M.E. Ali, M.M. Islam, S.B. Abd Hamid, Can We Optimize Arc Discharge and Laser Ablation for Well-Controlled Carbon Nanotube Synthesis?, *Nanoscale Res Lett* 11(1) (2016) 510. <https://doi.org/10.1186/s11671-016-1730-0>.
- [73] R.S. Edwards, K.S. Coleman, Graphene synthesis: relationship to applications, *Nanoscale* 5(1) (2013) 38-51. <https://doi.org/10.1039/c2nr32629a>.
- [74] L. Kong, J. Wang, F. Ma, M. Sun, J. Quan, Graphitic carbon nitride nanostructures: Catalysis, *Applied Materials Today* 16 (2019) 388-424. <https://doi.org/10.1016/j.apmt.2019.06.003>.

- [75] N. Rono, J.K. Kibet, B.S. Martincigh, V.O. Nyamori, A review of the current status of graphitic carbon nitride, *Critical Reviews in Solid State and Materials Sciences* 46(3) (2020) 189-217. <https://doi.org/10.1080/10408436.2019.1709414>.
- [76] E. Rafiee, M. Khodayari, Synthesis and characterization of PMoV/Fe₃O₄/g-C₃N₄ from melamine: An industrial green nanocatalyst for deep oxidative desulfurization, *Chinese Journal of Catalysis* 38(3) (2017) 458-468. [https://doi.org/10.1016/s1872-2067\(16\)62548-2](https://doi.org/10.1016/s1872-2067(16)62548-2).
- [77] N.M. Meman, B. Zarenezhad, A. Rashidi, Z. Hajjar, E. Esmacili, Application of palladium supported on functionalized MWNTs for oxidative desulfurization of naphtha, *Journal of Industrial and Engineering Chemistry* 22 (2015) 179-184. <https://doi.org/10.1016/j.jiec.2014.07.008>.
- [78] Y. Zhu, M. Zhu, L. Kang, F. Yu, B. Dai, Phosphotungstic Acid Supported on Mesoporous Graphitic Carbon Nitride as Catalyst for Oxidative Desulfurization of Fuel, *Industrial & Engineering Chemistry Research* 54(7) (2015) 2040-2047. <https://doi.org/10.1021/ie504372p>.
- [79] N. Mohammadi Meman, M. Pourkhalil, A. Rashidi, B. ZareNezhad, Synthesis, characterization and operation of a functionalized multi-walled CNT supported MnOx nanocatalyst for deep oxidative desulfurization of sour petroleum fractions, *Journal of Industrial and Engineering Chemistry* 20(6) (2014) 4054-4058. <https://doi.org/10.1016/j.jiec.2014.01.004>.
- [80] J. R. Ugal, R. B. Jima'a, W. Metaab Khamis Al-Jubori, B. Fadhel Abbas, N. Metaab Al-Jubori, Oxidative Desulfurization of Hydrotreated Gas Oil using Fe₂O₃ and Pd Loaded over Activated Carbon as Catalysts, *Oriental Journal of Chemistry* 34(2) (2018) 1091-1097. <https://doi.org/10.13005/ojc/340261>.
- [81] H.H. Alwan, A.A. Ali, H.F. Makki, Optimization of Oxidative Desulfurization Reaction with Fe₂O₃ Catalyst Supported on Graphene Using Box-Behnken Experimental Method, *Bulletin of Chemical Reaction Engineering & Catalysis* 15(1) (2020) 175-185. <https://doi.org/10.9767/bcrec.15.1.6670.175-185>.
- [82] E. Rafiee, M. Joshaghani, P. Ghaderi-Shekh Abadi, Oxidative desulfurization of diesel by potato based-carbon as green support for H₃PMo₁₀V₂O₄₀: Efficient composite nanorod catalyst, *Journal of Saudi Chemical Society* 21(5) (2017) 599-609. <https://doi.org/10.1016/j.jscs.2017.02.003>.
- [83] P. Huang, A. Liu, L. Kang, B. Dai, M. Zhu, J. Zhang, Heteropolyacid Supported on Nitrogen-doped Onion-Like Carbon as Catalyst for Oxidative Desulfurization, *ChemistrySelect* 2(14) (2017) 4010-4015. <https://doi.org/10.1002/slct.201700226>.
- [84] E. Rafiee, A. Shahbazirad, M. Khodayari, Preparation and characterization of nanocomposite of graphitic carbon nitride and TiO₂ as a porous support for nano catalyst for desulfurization process, *Journal of Saudi Chemical Society* 21(8) (2017) 943-953. <https://doi.org/10.1016/j.jscs.2017.04.006>.
- [85] A.A. Abdelrahman, M.A. Betiha, A.M. Rabie, H.S. Ahmed, M.F. Elshahat, Removal of refractory Organo-sulfur compounds using an efficient and recyclable {Mo₁₃₂} nanoball supported graphene oxide, *Journal of Molecular Liquids* 252 (2018) 121-132. <https://doi.org/10.1016/j.molliq.2017.12.124>.
- [86] C. Wang, A. Li, J. Xu, J. Wen, H. Zhang, L. Zhang, Preparation of WO₃/CNT catalysts in presence of ionic liquid [C₁₆mim]Cl and catalytic efficiency in oxidative desulfurization, *Journal of Chemical Technology & Biotechnology* 94(10) (2019) 3403-3412. <https://doi.org/10.1002/jctb.6154>.
- [87] Y. Gao, L. Cheng, R. Gao, G. Hu, J. Zhao, Deep desulfurization of fuels using supported ionic liquid-polyoxometalate hybrid as catalyst: A comparison of different types of ionic liquids, *Journal of Hazardous Materials* 401 (2021) 123267. <https://doi.org/10.1016/j.jhazmat.2020.123267>.
- [88] L. Zhuang, Q. Li, S. Chen, X. Hou, J. Lin, In-situ preparation of porous carbon-supported molybdenum dioxide and its performance in the oxidative desulfurization of thiophene, *Journal of Materials Science* 49(16) (2014) 5606-5616. <https://doi.org/10.1007/s10853-014-8273-5>.
- [89] Y. Gao, Z. Liu, R. Gao, G. Hu, J. Zhao, Support ionic liquid-heteropolyacid hybrid on mesoporous carbon aerogel with a high surface area for highly efficient desulfurization under mild conditions, *Microporous and Mesoporous Materials* 305 (2020) 110392. <https://doi.org/10.1016/j.micromeso.2020.110392>.
- [90] Z. Rongxiang, L. Xiuping, S. Jianxun, S. Weiwei, G. Xiaohan, The preparation of WO₃/C composite and its application in oxidative desulfurization of fuel, *China Petroleum Processing and Petrochemical Technology* 19(2) (2017) 65-73.
- [91] J. Xiao, L. Wu, Y. Wu, B. Liu, L. Dai, Z. Li, Q. Xia, H. Xi, Effect of gasoline composition on oxidative desulfurization using a phosphotungstic acid/activated carbon catalyst with hydrogen peroxide, *Applied Energy* 113 (2014) 78-85. <https://doi.org/10.1016/j.apenergy.2013.06.047>.

- [92] B.N. Bhadra, J.Y. Song, N.A. Khan, S.H. Jung, TiO₂-Containing Carbon Derived from a Metal–Organic Framework Composite: A Highly Active Catalyst for Oxidative Desulfurization, *ACS Applied Materials & Interfaces* 9(36) (2017) 31192-31202. <https://doi.org/10.1021/acsami.7b10336>.
- [93] N.A. Khan, B.N. Bhadra, S.W. Park, Y.S. Han, S.H. Jung, Tungsten Nitride, Well-Dispersed on Porous Carbon: Remarkable Catalyst, Produced without Addition of Ammonia, for the Oxidative Desulfurization of Liquid Fuel, *Small* 16(12) (2020) e1901564. <https://doi.org/10.1002/sml.201901564>.
- [94] N.T. do Prado, A.P. Heitmann, H.S. Mansur, A.A. Mansur, L.C.A. Oliveira, C.S. de Castro, PET-modified red mud as catalysts for oxidative desulfurization reactions, *Journal of Environmental Sciences* 57 (2017) 312-320. <https://doi.org/10.1016/j.jes.2017.01.011>.
- [95] C. Wang, Q. Miao, X. Huang, J. Li, Y. Duan, L. Yan, Y. Jiang, S. Lu, Fabrication of various morphological forms of a g-C₃N₄-supported MoO₃ catalyst for the oxidative desulfurization of dibenzothiophene, *New Journal of Chemistry* 44(43) (2020) 18745-18755. <https://doi.org/10.1039/d0nj04105j>.
- [96] R. Zhao, X. Li, J. Su, X. Gao, Preparation of WO₃/g-C₃N₄ composites and their application in oxidative desulfurization, *Applied Surface Science* 392 (2017) 810-816. <https://doi.org/10.1016/j.apsusc.2016.08.120>.
- [97] J. Zhu, P. Wu, L. Chen, J. He, Y. Wu, C. Wang, Y. Chao, L. Lu, M. He, W. Zhu, H. Li, 3D-printing of integrated spheres as a superior support of phosphotungstic acid for deep oxidative desulfurization of fuel, *Journal of Energy Chemistry* 45 (2020) 91-97. <https://doi.org/10.1016/j.jechem.2019.10.001>.
- [98] L.-p. Hou, R.-x. Zhao, X.-p. Li, X.-h. Gao, Preparation of MoO₂/g-C₃N₄ composites with a high surface area and its application in deep desulfurization from model oil, *Applied Surface Science* 434 (2018) 1200-1209. <https://doi.org/10.1016/j.apsusc.2017.10.076>.
- [99] J. Ye, J. Wen, D. Zhao, P. Zhang, A. Li, L. Zhang, H. Zhang, M. Wu, Macroporous 3D carbon-nitrogen (CN) confined MoO_x catalyst for enhanced oxidative desulfurization of dibenzothiophene, *Chinese Chemical Letters* 31(10) (2020) 2819-2824. <https://doi.org/10.1016/j.cclet.2020.08.004>.
- [100] R. Ghubayra, C. Nuttall, S. Hodgkiss, M. Craven, E.F. Kozhevnikova, I.V. Kozhevnikov, Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids, *Applied Catalysis B: Environmental* 253 (2019) 309-316. <https://doi.org/10.1016/j.apcatb.2019.04.063>.
- [101] R. Wang, F. Yu, G. Zhang, H. Zhao, Performance evaluation of the carbon nanotubes supported Cs_{2.5}H_{0.5}PW₁₂O₄₀ as efficient and recoverable catalyst for the oxidative removal of dibenzothiophene, *Catalysis Today* 150(1-2) (2010) 37-41. <https://doi.org/10.1016/j.cattod.2009.10.001>.
- [102] P. Xing, R. Zhao, X. Li, X. Gao, Preparation of CoWO₄/g-C₃N₄ and its Ultra-Deep Desulfurization Property, *Australian Journal of Chemistry* 70(3) (2017) 271-279. <https://doi.org/10.1071/ch16320>.
- [103] N.D.V. Quyen, T.N. Tuyen, D.Q. Khieu, H.V.M. Hai, D.X. Tin, K. Itatani, Oxidation of dibenzothiophene using the heterogeneous catalyst of tungsten-based carbon nanotubes, *Green Processing and Synthesis* 8(1) (2019) 68-77. <https://doi.org/10.1515/gps-2017-0189>.
- [104] Q. Wang, S. Wang, H. Yu, Oxidative desulphurization of model fuel by in situ produced hydrogen peroxide on palladium/active carbon, *The Canadian Journal of Chemical Engineering* 95(1) (2017) 136-141. <https://doi.org/10.1002/cjce.22636>.
- [105] G.X. Yu, R.X. Zhou, J.B. Li, X.L. Zhou, C.L. Li, L.F. Chen, J.A. Wang, Oxidative Removal of Dibenzothiophene by H₂O₂ over Activated Carbon-Supported Phosphotungstic Acid Catalysts, *Advanced Materials Research* 132 (2010) 126-132. <https://doi.org/10.4028/www.scientific.net/AMR.132.126>.
- [106] A. Mojaverian Kermani, A. Ahmadpour, T. Rohani Bastami, M. Ghahramaninezhad, Deep oxidative desulfurization of dibenzothiophene with {Mo-132} nanoballs supported on activated carbon as an efficient catalyst at room temperature, *New Journal of Chemistry* 42(14) (2018) 12188-12197. <https://doi.org/10.1039/c8nj01735b>.
- [107] L. Liu, Y. Zhang, W. Tan, Ultrasound-assisted oxidation of dibenzothiophene with phosphotungstic acid supported on activated carbon, *Ultrasonics Sonochemistry* 21(3) (2014) 970-4. <https://doi.org/10.1016/j.ultsonch.2013.10.028>.
- [108] L. Liu, Y. Zhang, W. Tan, Synthesis and characterization of phosphotungstic acid/activated carbon as a novel ultrasound oxidative desulfurization catalyst, *Frontiers of Chemical Science and Engineering* 7(4) (2013) 422-427. <https://doi.org/10.1007/s11705-013-1353-2>.
- [109] D. Piccinino, I. Abdalghani, G. Botta, M. Crucianelli, M. Passacantando, M.L. Di Vacri, R. Saladino, Preparation of wrapped carbon nanotubes poly(4-vinylpyridine)/MTO based heterogeneous catalysts for the

oxidative desulfurization (ODS) of model and synthetic diesel fuel, *Applied Catalysis B: Environmental* 200 (2017) 392-401. <https://doi.org/10.1016/j.apcatb.2016.07.037>.

[110] Z. Dini, M. Afsharpour, K. Tabar-Heydar, UV-assisted functionalization of carbon nanotube for synthesis of efficient desulfurization catalysts (NH₂/COOH)-MWNT/MoO₃, *Diamond and Related Materials* 91 (2019) 237-246. <https://doi.org/10.1016/j.diamond.2018.11.026>.

[111] M. Afsharpour, Z. Dini, One-pot functionalization of carbon nanotubes by WO₃/MoO₃ nanoparticles as oxidative desulfurization catalysts, *Fullerenes, Nanotubes and Carbon Nanostructures* 27(3) (2018) 198-205. <https://doi.org/10.1080/1536383x.2018.1538132>.

[112] B.N. Bhadra, N.A. Khan, S.H. Jung, Co supported on N-doped carbon, derived from bimetallic azolate framework-6: a highly effective oxidative desulfurization catalyst, *Journal of Materials Chemistry A* 7(30) (2019) 17823-17833. <https://doi.org/10.1039/c9ta03613j>.

[113] X. Liao, Y. Huang, Y. Zhou, H. Liu, Y. Cai, S. Lu, Y. Yao, Homogeneously dispersed HPW/graphene for high efficient catalytic oxidative desulfurization prepared by electrochemical deposition, *Applied Surface Science* 484 (2019) 917-924. <https://doi.org/10.1016/j.apsusc.2019.04.156>.

[114] R. Ma, J. Guo, D. Wang, M. He, S. Xun, J. Gu, W. Zhu, H. Li, Preparation of highly dispersed WO₃/few layer g-C₃N₄ and its enhancement of catalytic oxidative desulfurization activity, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 572 (2019) 250-258. <https://doi.org/10.1016/j.colsurfa.2019.04.006>.

[115] K. Chen, X.-M. Zhang, X.-F. Yang, M.-G. Jiao, Z. Zhou, M.-H. Zhang, D.-H. Wang, X.-H. Bu, Electronic structure of heterojunction MoO₃/g-C₃N₄ catalyst for oxidative desulfurization, *Applied Catalysis B: Environmental* 238 (2018) 263-273. <https://doi.org/10.1016/j.apcatb.2018.07.037>.

[116] S. Xun, Q. Ti, L. Wu, M. He, C. Wang, L. Chen, W. Yang, L. Zhu, W. Zhu, H. Li, Few layer g-C₃N₄ dispersed quaternary phosphonium ionic liquid for highly efficient catalytic oxidative desulfurization of fuel, *Energy & Fuels* 34(10) (2020) 12379-12387. <https://doi.org/10.1021/acs.energyfuels.0c02357>.

[117] J. Gu, M. Liu, S. Xun, M. He, L. Wu, L. Zhu, X. Wu, W. Zhu, H. Li, Lipophilic decavanadate supported by three-dimensional porous carbon nitride catalyst for aerobic oxidative desulfurization, *Molecular Catalysis* 483 (2020) 110709. <https://doi.org/10.1016/j.mcat.2019.110709>.

[118] S. Chen, W. Lu, Y. Yao, H. Chen, W. Chen, Oxidative desulfurization of dibenzothiophene with molecular oxygen catalyzed by carbon fiber-supported iron phthalocyanine, *Reaction Kinetics, Mechanisms and Catalysis* 111(2) (2013) 535-547. <https://doi.org/10.1007/s11144-013-0661-3>.

[119] S. Xun, Q. Ti, Z. Jiao, L. Wu, M. He, L. Chen, L. Zhu, W. Zhu, H. Li, Dispersing TiO₂ nanoparticles on graphite carbon for an enhanced catalytic oxidative desulfurization performance, *Industrial & Engineering Chemistry Research* 59(41) (2020) 18471-18479. <https://doi.org/10.1021/acs.iecr.0c03202>.

[120] Y. Gao, Z. Lv, R. Gao, G. Hu, J. Zhao, Dawson type polyoxometalate based-poly ionic liquid supported on different carbon materials for high-efficiency oxidative desulfurization with molecular oxygen as the oxidant, *New Journal of Chemistry* 44(46) (2020) 20358-20366. <https://doi.org/10.1039/d0nj04526h>.

[121] L. Chen, J.-T. Ren, Z.-Y. Yuan, Atomic heterojunction-induced electron interaction in P-doped g-C₃N₄ nanosheets supported V-based nanocomposites for enhanced oxidative desulfurization, *Chemical Engineering Journal* 387 (2020) 124164. <https://doi.org/10.1016/j.cej.2020.124164>.

[122] J. Zou, Y. Lin, S. Wu, Y. Zhong, C. Yang, Molybdenum Dioxide Nanoparticles Anchored on Nitrogen-Doped Carbon Nanotubes as Oxidative Desulfurization Catalysts: Role of Electron Transfer in Activity and Reusability, *Advanced Functional Materials* 31(22) (2021) 2100442. <https://doi.org/10.1002/adfm.202100442>.

[123] C. Wang, W. Zhu, Y. Xu, H. Xu, M. Zhang, Y. Chao, S. Yin, H. Li, J. Wang, Preparation of TiO₂/g-C₃N₄ composites and their application in photocatalytic oxidative desulfurization, *Ceramics International* 40(8) (2014) 11627-11635. <https://doi.org/10.1016/j.ceramint.2014.03.156>.

[124] X. Li, W. Zhu, X. Lu, S. Zuo, C. Yao, C. Ni, Integrated nanostructures of CeO₂/attapulgite/g-C₃N₄ as efficient catalyst for photocatalytic desulfurization: Mechanism, kinetics and influencing factors, *Chemical Engineering Journal* 326 (2017) 87-98. <https://doi.org/10.1016/j.cej.2017.05.131>.

[125] S. Ma, X. Li, X. Lu, S. Zuo, Z. Li, C. Yao, Carbon quantum dots/attapulgite nanocomposites with enhanced photocatalytic performance for desulfurization, *Journal of Materials Science: Materials in Electronics* 29(4) (2017) 2709-2715. <https://doi.org/10.1007/s10854-017-8197-3>.

- [126] G. Zhang, J. Ren, W. Zhao, M. Tian, W. Chen, Photocatalytic desulfurization of thiophene base on molecular oxygen and zinc phthalocyanine/g-C₃N₄, *Research on Chemical Intermediates* 44(9) (2018) 5547-5557. <https://doi.org/10.1007/s11164-018-3439-4>.
- [127] T.H.T. Vu, T.T.T. Nguyen, P.H.T. Nguyen, M.H. Do, H.T. Au, T.B. Nguyen, D.L. Nguyen, J.S. Park, Fabrication of photocatalytic composite of multi-walled carbon nanotubes/TiO₂ and its application for desulfurization of diesel, *Materials Research Bulletin* 47(2) (2012) 308-314. <https://doi.org/10.1016/j.materresbull.2011.11.016>.
- [128] W. Jiang, D. Zheng, S. Xun, Y. Qin, Q. Lu, W. Zhu, H. Li, Polyoxometalate-based ionic liquid supported on graphite carbon induced solvent-free ultra-deep oxidative desulfurization of model fuels, *Fuel* 190 (2017) 1-9. <https://doi.org/10.1016/j.fuel.2016.11.024>.
- [129] M.A. Astle, G.A. Rance, H.J. Loughlin, T.D. Peters, A.N. Khlobystov, Molybdenum Dioxide in Carbon Nanoreactors as a Catalytic Nanosponge for the Efficient Desulfurization of Liquid Fuels, *Advanced Functional Materials* 29(17) (2019) 1808092. <https://doi.org/10.1002/adfm.201808092>.
- [130] Z.C. Kampouraki, D.A. Giannakoudakis, K.S. Triantafyllidis, E.A. Deliyanni, Catalytic oxidative desulfurization of a 4,6-DMDBT containing model fuel by metal-free activated carbons: the key role of surface chemistry, *Green Chemistry* 21(24) (2019) 6685-6698. <https://doi.org/10.1039/c9gc03234g>.
- [131] J. He, P. Wu, L. Lu, H. Sun, Q. Jia, M. Hua, M. He, C. Xu, W. Zhu, H. Li, Synthesis of N,O-doped porous graphene from petroleum coke for deep oxidative desulfurization of fuel, *Energy & Fuels* 33(9) (2019) 8302-8311. <https://doi.org/10.1021/acs.energyfuels.9b01832>.
- [132] L.A. Gonzalez, P. Kracke, W.H. Green, J.W. Tester, L.M. Shafer, M.T. Timko, Oxidative desulfurization of middle-distillate fuels using activated carbon and power ultrasound, *Energy & Fuels* 26(8) (2012) 5164-5176. <https://doi.org/10.1021/ef201289r>.
- [133] K.-G. Haw, W.A.W.A. Bakar, R. Ali, J.-F. Chong, A.A.A. Kadir, Catalytic oxidative desulfurization of diesel utilizing hydrogen peroxide and functionalized-activated carbon in a biphasic diesel-acetonitrile system, *Fuel Processing Technology* 91(9) (2010) 1105-1112. <https://doi.org/10.1016/j.fuproc.2010.03.021>.
- [134] Q. Gu, Y. Ding, Z. Liu, Y. Lin, R. Schlögl, S. Heumann, D. Su, Probing the intrinsic catalytic activity of carbon nanotubes for the metal-free oxidation of aromatic thiophene compounds in ionic liquids, *Journal of Energy Chemistry* 32 (2019) 131-137. <https://doi.org/10.1016/j.jechem.2018.07.004>.
- [135] Q. Gu, G. Wen, Y. Ding, K.-H. Wu, C. Chen, D. Su, Reduced graphene oxide: a metal-free catalyst for aerobic oxidative desulfurization, *Green Chemistry* 19(4) (2017) 1175-1181. <https://doi.org/10.1039/c6gc02894b>.
- [136] W. Zhang, H. Zhang, J. Xiao, Z. Zhao, M. Yu, Z. Li, Carbon nanotube catalysts for oxidative desulfurization of a model diesel fuel using molecular oxygen, *Green Chemistry* 16(1) (2014) 211-220. <https://doi.org/10.1039/c3gc41106k>.
- [137] X. Zeng, X. Xiao, Y. Li, J. Chen, H. Wang, Deep desulfurization of liquid fuels with molecular oxygen through graphene photocatalytic oxidation, *Applied Catalysis B: Environmental* 209 (2017) 98-109. <https://doi.org/10.1016/j.apcatb.2017.02.077>.
- [138] M.T. Timko, J.A. Wang, J. Burgess, P. Kracke, L. Gonzalez, C. Jaye, D.A. Fischer, Roles of surface chemistry and structural defects of activated carbons in the oxidative desulfurization of benzothiophenes, *Fuel* 163 (2016) 223-231. <https://doi.org/10.1016/j.fuel.2015.09.075>.
- [139] G. Abdi, M. Ashokkumar, A. Alizadeh, Ultrasound-assisted oxidative-adsorptive desulfurization using highly acidic graphene oxide as a catalyst-adsorbent, *Fuel* 210 (2017) 639-645. <https://doi.org/10.1016/j.fuel.2017.09.024>.
- [140] H. Liu, Z. Li, J. Dong, D. Liu, C. Liu, Y. Chi, C. Hu, Polyoxometalates encapsulated into hollow double-shelled nanospheres as amphiphilic nanoreactors for an effective oxidative desulfurization, *Nanoscale* 12(31) (2020) 16586-16595. <https://doi.org/10.1039/d0nr03951a>.
- [141] Z. Yu, X. Huang, S. Xun, M. He, L. Zhu, L. Wu, M. Yuan, W. Zhu, H. Li, Synthesis of carbon nitride supported amphiphilic phosphotungstic acid based ionic liquid for deep oxidative desulfurization of fuels, *Journal of Molecular Liquids* 308 (2020) 113059. <https://doi.org/10.1016/j.molliq.2020.113059>.
- [142] X. Li, X. Yang, F. Zhou, J. Zhang, H. Yang, Y. Wang, Y. Zhao, X. Yuan, J. Ju, S. Hu, Construction of novel amphiphilic [Bmin]₃PMo₁₂O₄₀/g-C₃N₄ heterojunction catalyst with outstanding photocatalytic oxidative desulfurization performance under visible light, *Journal of the Taiwan Institute of Chemical Engineers* 100 (2019) 210-219. <https://doi.org/10.1016/j.jtice.2019.04.024>.

- [143] R.V. Mambrini, C.Z. Maia, J.D. Ardisson, P.P. de Souza, F.C.C. Moura, Fe/C and FeMo/C hybrid materials for the biphasic oxidation of fuel contaminants, *New Journal of Chemistry* 41(1) (2017) 142-150. <https://doi.org/10.1039/c6nj02718k>.
- [144] A.A.S. Oliveira, T. Christofani, I.F. Teixeira, J.D. Ardisson, F.C.C. Moura, Magnetic amphiphilic nanocomposites based on silica-carbon for sulphur contaminant oxidation, *New Journal of Chemistry* 39(7) (2015) 5445-5452. <https://doi.org/10.1039/c5nj00593k>.
- [145] A.A.S. Oliveira, I.F. Teixeira, T. Christofani, J.C. Tristão, I.R. Guimarães, F.C.C. Moura, Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue, *Applied Catalysis B: Environmental* 144 (2014) 144-151. <https://doi.org/10.1016/j.apcatb.2013.07.015>.
- [146] I.F. Teixeira, A.A.d.S. Oliveira, T. Christofani, F.C.C. Moura, Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process, *Journal of Materials Chemistry A* 1(35) (2013) 10203-10208. <https://doi.org/10.1039/c3ta11535f>.
- [147] S.-Y. Dou, R. Wang, The C-Si Janus nanoparticles with supported phosphotungstic active component for Pickering emulsion desulfurization of fuel oil without stirring, *Chemical Engineering Journal* 369 (2019) 64-76. <https://doi.org/10.1016/j.cej.2019.03.050>.
- [148] J.L. Diaz de Tuesta, M.C. Saviotti, F.F. Roman, G.F. Pantuzza, H.J.F. Sartori, A. Shinibekova, M.S. Kalmakhanova, B.K. Massalimova, J.M.T.A. Pietrobelli, G.G. Lenzi, H.T. Gomes, Assisted hydrothermal carbonization of agroindustrial byproducts as effective step in the production of activated carbon catalysts for wet peroxide oxidation of micro-pollutants, *Journal of Environmental Chemical Engineering* 9(1) (2021) 105004. <https://doi.org/10.1016/j.jece.2020.105004>.
- [149] A. Santos Silva, M. Seitovna Kalmakhanova, B. Kabykenovna Massalimova, J. G. Sgorlon, D.d.T. Jose Luis, H. T. Gomes, Wet peroxide oxidation of paracetamol using acid activated and Fe/Co-pillared clay catalysts prepared from natural clays, *Catalysts* 9(9) (2019) 705. <https://doi.org/10.3390/catal9090705>.
- [150] I.R. Guimarães, A.S. Giroto, W.F. de Souza, M.C. Guerreiro, Highly reactive magnetite covered with islands of carbon: Oxidation of N and S-containing compounds in a biphasic system, *Applied Catalysis A: General* 450 (2013) 106-113. <https://doi.org/10.1016/j.apcata.2012.10.017>.
- [151] S. Hasannia, M. Kazemeini, A. Rashidi, A. Seif, The oxidative desulfurization process performed upon a model fuel utilizing modified molybdenum based nanocatalysts: Experimental and density functional theory investigations under optimally prepared and operated conditions, *Applied Surface Science* 527 (2020) 146798. <https://doi.org/10.1016/j.apsusc.2020.146798>.
- [152] W.N.W. Abdullah, W.A.W.A. Bakar, N.H. Abdullah, W.N.A.W. Mokhtar, S.J.M. Rosid, N.M. Shukri, Effect of activated carbon supported Ce/Fe based catalyst for catalytic oxidative desulfurization of Malaysian diesel fuel, *AIP Conference Proceedings* 2068 (2019) 020075. <https://doi.org/10.1063/1.5089374>.
- [153] A.K. Dizaji, B. Mokhtarani, H.R. Mortaheb, Deep and fast oxidative desulfurization of fuels using graphene oxide-based phosphotungstic acid catalysts, *Fuel* 236 (2019) 717-729. <https://doi.org/10.1016/j.fuel.2018.09.076>.
- [154] A. Khodadadi Dizaji, H.R. Mortaheb, B. Mokhtarani, Complete oxidative desulfurization using graphene oxide-based phosphomolybdic acid catalyst: Process optimization by two phase mass balance approach, *Chemical Engineering Journal* 335 (2018) 362-372. <https://doi.org/10.1016/j.cej.2017.10.129>.
- [155] V. Tamborrino, G. Costamagna, M. Bartoli, M. Rovere, P. Jagdale, L. Lavagna, M. Ginepro, A. Tagliaferro, Catalytic oxidative desulfurization of pyrolytic oils to fuels over different waste derived carbon-based catalysts, *Fuel* 296 (2021) 120693. <https://doi.org/10.1016/j.fuel.2021.120693>.
- [156] Y. Gao, R. Gao, G. Zhang, Y. Zheng, J. Zhao, Oxidative desulfurization of model fuel in the presence of molecular oxygen over polyoxometalate based catalysts supported on carbon nanotubes, *Fuel* 224 (2018) 261-270. <https://doi.org/10.1016/j.fuel.2018.03.034>.
- [157] Y. Gao, Z. Lv, R. Gao, G. Zhang, Y. Zheng, J. Zhao, Oxidative desulfurization process of model fuel under molecular oxygen by polyoxometalate loaded in hybrid material CNTs@MOF-199 as catalyst, *Journal of Hazardous Materials* 359 (2018) 258-265. <https://doi.org/10.1016/j.jhazmat.2018.07.008>.
- [158] Y. Wang, G. Zhang, T. Guan, F. Xu, J. Wu, E. Zhou, J. Wang, K. Li, Ultra-deep oxidative desulfurization of model oil catalyzed by in situ carbon-supported vanadium oxides using cumene hydroperoxide as oxidant, *ChemistrySelect* 5(7) (2020) 2148-2156. <https://doi.org/10.1002/slct.201903893>.
- [159] W. Jiang, J. Xiao, L. Dong, C. Wang, H. Li, Y. Luo, W. Zhu, H. Li, Polyoxometalate-based poly(ionic liquid) as a precursor for superhydrophobic magnetic carbon composite catalysts toward aerobic oxidative

- desulfurization, *ACS Sustainable Chemistry & Engineering* 7(18) (2019) 15755-15761. <https://doi.org/10.1021/acsschemeng.9b04026>.
- [160] M.T. Timko, E. Schmois, P. Patwardhan, Y. Kida, C.A. Class, W.H. Green, R.K. Nelson, C.M. Reddy, Response of different types of sulfur compounds to oxidative desulfurization of jet fuel, *Energy & Fuels* 28(5) (2014) 2977-2983. <https://doi.org/10.1021/ef500216p>.
- [161] Y. Zhang, R. Wang, Synthesis of silica@C-dots/phosphotungstates core-shell microsphere for effective oxidative-adsorptive desulfurization of dibenzothiophene with less oxidant, *Applied Catalysis B: Environmental* 234 (2018) 247-259. <https://doi.org/10.1016/j.apcatb.2018.04.031>.
- [162] A.A.S. Oliveira, D.A.S. Costa, I.F. Teixeira, F.C.C. Moura, Gold nanoparticles supported on modified red mud for biphasic oxidation of sulfur compounds: A synergistic effect, *Applied Catalysis B: Environmental* 162 (2015) 475-482. <https://doi.org/10.1016/j.apcatb.2014.07.003>.
- [163] M.A. Rezvani, M. Shaterian, Z. Shokri Aghbolagh, R. Babaei, Oxidative desulfurization of gasoline catalyzed by IMID@PMA@CS nanocomposite as a high-performance amphiphilic nanocatalyst, *Environmental Progress & Sustainable Energy* 37(6) (2018) 1891-1900. <https://doi.org/10.1002/ep.12863>.
- [164] W.F. Souza, M.C. Pereira, L.C. A. Oliveira, Amphiphilic catalysts based on onion-like carbon over magnetic iron oxide for petrochemical industry use, *Fuel* 96 (2012) 604-607. <https://doi.org/10.1016/j.fuel.2012.01.011>.
- [165] A.A.S. Oliveira, A.R. Martins, R.V. Ferreira, I.T. Cunha, P. Serp, J.P. de Mesquita, F.C.C. Moura, N-doped carbon nanotubes grown on red mud residue: Hybrid nanocomposites for technological applications, *Catalysis Today* 344 (2020) 247-258. <https://doi.org/10.1016/j.cattod.2019.04.060>.
- [166] A.D. Purceno, B.F. Machado, A.P. Teixeira, T.V. Medeiros, A. Benyounes, J. Beausoleil, H.C. Menezes, Z.L. Cardeal, R.M. Lago, P. Serp, Magnetic amphiphilic hybrid carbon nanotubes containing N-doped and undoped sections: powerful tensioactive nanostructures, *Nanoscale* 7(1) (2015) 294-300. <https://doi.org/10.1039/c4nr04005h>.
- [167] S.H. Ammar, Y.S. Kareem, M.S. Mohammed, Catalytic-oxidative/adsorptive denitrogenation of model hydrocarbon fuels under ultrasonic field using magnetic reduced graphene oxide-based phosphomolybdic acid (PMo-Fe₃O₄/rGO), *Ultrasonics Sonochemistry* 64 (2020) 105050. <https://doi.org/10.1016/j.ultsonch.2020.105050>.
- [168] B.N. Bhadra, J.Y. Song, N. Uddin, N.A. Khan, S. Kim, C.H. Choi, S.H. Jung, Oxidative denitrogenation with TiO₂@porous carbon catalyst for purification of fuel: Chemical aspects, *Applied Catalysis B: Environmental* 240 (2019) 215-224. <https://doi.org/10.1016/j.apcatb.2018.09.004>.
- [169] M. Martin-Martinez, R.S. Ribeiro, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Role of Nitrogen Doping on the Performance of Carbon Nanotube Catalysts: A Catalytic Wet Peroxide Oxidation Application, *ChemCatChem* 8(12) (2016) 2068-2078. <https://doi.org/10.1002/cctc.201600123>.
- [170] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, S. Morales-Torres, J.L. Faria, A.M.T. Silva, H.T. Gomes, The pH effect on the kinetics of 4-nitrophenol removal by CWPO with doped carbon black catalysts, *Catalysis Today* 356 (2020) 216-225. <https://doi.org/10.1016/j.cattod.2019.08.033>.
- [171] J.L. Diaz de Tuesta, B. F. Machado, P. Serp, A.M. T. Silva, J.L. Faria, H. T. Gomes, Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide, *Catalysis Today* 356 (2020) 205-215. <https://doi.org/10.1016/j.cattod.2019.07.012>.
- [172] C.V. Diniz, J.V. Nascimento, I. Binatti, P.E. Freitas, R.V. Mambrini, Hybrid catalysts based on waste electrical and electronic equipment supported on bentonite for the removal of contaminants compounds in liquid phase, *Catalysis Today* 344 (2020) 75-83. <https://doi.org/10.1016/j.cattod.2018.10.030>.
- [173] X.-D. Wang, K. Vinodgopal, G.-P. Dai, Synthesis of Carbon Nanotubes by Catalytic Chemical Vapor Deposition, in: H.E.-D. Saleh, S.M.M. El-Sheikh (Eds.), *Perspective of Carbon Nanotubes*, InTechOpen, London, 2019, pp. 1-19. <https://doi.org/10.5772/intechopen.86995>.
- [174] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, *Nature* 363(6430) (1993) 603-605. <https://doi.org/10.1038/363603a0>.
- [175] P.K. Sonkar, Narvdeshwar, P.K. Gupta, Characteristics of carbon nanotubes and their nanocomposites, in: S. Thomas, N. Kalarikkal, A.R. Abraham (Eds.), *Fundamentals and Properties of Multifunctional Nanomaterials*, Elsevier, Amsterdam, Netherlands, 2021, pp. 99-118. <https://doi.org/10.1016/b978-0-12-822352-9.00011-0>.

- [176] M.M.-A. Aslam, H.-W. Kuo, W. Den, M. Usman, M. Sultan, H. Ashraf, Functionalized Carbon Nanotubes (CNTs) for water and wastewater treatment: Preparation to application, *Sustainability* 13(10) (2021) 5717. <https://doi.org/10.3390/su13105717>.
- [177] Y.J. Choi, E.J.C. Nacpil, J. Han, C. Zhu, I.S. Kim, I. Jeon, Recent Advances in dispersant technology for Carbon Nanotubes toward energy device applications, *Advanced Energy and Sustainability Research* 5(4) (2024) 2300219. <https://doi.org/10.1002/aesr.202300219>.
- [178] S. Zhang, J. Pang, Y. Li, F. Yang, T. Gemming, K. Wang, X. Wang, S. Peng, X. Liu, B. Chang, H. Liu, W. Zhou, G. Cuniberti, M.H. Rummeli, Emerging Internet of Things driven carbon nanotubes-based devices, *Nano Research* 15(5) (2022) 4613-4637. <https://doi.org/10.1007/s12274-021-3986-7>.
- [179] N. Mohd Nurazzi, M.R.M. Asyraf, A. Khalina, N. Abdullah, F.A. Sabaruddin, S.H. Kamarudin, S. Ahmad, A.M. Mahat, C.L. Lee, H.A. Aisyah, M.N.F. Norrrahim, R.A. Ilyas, M.M. Harussani, M.R. Ishak, S.M. Sapuan, Fabrication, functionalization, and application of Carbon Nanotube-reinforced polymer composite: An overview, *Polymers* 13(7) (2021) 1047. <https://doi.org/10.3390/polym13071047>.
- [180] N. Anzar, R. Hasan, M. Tyagi, N. Yadav, J. Narang, Carbon nanotube - A review on Synthesis, Properties and plethora of applications in the field of biomedical science, *Sensors International* 1 (2020) 100003. <https://doi.org/10.1016/j.sintl.2020.100003>.
- [181] R. Purohit, K. Purohit, S. Rana, R.S. Rana, V. Patel, Carbon Nanotubes and their growth methods, *Procedia Materials Science* 6 (2014) 716-728. <https://doi.org/10.1016/j.mspro.2014.07.088>.
- [182] E.F. Kukovitsky, S.G. L'Vov, N.A. Sainov, V.A. Shustov, L.A. Chernozatonskii, Correlation between metal catalyst particle size and carbon nanotube growth, *Chemical Physics Letters* 355(5-6) (2002) 497-503. [https://doi.org/10.1016/s0009-2614\(02\)00283-x](https://doi.org/10.1016/s0009-2614(02)00283-x).
- [183] A.A. Aboul-Enein, A.E. Awadallah, A.A.H. Abdel-Rahman, A.M. Haggag, Synthesis of multi-walled carbon nanotubes via pyrolysis of plastic waste using a two-stage process, *Fullerenes, Nanotubes and Carbon Nanostructures* 26(7) (2018) 443-450. <https://doi.org/10.1080/1536383x.2018.1447929>.
- [184] N.A. El Essawy, A.H. Konsowa, M. Elnouby, H.A. Farag, A novel one-step synthesis for carbon-based nanomaterials from polyethylene terephthalate (PET) bottles waste, *Journal of the Air & Waste Management Association* 67(3) (2017) 358-370. <https://doi.org/10.1080/10962247.2016.1242517>.
- [185] A. Veksha, A. Giannis, V.W.C. Chang, Conversion of non-condensable pyrolysis gases from plastics into carbon nanomaterials: Effects of feedstock and temperature, *Journal of Analytical and Applied Pyrolysis* 124 (2017) 16-24. <https://doi.org/10.1016/j.jaap.2017.03.005>.
- [186] P.K. Tripathi, S. Durbach, N.J. Coville, Synthesis of Multi-Walled Carbon Nanotubes from Plastic Waste Using a Stainless-Steel CVD Reactor as Catalyst, *Nanomaterials* 7(10) (2017) 284. <https://doi.org/10.3390/nano7100284>.
- [187] C. Wu, M.A. Nahil, N. Miskolczi, J. Huang, P.T. Williams, Production and application of carbon nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic reforming of waste plastic, *Process Safety and Environmental Protection* 103 (2016) 107-114. <https://doi.org/10.1016/j.psep.2016.07.001>.
- [188] C. Wu, M.A. Nahil, N. Miskolczi, J. Huang, P.T. Williams, Processing real-world waste plastics by pyrolysis-reforming for hydrogen and high-value carbon nanotubes, *Environmental Science & Technology* 48(1) (2014) 819-26. <https://doi.org/10.1021/es402488b>.
- [189] Y. Zhang, M.A. Nahil, C. Wu, P.T. Williams, Pyrolysis-catalysis of waste plastic using a nickel-stainless-steel mesh catalyst for high-value carbon products, *Environmental Technology* 38(22) (2017) 2889-2897. <https://doi.org/10.1080/09593330.2017.1281351>.
- [190] A.A. Aboul-Enein, H. Adel-Rahman, A.M. Haggag, A.E. Awadallah, Simple method for synthesis of carbon nanotubes over Ni-Mo/Al₂O₃ catalyst via pyrolysis of polyethylene waste using a two-stage process, *Fullerenes, Nanotubes and Carbon Nanostructures* 25(4) (2017) 211-222. <https://doi.org/10.1080/1536383x.2016.1277422>.
- [191] D. Yao, C. Wu, H. Yang, Y. Zhang, M.A. Nahil, Y. Chen, P.T. Williams, H. Chen, Co-production of hydrogen and carbon nanotubes from catalytic pyrolysis of waste plastics on Ni-Fe bimetallic catalyst, *Energy Conversion and Management* 148 (2017) 692-700. <https://doi.org/10.1016/j.enconman.2017.06.012>.
- [192] A. Mukherjee, B. Debnath, S.K. Ghosh, Carbon Nanotubes as a Resourceful Product Derived from Waste Plastic—A Review, in: S.K. Ghosh (Ed.), *Waste Management and Resource Efficiency*, Springer Singapore, Singapore, 2019, pp. 915-934. https://doi.org/10.1007/978-981-10-7290-1_77.

- [193] J.L. Diaz de Tuesta, A.S. Silva, F.F. Roman, L.F. Sanches, F.A. da Silva, A.I. Pereira, A.M.T. Silva, J.L. Faria, H.T. Gomes, Polyolefin-derived carbon nanotubes as magnetic catalysts for wet peroxide oxidation of paracetamol in aqueous solutions, *Catalysis Today* 419 (2023) 114162. <https://doi.org/10.1016/j.cattod.2023.114162>.
- [194] Q.-L. Li, R. Shan, S.-X. Wang, H.-R. Yuan, Y. Chen, Production of carbon nanotubes via catalytic pyrolysis of waste plastics over Ni/Al₂O₃ catalyst: The influence of plastic types, *Journal of Analytical and Applied Pyrolysis* 177 (2024) 106318. <https://doi.org/10.1016/j.jaap.2023.106318>.
- [195] Q. Wu, X. Lv, N. Xu, L. Xin, G. Lin, K. Chen, M. He, Upcycling plastic polymers into single-walled carbon nanotubes from a magnesia supported iron catalyst, *Carbon* 215 (2023) 118492. <https://doi.org/10.1016/j.carbon.2023.118492>.
- [196] R.S. Ribeiro, O. Vieira, R. Fernandes, F.F. Roman, J.L. Diaz de Tuesta, A.M.T. Silva, H.T. Gomes, Synthesis of low-density polyethylene derived carbon nanotubes for activation of persulfate and degradation of water organic micropollutants in continuous mode, *Journal of Environmental Management* 308 (2022) 114622. <https://doi.org/10.1016/j.jenvman.2022.114622>.
- [197] A. Pattanshetti, N. Pradeep, V. Chaitra, V. Uma, Synthesis of multi-walled carbon nanotubes (MWCNTs) from plastic waste & analysis of garlic coated gelatin/MWCNTs nanocomposite films as food packaging material, *SN Applied Sciences* 2(4) (2020) 730. <https://doi.org/10.1007/s42452-020-2442-8>.
- [198] C. Zhuo, Y.A. Levendis, Upcycling waste plastics into carbon nanomaterials: A review, *Journal of Applied Polymer Science* 131(4) (2014) 39931. <https://doi.org/10.1002/app.39931>.
- [199] N. Cai, Q. Liu, Y. Zhu, H. Yang, H. Chen, Preparation of high-value carbon nanotubes from real waste plastic towards the negative carbon technology, *Carbon Capture Science & Technology* 13 (2024) 100258. <https://doi.org/10.1016/j.cccst.2024.100258>.
- [200] A. Abbas, Y.M. Yi, F. Saleem, Z. Jin, A. Veksha, Q. Yan, G. Lisak, T.M. Lim, Multiwall carbon nanotubes derived from plastic packaging waste as a high-performance electrode material for supercapacitors, *International Journal of Energy Research* 45(13) (2021) 19611-19622. <https://doi.org/10.1002/er.6967>.
- [201] E. Nam, G. Park, J.Y. Nam, S. Park, Y. Jo, J. Kim, B.G. Park, K. Baek, S.J. Kang, H.W. Ra, Y. Park, M.W. Seo, K.J. Lee, K. An, Upcycling of plastic waste into carbon nanotubes as efficient battery additives, *Green Chemistry* 25(20) (2023) 8007-8018. <https://doi.org/10.1039/d3gc02100a>.
- [202] D. Yao, H. Yang, Q. Hu, Y. Chen, H. Chen, P.T. Williams, Carbon nanotubes from post-consumer waste plastics: Investigations into catalyst metal and support material characteristics, *Applied Catalysis B: Environmental* 280 (2021) 119413. <https://doi.org/10.1016/j.apcatb.2020.119413>.
- [203] N. Cai, X. Li, S. Xia, L. Sun, J. Hu, P. Bartocci, F. Fantozzi, P.T. Williams, H. Yang, H. Chen, Pyrolysis-catalysis of different waste plastics over Fe/Al₂O₃ catalyst: High-value hydrogen, liquid fuels, carbon nanotubes and possible reaction mechanisms, *Energy Conversion and Management* 229 (2021) 113794. <https://doi.org/10.1016/j.enconman.2020.113794>.
- [204] P. Zhang, M. Wu, C. Liang, D. Luo, B. Li, J. Ma, In-situ exsolution of Fe-Ni alloy catalysts for H₂ and carbon nanotube production from microwave plasma-initiated decomposition of plastic wastes, *Journal of Hazardous Materials* 445 (2023) 130609. <https://doi.org/10.1016/j.jhazmat.2022.130609>.

CHAPTER 3 – METHODOLOGIES

Chapter 3

Methodologies

This chapter outlines the methodologies, materials, and equipment employed in this study, providing a detailed account of the experimental procedures. It begins with the synthesis of carbon nanotubes (CNTs), describing the preparation of catalysts for chemical vapor deposition purposes, synthesis conditions for CNT growth, and any modifications applied to optimize their properties for catalytic applications. The chapter then covers the characterization techniques used to analyze the structural, textural, and chemical properties of the synthesized materials. Subsequently, the procedures and reaction conditions for catalytic testing in oxidative desulfurization (ODS) and denitrogenation (ODN) systems are detailed. Finally, the analytical techniques used to assess catalytic efficiency, including sulfur and nitrogen content analysis, are described.

3.1 Reagents and Materials

Material synthesis

Two different types of materials are produced in this work: (i) the metal-based catalysts used for the growth of the carbon nanotubes and (ii) the carbon nanotubes themselves.

(i) For the synthesis of metal-based catalysts: Alumina (Al_2O_3) was obtained from BASF (Nienburg, Germany) in the form of pellets. Before being used, it was ground and sieved in the 53–106 μm range. Ethanol absolute ($\text{C}_2\text{H}_6\text{O}$, 99.8%), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%) and nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, analytical reagent grade) were provided by Fisher Scientific (Waltham, MA, USA). Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 98%) was provided by Acros Organics (Geel, Belgium). Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) was obtained from VWR Chemicals (Radnor, PA, USA).

(ii) For carbon nanotubes synthesis: High-density polyethylene (**HDPE**, melt index 2.2 g/10 min), low-density polyethylene (**LDPE**, weight average molecular weight $\sim 35,000 \text{ g mol}^{-1}$, number average molecular weight ~ 7700), polypropylene (**PP**, weight average molecular weight $\sim 250,000 \text{ g mol}^{-1}$, number average molecular weight $\sim 67,000$) and polystyrene (**PS**; Average Mw – 192,000) were obtained from Sigma-Aldrich (St. Louis, MI, USA). Nitric acid (HNO_3 , 69%) was provided by PanReac AppliChem (Darmstadt, Germany). Sulfuric acid (H_2SO_4 , 98%) was obtained from Labkem (Lucknow, India).

Materials characterization

Spray mount was obtained from 3M (St. Paul, Minnesota, USA). Hydrochloric acid (HCl , 37%) was provided by VWR Chemicals (Radnor, PA, USA). Potassium bromide (KBr , 99%) was obtained from Acros Organics (Geel, Belgium). Sodium hydroxide pearls (NaOH , 98%) were obtained from Labkem (Lucknow, India).

Reaction runs and analytical methods

Acetonitrile (**ACN**, $\text{C}_2\text{H}_3\text{N}$, 99.9%) and orthophosphoric acid (H_3PO_4 , 85%) were provided by Fisher Chemical (Waltham, MA, USA). Hydrogen peroxide (H_2O_2 , 30%), 2,2,4-trimethylpentane (C_8H_{18} , 99.9%), pyridine (**PYR**, $\text{C}_5\text{H}_5\text{N}$, 99.9%), and sodium hydroxide (NaOH , 99.2%) were obtained from VWR Chemicals (Radnor, PA, USA). Titanium(IV) oxysulfate (TiOSO_4 , $\sim 15 \text{ wt.}\%$ in diluted sulfuric acid, 99.99% trace metal basis), and multi-walled carbon nanotubes (**CNT-C**, O.D. $\times$ L 6–9 nm $\times$ 5 μm , $>95\%$ carbon) were obtained from Sigma-Aldrich (St. Louis, MI, USA). Quinoline (**QN**, $\text{C}_9\text{H}_7\text{N}$, 98%) and n-hexadecane ($\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$, 99%) were provided by Alfa Aesar (Haverhill, MA, USA). Sulfuric

acid (H_2SO_4 , 98%) and formic acid (**FA**, CH_2O_2 , 98%) were obtained from Labkem (Lucknow, India). Dibenzothiophene (**DBT**, $\text{C}_{12}\text{H}_8\text{S}$, 98%) was obtained from Merck Chemicals (Darmstadt, Germany). Dibenzothiophene 5,5-dioxide (**DBT 5,5-dioxide**, $\text{C}_{12}\text{H}_8\text{O}_2\text{S}$, 97%) and dibenzothiophene 5-oxide (**DBT 5-oxide**, $\text{C}_{12}\text{H}_8\text{OS}$, 97%) were supplied by Sigma-Aldrich Chemistry (Taufkirchen, Germany).

All reactants were used without modifications. Ultrapure water was used throughout the work unless stated otherwise.

3.2 Synthesis of Catalysts for Chemical Vapor Deposition

The chemical vapor deposition (CVD) catalysts were obtained by sol-gel [1]. Two CVD catalysts were synthesized: an iron-based catalyst ($\text{Fe}/\text{Al}_2\text{O}_3$) and a nickel/iron catalyst ($\text{NiFe}/\text{Al}_2\text{O}_3$). In both cases, 20% of the active phase was deposited on the support (Al_2O_3).

The sol-gel procedure was conducted as follows: 10 mmol of M^{2+} ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 20 mL of ethanol and heated until reaching its boiling point, and 20 mmol of M^{3+} (in both cases, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved in 80 mL of ethylene glycol and heated to 60 °C for 5 min. Both solutions were then inserted into an ice bath until reaching temperature equilibrium. The choice of the $\text{M}^{2+}/\text{M}^{3+}$ molar ratio of 2 was based on previous works on the sol-gel synthesis of other ferrites [2, 3]. The solutions were mixed in one beaker with Al_2O_3 (6.6 g), and the mixture was heated to 60 °C for 2 h in a heating plate with stirring. Then, the temperature was increased to 120 °C, and the mixture was left at this temperature until reaching a gel-like texture (*ca.* 3 h). Once the gel-like texture was achieved, the temperature was increased to 200 °C until a powder texture was reached.

After sol-gel synthesis, the obtained powder was subjected to a thermal treatment. The iron-based catalyst was subjected to thermal treatment under nitrogen flow ($100 \text{ cm}^3 \text{ min}^{-1}$) at 300 °C for 12 h and 600 °C for 24 h, leading to $\text{Fe}/\text{Al}_2\text{O}_3$. The nickel ferrite-based catalyst was subjected to thermal treatment under an air atmosphere at 850 °C for 3 h, leading to $\text{NiFe}/\text{Al}_2\text{O}_3$.

The yield was calculated based on the theoretical ($m_{\text{theoretical}}$, in g) versus the actual mass (m_{obtained} , in g) obtained, as shown in Equation (3.1).

$$\text{Yield (\%)} = \frac{m_{\text{obtained}}}{m_{\text{theoretical}}} \times 100 \quad (3.1)$$

3.3 Synthesis of Carbon Nanotubes

The CVD growth of the carbon nanostructures was carried out in a vertical oven (TH/TV, Termolab), as shown in Figure 3.1. The oven has an upper and a lower crucible and three regions of temperature control (T_1 , T_2 , and T_3). For the growth of carbon materials, 1 g of the catalyst of choice was loaded in

the lower crucible and 5 g of the desired polymer (or a mixture of polymers) on the upper crucible. The synthesis was conducted at $T_3 = 600\text{--}800\text{ }^{\circ}\text{C}$ with a 30 min hold time upon reaching the desired temperature under nitrogen flow ($50\text{ cm}^3\text{ min}^{-1}$). The mass yield was calculated according to Equation (3.2).

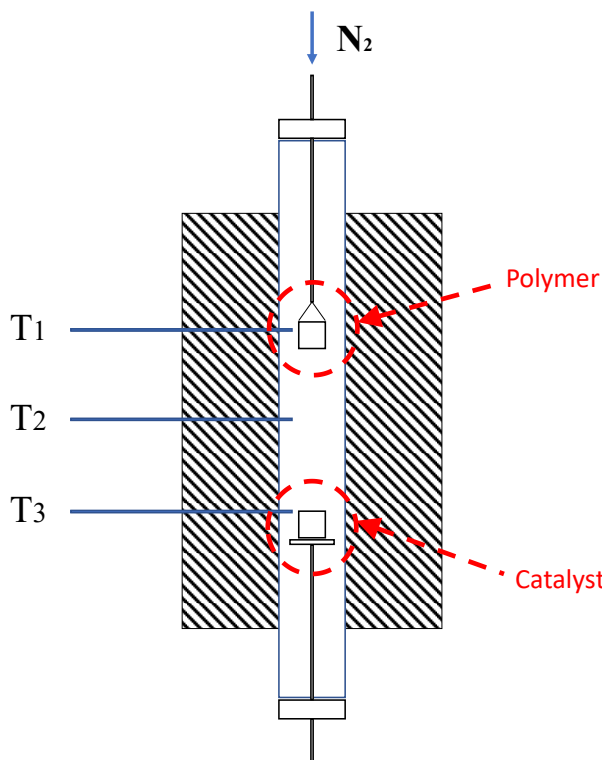


Figure 3.1. Vertical oven used for growth of carbon nanotubes.

$$\text{Yield (\%)} = \frac{m_{\text{recovered}} - m_{\text{catalyst}}}{m_{\text{polyolefin}} \times \%C_{\text{polymer}}} \quad (3.2)$$

in which $m_{\text{recovered}}$ is the mass of the sample recovered by the end of the CVD process accounting for both organic and inorganic phases (in g), m_{catalyst} is the mass of catalyst loaded in the reactor (in g), $m_{\text{polyolefin}}$ is the mass of the polymer used for the CVD process (in g), and $\%C_{\text{polymer}}$ is the content of carbon in the polymeric materials (85.6 wt.% for LDPE, HDPE and PP and 92.2 wt.% for PS [4]). A blank experiment was performed consisting of an equal thermal treatment of the catalyst (without using carbon feedstock) to know whether the catalyst showed significant mass changes, *i.e.*, affected the yield calculation.

Different polymer and polymer mixtures were used as carbon sources (including samples using real PSW) for the CVD reaction, considering the two CVD catalysts prepared in this work. For this matter, mixed PSW provided by the local waste management company (Resíduos do Nordeste) was manually sorted into the desired fractions (LDPE, HDPE and PP). The selected fractions were cut into pieces smaller than 1 cm^2 , with no additional pre-treatment applied. Table 3.1 describes the catalyst, carbon

source, temperature used for each synthesis, and nomenclature adopted for the distinct materials produced in this work.

Table 3.1 Carbon source, catalyst, temperature, and nomenclature adopted for each CNT sample.

Carbon source	Catalyst	Temperature (°C)	Nomenclature
LDPE	Fe/Al ₂ O ₃	600	LDPE-600@Fe
LDPE	Fe/Al ₂ O ₃	800	LDPE-800@Fe
HDPE	Fe/Al ₂ O ₃	800	HDPE@Fe
PP	Fe/Al ₂ O ₃	800	PP@Fe
35%LDPE, 25%HDPE and 40%PP*	Fe/Al ₂ O ₃	800	POL@Fe
35%LDPE, 25%HDPE and 40%PP*	NiFe/Al ₂ O ₃	800	POL@NiFe
PS	NiFe/Al ₂ O ₃	800	PS@NiFe
31%LDPE, 22%HDPE, 36%PP and 11%PS*	NiFe/Al ₂ O ₃	800	MIX@NiFe
35%LDPE, 25%HDPE and 40%PP* (real PSW supplied by Resíduos do Nordeste)	NiFe/Al ₂ O ₃	800	POL _{PSW} @NiFe

*The proportion between the different polymers (in mass basis) in the mixtures was based on the typically found composition of municipal solid waste as reported in [5].

3.3.1 Purification of carbon nanotubes

After synthesis, the CNTs were subjected to acid washing (purification) to reduce the quantity of metallic particles attached to the structure (50 vol.% of H₂SO₄, 140 °C, 3 h, 20 g_{CNT} L⁻¹, under reflux), as described elsewhere [6]. After cooling to room temperature, the material was abundantly washed with distilled water to remove excess acid and dried at 60 °C for 12 h. To identify purified samples, a **P** was included after the nomenclature, leading to LDPE-600-P@Fe, LDPE-800-P@Fe, HDPE-P@Fe, PP-P@Fe, POL-P@Fe, POL-P@NiFe, and POL_{PSW}-P@NiFe. The mass loss of purified CNTs was calculated according to Equation (3.3):

$$\text{Mass loss (\%)} = 1 - \frac{m_{\text{CNT},P}}{m_{\text{CNT}}} \times 100 \quad (3.3)$$

in which $m_{\text{CNT},P}$ is the mass of CNT recovered after washing (in g) and m_{CNT} is the mass of CNT used for the washing process (in g).

3.3.2 Changing the surface chemistry

Some samples were also subjected to a more drastic acid attack to introduce oxygenated groups on their surface. PS@NiFe, POL@NiFe, MIX@NiFe and POL_{PSW}@NiFe were treated with nitric acid (65-69 wt.%), considering 20 mL for 1 g of material at 130 °C for 24 h, as reported elsewhere [7]. After the reaction, the materials were abundantly washed with distilled water until reaching a neutral pH. The materials were named as PS-OX@NiFe, POL-OX@NiFe, MIX-OX@NiFe, and POL_{PSW}-OX@NiFe. Mass loss was calculated according to Equation 3.3.

POL-OX@NiFe was further thermally treated under N₂ atmosphere (400 °C for 4 h, temperature ramp of 120 °C min⁻¹) to remove some of the oxygenated groups, leading to POL-400@NiFe [8].

3.4 Materials Characterization

X-ray diffraction (XRD) analyses were made at room temperature with a PANalytical X' Pert Pro diffractometer (Malvern Pananalytical Ltd, Malvern, United Kingdom) equipped with an X' Celerator detector and secondary monochromator in $\theta/2\theta$ Bragg-Brentano geometry. The measurements were carried out using 40 kV and 30 mA, a CuK α radiation ($\lambda_{\alpha_1} = 1.54060 \text{ \AA}$ and $\lambda_{\alpha_2} = 1.54443 \text{ \AA}$), $0.017^\circ/\text{step}$, and 100 s/step , in a $10\text{--}80^\circ 2\theta$ angular range. XRD data were used to estimate crystallite size using Halder-Wagner and size strain plot, as given by Equations (3.4) and (3.5), respectively [9]:

$$\left(\frac{\beta_{hkl}}{d_{hkl}}\right)^2 = \frac{1}{D} \cdot \frac{\beta_{hkl}}{d_{hkl}^2} + \left(\frac{\epsilon}{2}\right)^2 \quad (3.4)$$

$$(d_{hkl} \cdot \beta_{hkl} \cdot \cos \theta)^2 = \frac{k\lambda}{D} \cdot (d_{hkl}^2 \cdot \beta_{hkl} \cdot \cos \theta) + \frac{\epsilon^2}{4} \quad (3.5)$$

in which β_{hkl} is the full width at half of the maximum intensity (FWMH), λ is the incident radiation, k is the shape factor (assumed to be 0.9), D is the average crystallite size, ϵ is the strain induced in powders, θ is the angle, and d_{hkl} is the lattice distance between (hkl) planes for the cubic crystal.

The FT-IR spectrum was acquired using a Perkin Elmer Spectrum Two FTIR (Shelton, CT, USA) with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} . Pellets were prepared by mixing *ca.* 1 mg of material with 100 mg of KBr. Before analysis, the KBr solid and the materials were carefully dried in an oven at 100°C overnight to remove excess moisture.

TEM images were obtained using a JEOL 1011 (JEOL USA, Inc, Peabody, MA, USA) transmission electron microscope operating at 200 kV. Images were processed using ImageJ.

Thermogravimetric analysis (TGA) was conducted using a NETZSCH TG 209F3 (Selb, Germany) in an air atmosphere from 30 to 930°C at a rate of $10^\circ\text{C min}^{-1}$.

Textural properties of the materials were determined from N_2 adsorption/desorption isotherms at -196°C obtained in a Quantachrome instrument NOVA TOUCH LX4 (Quantachrome Instruments, Florida, USA). The specific surface area (S_{BET}) was calculated using the BET method in the p/p^0 range of $0.05\text{--}0.35$. The total pore volume (V_{Total}) was determined at $p/p^0 = 0.98$. Calculations were done with TouchWinTM software v1.21. Before analysis, the samples were degassed under vacuum at 300°C for 6 h.

The Fe and Ni content of the CNTs was determined by digesting the ashes of the CNTs with *aqua regia* ($\text{HNO}_3\text{:HCl} = 1\text{:}3$, molar ratio) at 105°C for 12 h [6]. The resulting liquid was filtered with a $0.45 \mu\text{m}$

syringe filter and analyzed via atomic absorption spectroscopy (PinAacle 900T, Perkin Elmer, Hongkong, China).

The elemental analysis (CHNS-O) was carried out in a Flash 2000 analyzer (Thermo Fisher Scientific, Waltham, MA, USA) provided with a thermal conductivity detector (TCD).

The hydrophobicity/hydrophilicity of the samples was estimated by static water contact angle measurements using the sessile-drop method in an Attension optical tensiometer (model theta, Biolin Scientific, Göteborg, Sweden) for image acquisition. The measurements were performed in a glass-slide covered by the materials with the aid of a spray adhesive from 3M, prepared according to a procedure described elsewhere [11]. Before analysis, the samples immobilized in the glass slide were dried in an oven at 40 °C to remove moisture. The contact angles reported are an average of at least 3 measurements in different locations of the slides. The obtained images were analyzed using ImageJ software.

The concentrations of acidic and basic sites of the materials were determined following the methodology described in previous work for carbon-based materials [12]. Briefly, the concentration of acidic sites was determined by adding 0.1 g of each material to 20 mL of a 0.02 mol L⁻¹ NaOH solution. The resulting suspensions were left under stirring for 48 h at room temperature. After filtration to remove the solid material, the unreacted OH⁻ was titrated with a 0.01 mol L⁻¹ HCl solution. The initial concentration of acidic functionalities was then calculated by the difference between the amount of NaOH initially present in the suspension, and the amount of NaOH determined by titration, and this value was divided by the mass of the material. The concentration of basic sites was determined in a similar way, this time by adding the carbon sample to a 0.02 mol L⁻¹ HCl solution and titration with a 0.01 mol L⁻¹ NaOH solution. Phenolphthalein was used as an indicator in both titrations.

Raman spectra were acquired in an Alpha 300 equipment (WiTec, Ulm, Germany) at a 532 nm monochromatic wavelength. The acquired spectra were then processed using the software Project FIVE v5.3 to remove cosmic ray and eliminate the background. The data was then normalized, and the D/G ratio was estimated using the area of the peaks obtained by deconvolution.

3.5 Reaction Runs

3.5.1 Nitrogenated compounds

3.5.1.1 Catalytic wet peroxide oxidation (CWPO)

A QN solution ([QN]₀ = 100 mg L⁻¹) in ultrapure water at pH 3.0 (adjusted using H₂SO₄ 0.5 M, not buffered) was placed in a reaction vessel and heated to the desired temperature (80 °C). Upon reaching the temperature, hydrogen peroxide was added ([H₂O₂]₀ = 6.2 g L⁻¹). Then, the catalyst (*C_{cat}* = 2.5 g L⁻¹)

was added, considering this as $t_0 = 0 \text{ min}$. QN and H_2O_2 concentrations along the reaction were monitored via HPLC and UV-Vis, respectively. Upon withdrawing the reaction samples, they were immediately submerged in an ice bath and kept at 4°C for subsequent analysis. By the end of the reaction, the catalyst was separated from the reaction, and the resulting liquid was analyzed by TOC, pH, and other aromatic compounds (ARM). A non-catalytic (N.C.) run was carried out under the same conditions without the catalyst.

3.5.1.2 Extraction and adsorption

The pure extraction effect was estimated considering different initial concentrations of QN in 2,2,4-trimethylpentane ($[\text{QN}]^{\text{oil}}_0 = 250 - 1000 \text{ mg L}^{-1}$, equivalent to $[\text{N}]^{\text{oil}}_0 = 27 - 108 \text{ mg L}^{-1}$). The QN solution was placed in a reaction vessel and heated to 80°C . Upon reaching the desired temperature, a volume of ultrapure water at pH 3.0 (adjusted using H_2SO_4 1 M, not buffered) at 80°C was added, considering this $t_0 = 0 \text{ min}$. The ratio between 2,2,4-trimethylpentane and water was kept at an oil-to-water (O/W) volume ratio of 80:20, and the medium was well stirred (600 rpm). The concentration of QN in both oil and water phases ($[\text{QN}]^{\text{oil}}$ and $[\text{QN}]^{\text{water}}$, respectively) was followed by UV-Vis. The samples were withdrawn in such a way as to ensure that the O/W volume ratio was not affected.

The adsorption effect in the oil phase was also evaluated by placing a QN solution ($[\text{QN}]^{\text{oil}}_0 = 1000 \text{ mg L}^{-1}$, $[\text{N}]^{\text{oil}}_0 = 108 \text{ mg L}^{-1}$) in a reaction vessel and heating to 80°C . The adsorbent ($C_{\text{adsorbent}} = 2.5 \text{ g L}^{-1}$) was added, considering this $t_0 = 0 \text{ min}$, and the concentration of QN in 2,2,4-trimethylpentane was estimated via UV-Vis.

Experiments combining simultaneous adsorption and extraction were also evaluated, following a similar procedure described above. The QN solution ($[\text{QN}]^{\text{oil}}_0 = 1000 \text{ mg L}^{-1}$, $[\text{N}]^{\text{oil}}_0 = 108 \text{ mg L}^{-1}$) was placed in a reaction vessel and heated to 80°C . The desired volume of ultrapure water at pH 3.0, considering an O/W volume ratio = 80:20 and at $T = 80^\circ\text{C}$ was added, immediately followed by the adsorbent ($C_{\text{adsorbent}} = 2.5 \text{ g L}^{-1}$, considering the total volume of the system), considering this $t_0 = 0 \text{ min}$. QN concentration, both in the oil and water phases, was measured by UV-Vis.

3.5.1.3 Oxidation reactions

A QN solution ($[\text{QN}]^{\text{oil}}_0 = 500\text{-}1000 \text{ mg L}^{-1}$, $[\text{N}]^{\text{oil}}_0 = 54\text{-}108 \text{ mg L}^{-1}$) in 2,2,4-trimethylpentane was placed in a reaction vessel and heated to the desired temperature ($50\text{-}80^\circ\text{C}$). Upon reaching the desired temperature, a volume of H_2O_2 solution ($[\text{H}_2\text{O}_2]_0 = 1.2\text{-}247 \text{ g L}^{-1}$) at pH 1.0-11.0, adjusted with 1 M H_2SO_4 and 1 M NaOH (not buffered), was added to achieve an oil-to-water (O/W) volume ratio of 80:20. Around 2-3 min were waited before adding the catalyst ($C_{\text{cat}} = 0.25\text{-}5 \text{ g L}^{-1}$, considering the whole volume of the system), representing the beginning of the reaction ($t_0 = 0 \text{ min}$). Samples were periodically withdrawn to monitor the concentration of QN in oil ($[\text{QN}]^{\text{oil}}$) and water ($[\text{QN}]^{\text{water}}$) phases (GC-FID and

HPLC, respectively) and H_2O_2 in the water phase (UV-Vis). Samples were collected by respecting the O/W volume ratio to avoid altering the phase equilibria, and the total amount removed from the reaction during sampling was maintained below 15% in volume. By the end of the reaction, the catalyst was separated from the liquid medium, and the oily and water phases were stored separately. The water phase was further analyzed regarding total organic carbon (TOC) content. The catalyst was dried at 60 °C overnight and reused. A non-catalytic run was also conducted without a catalyst, and oxidation reactions in the absence of the pollutant were also carried out to evaluate the possible oxidation of 2,2,4-trimethylpentane; negligible oxidation was observed.

ODN was also carried out for a simulated fuel containing (i) pyridine (PYR) with a concentration of $[\text{PYR}]^{\text{oil}}_0 = 610 \text{ mg L}^{-1}$ (to achieve the same concentration of N as in the QN experiments, equivalent to $[\text{N}]^{\text{oil}}_0 = 108 \text{ mg L}^{-1}$) in 2,2,4-trimethylpentane, and (ii) a mixture of QN and PYR with a concentration of $[\text{QN}]^{\text{oil}}_0 = 500 \text{ mg L}^{-1}$ ($[\text{N}]^{\text{oil}}_0 = 54 \text{ mg L}^{-1}$) and $[\text{PYR}]^{\text{oil}}_0 = 305 \text{ mg L}^{-1}$ ($[\text{N}]^{\text{oil}}_0 = 54 \text{ mg L}^{-1}$), amounting to a total of $[\text{N}]^{\text{oil}}_0 = 108 \text{ mg L}^{-1}$.

Reutilization runs were also conducted. The same procedure described above was followed, and the reaction was allowed to continue for 1-2 h. Then, the phases were separated and stored. The catalyst was recovered with a membrane filter (pore: 0.45 μm), washed with distilled water and ethanol, and dried overnight at 105 °C.

3.5.2 Sulfonated compounds

3.5.2.1 Adsorption and extraction runs

The adsorption ability of the materials towards dibenzothiophene ($[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane) was evaluated considering only the oily phase (2,2,4-trimethylpentane). A volume of the DBT solution was placed in a reaction vessel and heated to 70 °C. Upon reaching the desired temperature, the adsorbent was added ($C_{\text{adsorbent}} = 2.5 \text{ g L}^{-1}$), considering this time $t = 0 \text{ min}$ and the material was allowed to contact DBT for 2 h. The DBT was measured using UV-Vis.

Extraction runs were conducted by placing the oily phase in contact with distinct extractant phases (water, ACN, $\text{ACN}/\text{H}_2\text{SO}_4$, and ACN/FA) at an oil-to-extractant (O/E) volume ratio of 80:20 and 70 °C, and samples were withdrawn to measure the concentration of DBT in each phase by UV-Vis.

3.5.2.2 Oxidation runs

The ODS reaction was carried out at 70 °C for 8 h of reaction. The DBT ($[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$) solution in 2,2,4-trimethylpentane was heated to 70 °C. Upon reaching the desired temperature, the extractant phase was added to achieve an O/E volume ratio of 80:20 and immediately followed by hydrogen peroxide ($[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/S$ molar ratio = 15) and catalyst ($C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, considering the

whole volume of the system), marking this instant as $t = 0 \text{ min}$. The reaction was periodically monitored by removing samples (respecting the O/E volume ratio). DBT concentration and intermediates were followed in the oily and aqueous phases by GC-FID and HPLC, respectively, and H_2O_2 in the extractant phase was followed by UV-Vis. By the end of the reaction, the catalyst was separated from the reaction medium by filtration, and each phase was stored separately. The adsorbed products in the catalyst phase were extracted by sonication with acetone (30 min, $1 \text{ mg}_{\text{CNT}} \text{ mL}^{-1}$) and analyzed by HPLC. A non-catalytic run was carried out in the absence of a catalyst.

The reactions were also carried out with ACN as extractant, with every other conditions maintained the same ($([\text{DBT}]_0 = 500 \text{ mg L}^{-1}, ([\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1} (\text{H}_2\text{O}_2/S \text{ molar ratio} = 15), T = 70 \text{ }^\circ\text{C}, C_{\text{cat}} = 2.5 \text{ g L}^{-1}, O/E \text{ volume ratio} = 80:20)$). Two co-catalysts (formic acid (FA) and sulfuric acid) were also added to the oil-ACN system ($0.1 \text{ vol}_{\text{extractant}}\%$ of a 1 M solution).

The effect of formic acid was evaluated by a reaction carried out in the presence of POL-OX@NiFe and in the absence of hydrogen peroxide (following every other condition as already mentioned), and by delayed addition of formic acid to the oil-ACN/FA system (FA added at 60 min of reaction; all remaining experimental conditions maintained the same). The role of hydroxyl radicals was assessed by adding ethanol (molar ratio $\text{H}_2\text{O}_2:\text{EtOH}$ of 2) to the oil-ACN/FA and oil-ACN/ H_2SO_4 systems.

3.6 Analytical Techniques

H_2O_2 concentration was determined using a TiOSO_4 methodology and measured using UV-Vis (UV-VIS Spectrometer, T70, PG Instrument Ltd., Lutterworth, UK) at 405 nm, as described elsewhere [13]. TOC was measured in a TOC-L (Shimadzu, Kyoto, Japan) equipment.

3.6.1 Nitrogenated compounds

QN concentration in the water phase was followed via high-performance liquid chromatography (HPLC). The separation of QN and reaction products was achieved using a JASCO HPLC system (Tokyo, Japan) coupled to a Nucleosil 100-5C18 ($150 \times 2.1 \text{ mm}$) column (alternatively, an Interchim Uptisphere strategy biphenyl column ($150 \times 2.1 \text{ mm}$)). A mobile phase consisting of 20% acetonitrile and 80% of an ammonium acetate buffer solution (10 mmol) at pH 5.75 (isocratic) was delivered at a 0.4 mL min^{-1} flow rate by a quaternary gradient pump (PU-2089). Detection was achieved in a UV-Vis detector (UV-2075) at 313 nm. During extraction and adsorption runs, QN concentration was estimated using UV-Vis at 313 nm for oily ($[\text{QN}]^{\text{oil}}$) and aqueous ($[\text{QN}]^{\text{water}}$) phases. Aromatic compounds (ARM) in water phases were estimated by diluting the aqueous samples with a phosphate buffer solution at a pH of 7.0 and analyzed via UV-Vis at 254 nm [6]. The detection of QN in the oily phase during oxidation reactions was performed in a GC-FID (Varian 3800, Palo Alto, CA, USA) coupled with a SupelcoWax10 column. The oven temperature was set to $60 \text{ }^\circ\text{C}$ for 2 min, followed by a $10 \text{ }^\circ\text{C min}^{-1}$

ramp up to 210 °C (hold for 2 min), with helium as carrier gas under a 1 mL min⁻¹ flow. Detection was set to 200 °C and injection to 250 °C with a split ratio of 20. N-hexadecane was used as an internal standard (1 mg mL⁻¹).

3.6.1.1 Calculations

QN concentration was monitored throughout the ODN runs by HPLC and GC-FID for water and oily phases, respectively, and the concentrations obtained were transformed into the number of mols, according to Equation (3.7).

$$n_{QN,t}^i = \frac{[QN]_t^i V^i}{MM_{QN}} \quad (3.7)$$

in which i can be either the oil ($i = oil$) or aqueous ($i = water$) phase, $n_{QN,t}^i$ is the number of mols of QN at the time t and the phase i (in μmol), $[QN]_t^i$ is the concentration of QN at time t in phase i (in g L⁻¹), V^i is the volume of phase i (in L), and MM_{QN} is the molar mass of QN (in g mol⁻¹). The total number of mols of QN for each reaction time t ($n_{QN,t}^{total}$) was calculated according to Equation (3.8), and the total conversion of QN ($X_{QN,total}$) according to Equation (3.9).

$$n_{QN,t}^{total} = n_{QN,t}^{water} + n_{QN,t}^{oil} \quad (3.8)$$

$$X_{QN,total} = \left(1 - \frac{n_{QN,t}^{total}}{n_{QN,0}^{total}} \right) \times 100 \quad (3.9)$$

in which $X_{QN,total}$ is the global conversion of QN, accounting for both QN in the oily and aqueous phase (in %) and $n_{QN,0}^{total}$ is the number of mols of QN at the beginning of the reaction ($t = 0 \text{ min}$) in both phases (in mol).

The conversion of TOC (X_{TOC} , in %) was calculated according to Equation (3.10).

$$X_{TOC} = \left(1 - \frac{(TOC_{measured}^{water} + TOC_{QN}^{oil})}{TOC_{QN,0}} \right) \times 100 \quad (3.10)$$

in which $TOC_{measured}^{water}$ is the TOC measured in the water phase by the end of the reaction (in mg L⁻¹), TOC_{QN}^{oil} is the TOC contribution arising from QN still in the oil phase (obtained based on the concentration of QN calculated by GC-FID) (in mg L⁻¹), and $TOC_{QN,0}$ is the TOC contribution from the QN at the beginning of the process (obtained based on the concentration of QN as determined by GC-FID and HPLC for oil and water phases, respectively) (in mg L⁻¹).

The efficiency of hydrogen peroxide consumption ($\eta_{H_2O_2}^{ODN}$) during ODN reactions was calculated according to Equation (3.11):

$$\eta_{H_2O_2}^{ODN} = \frac{X_{TOC,t}}{X_{H_2O_2,t}} \quad (3.11)$$

in which $X_{TOC,t}$ is the conversion of TOC at time t obtained from Equation (3.10) (in %) and $X_{H_2O_2,t}$ is the conversion of hydrogen peroxide at time t (in %).

3.6.1.2 Kinetic modeling of ODN reactions

Kinetic modeling of the biphasic oxidation reactions was carried out. The methodology considered is based on previous reports on the catalytic wet peroxide oxidation (in the aqueous phase) of phenol [14] and the biphasic oxidation of 2-nitrophenol [15]. The disappearance rate of each species j ($-r_j$) is given by Equation (3.12).

$$-r_j = \frac{1}{W_{cat}} \cdot \frac{dn_j}{dt} \quad (3.12)$$

in which n_j is the mols of compound j (calculated according to Equation (3.7)), and W_{cat} is the mass of the catalyst (in g). The solution of the rate equations and estimation of kinetic parameters was achieved by minimizing the sum of squared errors (SSE_{model}), which was calculated based on the relative number of mols of each species ($n_j/n_{j,0}$) for experimental (*exp*) and predicted (*model*) values, according to Equation (3.13).

$$SSE_{model} = \sum_{n=1}^N \left[\left(\frac{n_j}{n_{j,0}} \right)_{exp} - \left(\frac{n_j}{n_{j,0}} \right)_{model} \right]^2 \quad (3.13)$$

Kinetic models were evaluated by the coefficient of determination (R^2) and parity plots.

3.6.2 Sulfonated compounds

DBT was followed by UV-Vis at 235 nm for adsorption and extraction runs, both for oily and water phases. For ODS runs, DBT in the oily phase was followed by GC-FID using n-hexadecane as the internal standard (1 mg mL⁻¹). The operating conditions used for GC analysis were a helium flow (carrier gas) of 1 mL min⁻¹ and an initial oven temperature of 50 °C, which was held for 5 min. Then, a ramp was done up to 270 °C at a 15 °C min⁻¹ rate, held for 2 min, leading to a total running time of 20 min. The injection temperature was 250 °C, the detector temperature was 200 °C, and a split ratio of 20 was used. DBT and its oxidized intermediates (DBT 5-oxide and DBT 5,5-dioxide) in the extractant phases were followed by High-Pressure Liquid Chromatography (JASCO System). The separation of the reaction products was achieved in a Restek Ultra Biphenyl column (15 cm x 2.1 mm, particle size 5 µm)

and an isocratic mobile phase (50% acetonitrile and 50% ultrapure water with orthophosphoric acid (0.1%)) with a 0.3 mL min^{-1} flow delivered by a quaternary pump (PU-2089). The detection was achieved in a UV-Vis at 235 nm (UV-2075). The reaction products in the extractant phase and oily phase were further confirmed by gas chromatography coupled with mass spectroscopy (GCMS-QP2020, Shimadzu, Kyoto, Japan). The operating conditions for the oven were a helium flow (carrier gas) of 1 mL min^{-1} and an initial oven temperature of $50 \text{ }^{\circ}\text{C}$ (held for 3.5 min), followed by a ramp up to $300 \text{ }^{\circ}\text{C}$ at $3 \text{ }^{\circ}\text{C min}^{-1}$ rate (held for 15 min), leading to a total running time of 101 min, using a split ratio of 20. The injection temperature was $250 \text{ }^{\circ}\text{C}$. N-hexadecane was used as an internal standard (1 mg mL^{-1}).

3.6.2.1 Calculations

DBT concentration was monitored throughout the ODS runs by HPLC and GC-FID for water and oily phases, respectively, and the concentrations obtained were transformed into mass of DBT, according to Equation (3.14).

$$m_{DBT_t^i} = [DBT]_t^i V^i \times 1000 \quad (3.14)$$

in which i can be either the oil ($i = oil$) or extractant ($i = ext.$) phase, $m_{DBT_t^i}$ is the mass of DBT at the time t and the phase i (in μg), $[DBT]_t^i$ is the concentration of DBT at time t in phase i (in mg L^{-1}), and V^i is the volume of phase i (in L). The total mass of DBT for each reaction time t ($m_{DBT,t}^{total}$) was calculated according to Equation (3.15), and the total conversion of DBT ($X_{DBT,t}^{total}$) according to Equation (3.16).

$$m_{DBT,t}^{total} = m_{DBT,t}^{ext.} + m_{DBT,t}^{oil} \quad (3.15)$$

$$X_{DBT,t}^{total} = \left(1 - \frac{m_{DBT,t}^{total}}{m_{DBT,t=0}^{total}} \right) \times 100 \quad (3.16)$$

in which $m_{DBT,t}^{oil}$ is the mass of DBT at the time t in the oil phase (in μg), $m_{DBT,t}^{ext.}$ is the mass of DBT at the time t in the extractant phase (in μg), and $m_{DBT,t=0}^{total}$ is the total mass of DBT, accounting for both oil and extractant phases, at time $t = 0 \text{ min}$ (in μg).

The mass of S (m_S^j) in each phase j ($j = \text{oil, extractant or catalyst phase}$) by the end of the reaction and the distribution of S (S^j (%)) in each phase j at the end of the reaction run was calculated according to Equations (3.17) and (3.18), respectively.

$$m_S^j = m_{x_{t=480}^j} \times \frac{MW_S}{MM_x} \quad (3.17)$$

$$S^j (\%) = \frac{m_S^j}{m_{S,t=0}^{oil} + m_{S,t=0}^{ext.}} \quad (3.18)$$

in which j can be either the oil ($j = \text{oil}$), extractant ($j = \text{ext.}$) or catalyst ($j = \text{cat.}$) phase, $m_{x,t=480}^j$ is the mass of x ($x = \text{DBT, DBT 5-oxide or DBT 5,5-dioxide}$) at 480 min in phase j (in μg), MW_S is the molar weight of S ($32.0655 \text{ g mol}^{-1}$), MM_x is the molar mass of x ($184.26, 200.26$ and $216.26 \text{ g mol}^{-1}$ for DBT, DBT 5-oxide and DBT 5,5-dioxide, respectively), $m_{S,t=0}^{oil}$ and $m_{S,t=0}^{ext.}$ is the mass of S at the oil and extractant phases, respectively, at the beginning of the reaction.

The efficiency of consumption of hydrogen peroxide ($\eta_{H_2O_2}^{ODS}$) for the ODS reaction was calculated based on the percentage of DBT removed per conversion of H_2O_2 , according to Equation (3.19).

$$\eta_{H_2O_2}^{ODS} = \frac{X_{DBT,t}^{total}}{X_{H_2O_2,t}} \quad (3.19)$$

in which $X_{DBT,t}^{total}$ is the total conversion of DBT at time t (in %) and $X_{H_2O_2,t}$ is the conversion of H_2O_2 at time t (in %).

3.7 References

- [1] A.S. Silva, J.L. Diaz de Tuesta, T. Sayuri Berberich, S. Delezuk Inglez, A.R. Bertao, I. Caha, F.L. Deepak, M. Bañobre-Lopez, H.T. Gomes, Doxorubicin delivery performance of superparamagnetic carbon multi-core shell nanoparticles: pH dependence, stability and kinetic insight, *Nanoscale* 14(19) (2022) 7220-7232. <https://doi.org/10.1039/d1nr08550f>.
- [2] T. Giannakopoulou, L. Kompotiatis, A. Kontogeorgakos, G. Kordas, Microwave behavior of ferrites prepared via sol-gel method, *Journal of Magnetism and Magnetic Materials* 246(3) (2002) 360-365. [https://doi.org/10.1016/s0304-8853\(02\)00106-3](https://doi.org/10.1016/s0304-8853(02)00106-3).
- [3] A.S. Silva, F.F. Roman, A.V. Dias, J.L. Diaz de Tuesta, A. Narcizo, A.P.F. da Silva, I. Caha, F.L. Deepak, M. Bañobre-López, A.M.C. Ferrari, H.T. Gomes, Hybrid multi-core shell magnetic nanoparticles for wet peroxide oxidation of paracetamol: Application in synthetic and real matrices, *Journal of Environmental Chemical Engineering* 11(5) (2023) 110806. <https://doi.org/10.1016/j.jece.2023.110806>.
- [4] C. Zhuo, Y.A. Levendis, Upcycling waste plastics into carbon nanomaterials: A review, *Journal of Applied Polymer Science* 131(4) (2014) 39931. <https://doi.org/10.1002/app.39931>.
- [5] PlasticsEurope, *Plastics - the facts 2021*, 2021. Available at: <https://plasticseurope.org/wp-content/uploads/2021/12/Plastics-the-Facts-2021-web-final.pdf>. (Accessed on January, 24th 2024)
- [6] F.F. Roman, J.L. Diaz de Tuesta, F.K.K. Sanches, A.S. Silva, P. Marin, B.F. Machado, P. Serp, M. Pedrosa, A.M.T. Silva, J.L. Faria, H.T. Gomes, Selective denitrification of simulated oily wastewater by oxidation using Janus-structured carbon nanotubes, *Catalysis Today* (2023) 114001. <https://doi.org/10.1016/j.cattod.2023.01.008>.
- [7] C. Herrera, L. Barrientos, A. Rosenkranz, C. Sepulveda, J.L. García-Fierro, M.A. Laguna-Bercero, N. Escalona, Tuning amphiphilic properties of Ni/Carbon nanotubes functionalized catalysts and their effect as emulsion stabilizer for biomass-derived furfural upgrading, *Fuel* 276 (2020) 118032. <https://doi.org/10.1016/j.fuel.2020.118032>.
- [8] R. Rocha, O. Soares, J. Figueiredo, M. Pereira, Tuning CNT Properties for Metal-Free Environmental Catalytic Applications, *C* 2(3) (2016) 17. <https://doi.org/10.3390/c2030017>.
- [9] S. Moretto, A. Santos Silva, J.L. Diaz de Tuesta, F. F. Roman, R. Cortesi, A.R. Bertão, M. Bañobre-López, M. Pedrosa, A. M.T. Silva, H. T. Gomes, Comprehensive characterization and development of multi-core shell superparamagnetic nanoparticles for controlled delivery of drugs and their kinetic release modelling, *Materials Today Chemistry* 33 (2023) 101748. <https://doi.org/10.1016/j.mtchem.2023.101748>.
- [10] A.O. Onokwai, E.S.A. Ajisegiri, I.P. Okokpujie, R.A. Ibikunle, M. Oki, J.O. Dirisu, Characterization of lignocellulose biomass based on proximate, ultimate, structural composition, and thermal analysis, *Materials Today: Proceedings* 65 (2022) 2156-2162. <https://doi.org/10.1016/j.matpr.2022.05.313>.
- [11] E. Nowak, G. Combes, E.H. Stitt, A.W. Pacek, A comparison of contact angle measurement techniques applied to highly porous catalyst supports, *Powder Technology* 233 (2013) 52-64. <https://doi.org/10.1016/j.powtec.2012.08.032>.
- [12] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez, P-, B- and N-doped carbon black for the catalytic wet peroxide oxidation of phenol: Activity, stability and kinetic studies, *Catalysis Communications* 102 (2017) 131-135. <https://doi.org/10.1016/j.catcom.2017.09.012>.
- [13] A. Santos Silva, M. Seitovna Kalmakhanova, B. Kabykenovna Massalimova, J. G. Sgorlon, D.d.T. Jose Luis, H. T. Gomes, Wet Peroxide Oxidation of Paracetamol Using Acid Activated and Fe/Co-Pillared Clay Catalysts Prepared from Natural Clays, *Catalysts* 9(9) (2019) 705. <https://doi.org/10.3390/catal9090705>.
- [14] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez, Kinetic modeling of wet peroxide oxidation with a carbon black catalyst, *Applied Catalysis B: Environmental* 209 (2017) 701-710. <https://doi.org/10.1016/j.apcatb.2017.03.031>.
- [15] J.L. Diaz de Tuesta, B. F. Machado, P. Serp, A.M. T. Silva, J.L. Faria, H. T. Gomes, Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide, *Catalysis Today* 356 (2020) 205-215. <https://doi.org/10.1016/j.cattod.2019.07.012>.

CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF MATERIALS

Chapter 4

Synthesis and characterization of materials

This chapter presents the synthesis and characterization of carbon nanotubes (CNTs) and the chemical vapor deposition (CVD) catalysts used in their production. It focuses on the influence of key synthesis parameters, including the composition of the CVD catalyst and the choice of carbon sources, on the structural and physicochemical properties of the resulting CNTs. Characterization techniques, including transmission electron microscopy (TEM), Raman spectroscopy, elemental analysis, thermogravimetric analysis (TGA), basicity/acidity content, metal content, water contact angle, and surface area analysis, are employed to evaluate the structural, textural, and chemical properties of synthesized CNTs. The findings provide insights into the relationship between synthesis conditions and CNT quality, serving as a foundation for their application in catalytic processes.

This chapter contains results published in the following research papers:

- Fernanda F. Roman, Larissa de G. Piccinin, Adriano S. Silva, Jose L. Diaz de Tuesta, Isabella V. K. Freitas, Admilson Vieira, Giane G. Lenzi, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Carbon nanomaterials from polyolefin waste: effective catalysts for quinoline degradation through catalytic wet peroxide oxidation. *Catalysts* 13 (2023) 1259. <https://doi.org/10.3390/catal11101239>
- Fernanda F. Roman, Larissa de G. Piccinin, Adriano S. Silva, Jose L. Diaz de Tuesta, Admilson Vieira, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Selective biphasic oxidation of nitrogenated contaminants with H₂O₂ using polyolefin-derived carbon nanotubes. *Journal of Environmental Chemical Engineering* 13 (2025) 115128. <https://doi.org/10.1016/j.jece.2024.115128>
- Fernanda F. Roman, Maria C. Batista, Ana J. Briganti, Adriano S. Silva, Jose L. Diaz de Tuesta, Raquel V. Mambrini, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Polyolefin and polystyrene-derived carbon nanotubes: Catalysts for oxidative desulfurization under a biphasic system. *ChemCatChem*, 2025, e202500233. <https://doi.org/10.1002/cctc.202500233> [Accepted – In press].

4.1 Catalysts for Chemical Vapor Deposition

X-ray diffraction (XRD) of the CVD catalyst used to grow the CNT structures is shown in Figure 4.1a. The results were analyzed using the software X'Pert HighScore Plus (v4.5) loaded with Crystallography Open Database (COD) cards. The qualitative analysis revealed that both samples contain alumina, both gamma (γ) and alpha (α) phases (COD card 96-152-8248 and 96-201-5531, respectively, Figure 4.2.). Fe-based catalyst displayed peaks related to hematite and magnetite, according to cards 96-900-9783 and 96-900-2318 from COD, respectively. NiFe-based catalyst has peaks related to the nickel ferrite spinel, hematite and nickel oxide, according to COD cards 96-100-6116, 96-900-9783, and 96-101-0094, respectively. Crystallite sizes were estimated using Halder-Wagner and size strain plot. Hematite in Fe/ Al_2O_3 was estimated to be 9.17 and 9.83 nm, respectively. In NiFe/ Al_2O_3 , hematite was estimated at 7.26 and 9.76 nm, respectively, nickel ferrite at 7.32 and 11.95 nm, respectively, and nickel oxide at 7.35 and 9.63 nm, respectively.

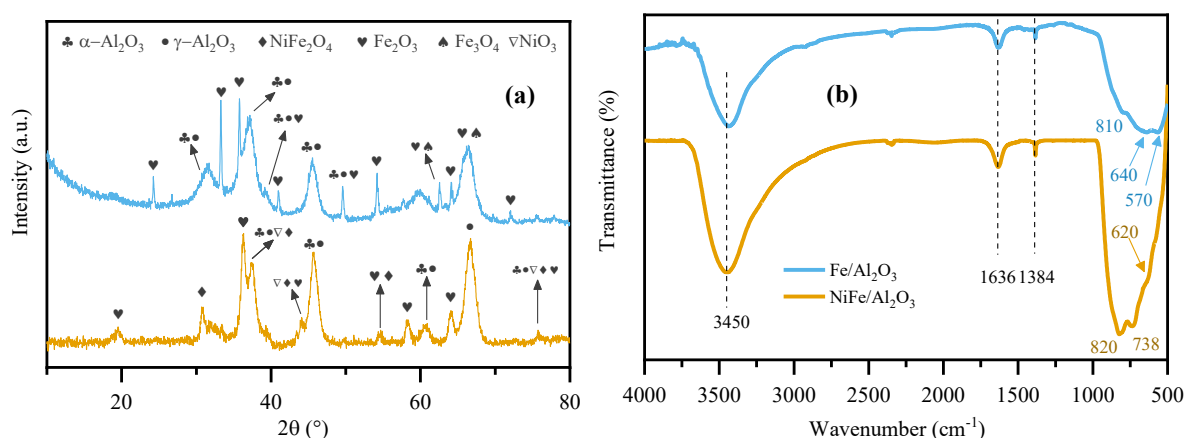


Figure 4.1. (a) XRD and (b) FTIR of the metal catalysts used in CVD.

The semi-quantitative analysis, also obtained with the aid of X'Pert HighScore Plus, revealed that Fe/ Al_2O_3 has 78% alumina, with 52% from γ - Al_2O_3 and 26% from α - Al_2O_3 , 19% hematite (Fe_2O_3), and 3% magnetite (Fe_3O_4). The analysis results demonstrate that the material is composed of mixed iron oxide phases supported on alumina, and the iron oxide content is similar to the intended content of 20%. A similar metal substrate composition was found in previous studies using a similar procedure to prepare the metal substrate for CNTs growth via CVD [1]. The content of Fe (Table 4.1), as obtained via atomic absorption, was determined to be 15 wt.% (which corresponds to approximately 21 wt.% of hematite), close to the values observed via XRD. The NiFe/ Al_2O_3 is comprised of 82% alumina (where 54% and 28% from γ - and α - Al_2O_3 , respectively). Three metal phases were identified in XRD analysis: spinel NiFe_2O_4 , hematite, and nickel oxide, each corresponding to 6% of the material, amounting to 18% of the active phase. The content of Ni and Fe (Table 4.1), as determined by atomic absorption, was estimated at 4.9 and 8.8 wt.%, respectively. The yield of the CVD catalysts, calculated according to Equation 3.1, was estimated as 92-96% (Table 4.1).

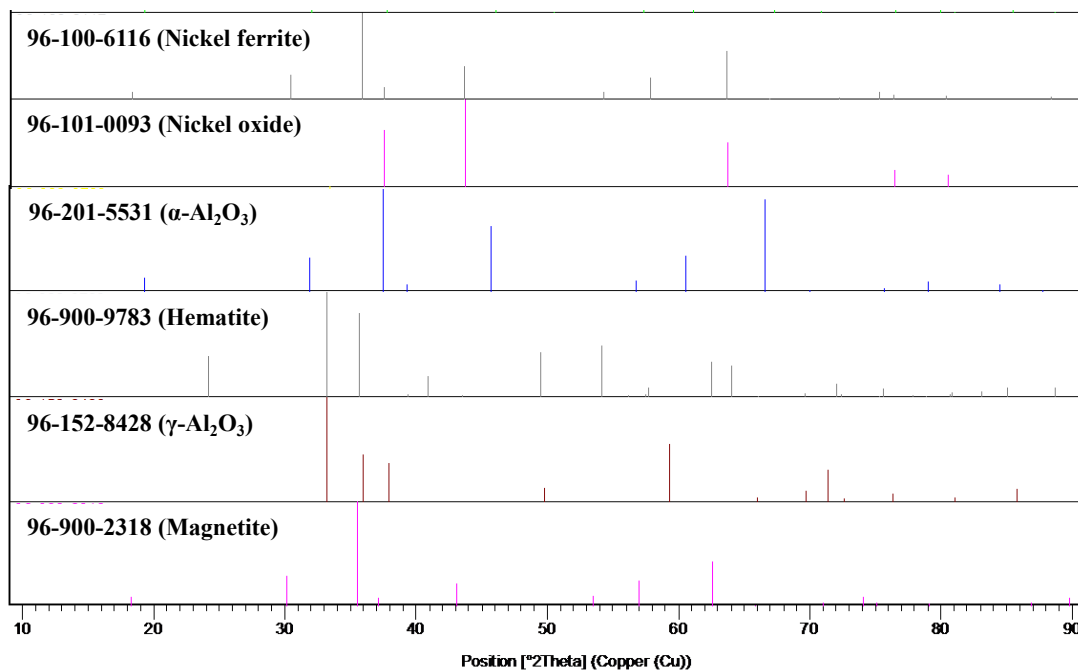


Figure 4.2. XRD reference cards of α - and γ -alumina, hematite, magnetite, nickel ferrite and nickel oxide from the COD database.

FTIR of $\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{NiFe}/\text{Al}_2\text{O}_3$ are displayed in Figure 4.1b. Bands related to adsorbed water were identified ($-\text{OH}$ stretching vibration at 3450 , 1636 and 1384 cm^{-1} for both materials [2]). The bands at 640 and 570 cm^{-1} were ascribed to the vibration of $\text{Fe}-\text{O}$ bonds related to iron oxide phases [3]. The band located around 620 cm^{-1} can be attributed to the intrinsic stretching of the NiFe_2O_4 at the tetrahedral vibration site [4] or from $\text{Ni}-\text{O}$ bands from nickel oxide particles [2]. The band at $810\text{--}820\text{ cm}^{-1}$ was ascribed to the $\text{Al}-\text{O}$ stretch from alumina [5], and the band at 738 cm^{-1} was ascribed to the $\text{Al}-\text{O}-\text{Al}$ stretching vibration [6]. The broad band in the region $400\text{--}1000\text{ cm}^{-1}$ is also a characteristic of amorphous and disordered γ -alumina [7], which was identified in most abundance in the samples by XRD.

The N_2 adsorption-desorption isotherms of the CVD catalyst are shown in Figure 4.3, and the textural properties calculated from the data are shown in Table 4.1. As can be seen, the S_{BET} of alumina is much higher than that of both prepared catalysts, indicating that the deposition of the active phases blocks pore access, especially for $\text{Fe}/\text{Al}_2\text{O}_3$. The pore size distribution of the materials is shown in Figure 4.4, and it is possible to observe that $\text{NiFe}/\text{Al}_2\text{O}_3$ displays a similar profile compared to Al_2O_3 , with most pores centered around $4\text{--}5\text{ nm}$. $\text{Fe}/\text{Al}_2\text{O}_3$, on the other hand, has a shift towards slightly bigger pores centered around 7 nm .

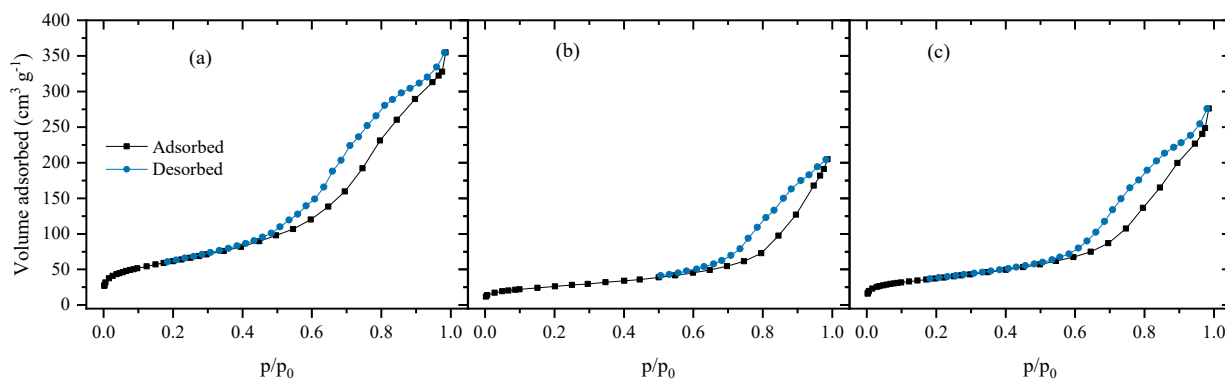


Figure 4.3. Nitrogen adsorption-desorption isotherms of (a) Al_2O_3 , (b) $\text{Fe}/\text{Al}_2\text{O}_3$ and (c) $\text{NiFe}/\text{Al}_2\text{O}_3$.

Table 4.1. Yield, textural properties and surface chemistry of CVD catalysts and support.

Material	Yield (%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{mm}^3 \text{g}^{-1}$)	Fe (wt.%)	Ni (wt.%)	Acidic groups ($\mu\text{mol g}^{-1}$)	Basic groups ($\mu\text{mol g}^{-1}$)	Contact angle ($^\circ$)	Image
Al_2O_3	-	221	508	-	-	1836	1270	15 $\pm$ 4	
$\text{Fe}/\text{Al}_2\text{O}_3$	92	98	273	15	-	742	498	96 $\pm$ 4	
$\text{NiFe}/\text{Al}_2\text{O}_3$	96	134	427	8.8	4.9	1840	796	105 $\pm$ 5	

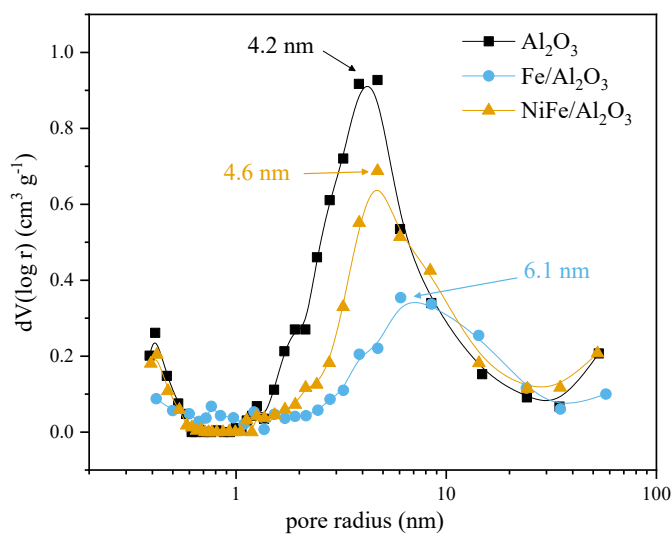


Figure 4.4. Pore size distribution for Al_2O_3 , $\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{NiFe}/\text{Al}_2\text{O}_3$.

The surface chemistry of the CVD catalysts and alumina is shown in Table 4.1. The metal catalysts ($\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{NiFe}/\text{Al}_2\text{O}_3$) displayed a contact angle of 96° and 105°, respectively. Hematite, identified in both CVD-catalysts, has been correlated to higher contact angles than other iron oxide phases [8]. No reports were found regarding specific contact angles of γ -alumina surfaces.

4.2 Carbon Nanotubes

4.2.1 Yield of carbon materials

The yields of as-synthesized materials are reported in Figure 4.5a. The mass yields were obtained in the range of 5.3-30 wt.% (calculated according to Equation 3.2), depending on CVD reaction conditions, catalyst and polymer source. Those values are within the range of previously reported yields using LDPE or waste PE as carbon source on NiFe-based catalysts (7-20 wt.% [9, 10]), PP over a MnFe-derived catalyst (23-42 wt.% [11]), waste plastic over Fe-based catalyst (*ca.* 20% [12]), waste HDPE over a Ni-based catalyst (4.2-11.4 wt.% [13]), and PS over a NiFe/Al₂O₃ catalyst (*ca.* 29% [14]).

The lowest yield was obtained for the sample synthesized at 600 °C (5.3 wt.%) using Fe-based catalyst. The CNTs synthesized using Fe/Al₂O₃ at higher temperatures displayed a yield ranging from 11–14 wt.%, depending on the carbon source. The increase in carbonaceous material yields when the temperature increases has been previously reported [15-18]. The highest yield (for monometallic catalyst, Fe/Al₂O₃) was obtained from the cracking of LDPE at 800 °C (14.3 wt.%), representing an increase of 2.7× compared to 600 °C. Previous studies in the catalytic cracking of polyolefins to produce liquid fuels have found that LDPE resulted in the highest selectivity towards C₁-C₄ hydrocarbons compared to HDPE [19] and compared to PP [20], especially towards methane, ethane, and ethylene gases [21], which may explain the higher mass yield using LDPE compared to HDPE and PP.

Changing from a mono- to a bimetallic catalyst also significantly influenced the yield of CNTs. Catalyst NiFe/Al₂O₃ resulted in a yield 2× greater using POL as a carbon source compared to Fe/Al₂O₃ at the same reaction temperature. This behavior has been previously reported for several catalysts in the CVD of carbonaceous materials, with a mass yield increase in the range of 1.15-1.30× for NiMo, CoMo and FeMo comparing to Ni, Fe, or Co alone [22], 1.25-2.5× for NiFe versus Fe and Ni [10], 1.25-1.60× for MnFe versus Fe [11], 1.25-1.95× for NiFe-based compared to Ni or Fe alone [12].

Several aspects may influence CNT growth, impacting mass yield. Among them, carbon solubility and diffusivity are relevant ones, combined with particle size [23]. Previous works have reported that carbon solubility is higher for Fe particles than Ni [24-27]. On the other hand, the diffusion coefficient of carbon in Ni is higher than in Fe ($1.6 \cdot 10^{-7}$ versus $1.1 \cdot 10^{-7}$ cm²s⁻¹ at 950 °C, respectively [28]), favoring the growth of carbon nanotubes compared to other carbon forms. Thus, a significantly higher yield can be obtained by combining high carbon solubility from Fe with high carbon diffusion from Ni.

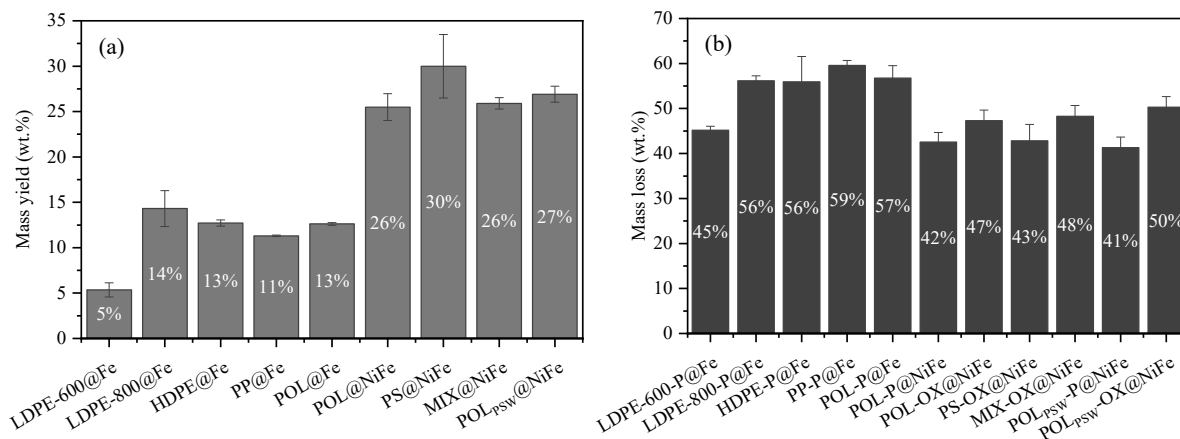


Figure 4.5. (a) Yield of the materials after CVD and (b) mass loss after acid washing.

The mass loss after acid washing (calculated according to Equation 3.3) is reported in Figure 4.5b. This mass loss is mostly related to the dissolution of the inorganic fraction of the materials (CVD catalyst, Fe/Al₂O₃ or NiFe/Al₂O₃), removal of amorphous carbon phases [29] and even the destruction of the outer layers in CNTs [30]. POL_{PSW}@NiFe resulted in a similar yield and mass loss with the different acid treatments compared to the material obtained using simulated mixed waste (POL@NiFe).

4.2.2 Morphology and elemental composition of CNT samples

The morphology of the treated CNT samples (with both H₂SO₄ and HNO₃) was observed via TEM, and the images are shown in Figure 4.6 for Fe-based CNTs, Figure 4.7 for NiFe-based materials using pure polymers and Figure 4.8 for CNTs synthesized using real PSW. As observed (Figure 4.6a-c), the synthesis carried out at 600 °C did not allow for obtaining filamentous structures, as expected. However, a crystalline carbon phase can be observed encapsulating an iron particle on the left side of the figure (Figure 4.6a,c). Similar observations have been reported, with CNTs obtained only at T > 680 °C [31]. All samples obtained at 800 °C resulted in filamentous structures with hollow cavities. Samples derived from Fe/Al₂O₃ as the catalyst have a similar configuration, with straight walls and a similar number of walls (25–27). The outer diameter was also similar for all samples, with average diameters of 32±5 nm, 29±1 nm, 26±1 nm, and 33±3 nm for LDPE-800-P@Fe, HDPE-P@Fe, PP-P@Fe, and POL-P@Fe, respectively, indicating that the morphology of the CNTs is not affected for the distinct polyolefins used in this work. For LDPE-600-P@Fe, the average particle size could not be determined. In some samples, an encapsulated metal particle can be observed (Figure 4.6f,g,m,o) because iron nanoparticles are taken from alumina support during synthesis, as is well-known in the mechanism of CNTs growth [1]. As metallic particles are inside the nanotubes, purification methods are not able to remove them without destroying the whole structure. Nevertheless, the metallic phases can work as active phases for the catalytic application of the CNTs and are typically protected against deactivation mechanisms, such as leaching [9].

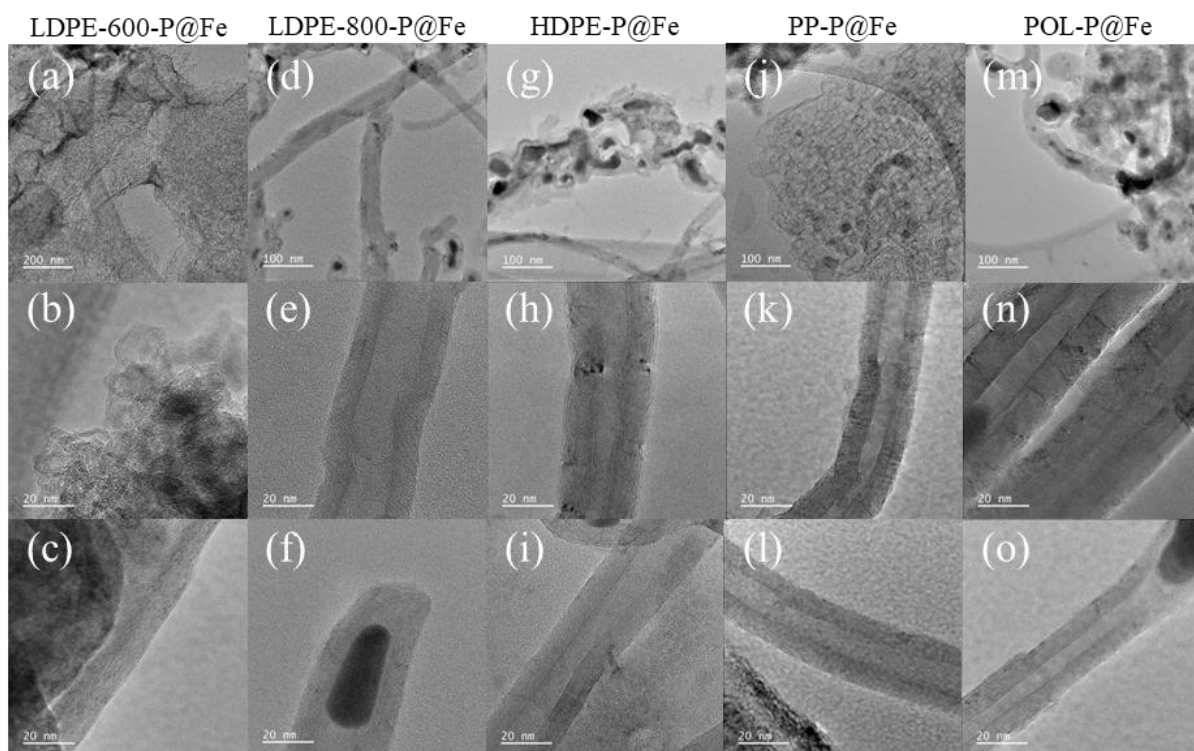


Figure 4.6. TEM images of Fe/Al₂O₃-derived CNTs. (a–c) LDPE-600-P@Fe, (d–f) LDPE-800-P@Fe, (g–i) HDPE-P@Fe, (j–l) PP-P@Fe, and (m–o) POL-P@Fe.

TEM images of POL-P@NiFe and POL-OX@NiFe are shown in Figure 4.7a–f. Both samples display tubes with straight walls, although some disordered structures can also be observed, such as cup-stacked (Figure 4.7a,d,e), differently from what was seen for Fe-derived CNTs, where CNTs displayed only straight walls. This behavior has been previously reported with Fe yielding CNTs with straight walls and Ni yielding helical tubes [32]. Outer diameters were estimated as 28.2 ± 0.6 nm and 22.8 ± 0.6 nm for POL-P@NiFe and POL-OX@NiFe, respectively (a reduction of *ca.* 20% between the samples). Several metallic particles can be found encapsulated in the walls of the tubes, especially for POL-P@NiFe (Figure 4.7a). MIX-OX@NiFe (Figure 4.7j–l) resulted in some structures with straight walls (Figure 4.7l), but it is also possible to see some CNTs with more disordered walls (Figure 4.7j–k), with an average outer diameter of 24.8 ± 0.7 nm. PS-OX@NiFe resulted in more disordered CNTs, with some growing with a cup-stacked structure (Figure 4.7i) and including some coiled CNT bundles (Figure 4.7g, h) and an average diameter of 18.6 ± 1.4 nm. The lower outer diameter obtained for the HNO₃-treated samples likely indicates the stripping of outer layers of the CNTs due to harsher oxidation conditions [33, 34]. Other works also reported that PS yields CNTs with more irregular and defective walls than PP [14] and other polyolefins [35]. While the distinct polyolefins do not seem to affect the samples' overall morphology and diameter distribution (Figure 4.6), PS seems to affect the sample obtained significantly. This difference observed in the morphology of CNTs grown from PS compared to polyolefins is generally associated with the gases generated during pyrolysis of the polymer source. While polyolefins tend to generate linear alkanes with carbon lengths varying from C₁–C₆₀ (including

gaseous products with 1-4 carbons [19]), PS generates cyclic products, mainly styrene [14]. The generation of distinct gases may affect the morphology of the obtained sample.

The morphology of PSW-derived CNTs grown over NiFe/Al₂O₃ is similar to the morphology obtained for CNTs synthesized from pure polyolefins with straight walls (Figure 4.8b,c,e,f) and also some other structures (Figure 4.8a,c,d,e), indicating that the process proposed is suitable to synthesize CNTs from a wide range of solid precursors. Outer diameters of 23.8 ± 0.6 nm and 18.1 ± 1.7 nm were obtained for POL_{PSW}-P@NiFe and POL_{PSW}-OX@NiFe, respectively (reduction of *ca.* 24% between the samples). The outer diameters were slightly lower than for their counterparts derived from simulated PSW (reduction of 15% and 20% for POL_{PSW}-P@NiFe and POL_{PSW}-OX@NiFe, respectively, in comparison with their counterparts derived from virgin plastic), likely indicating that they present more defects and are more prone to oxidation compared to pure POL.

The outer diameters reported here are similar to previously reported values for polymer-derived CNTs: 37–44 nm for polyolefin-derived CNTs [1], 4–63 nm for LDPE-derived CNTs [9], 1–40 nm for a mixture of polyolefins [36], and 5–25 nm for polyolefins and polystyrene-derived CNTs [37].

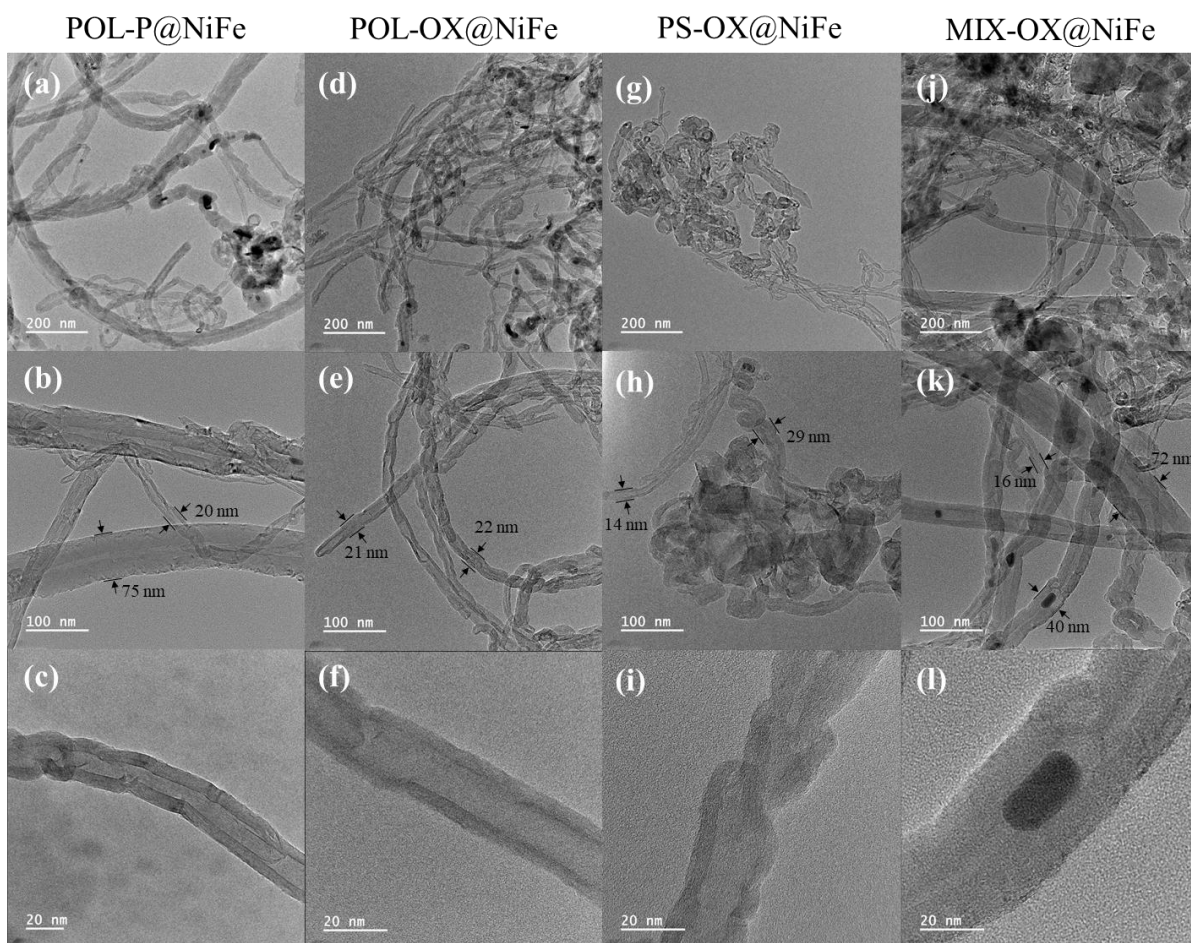


Figure 4.7. TEM images of (a-c) POL-P@NiFe, (d-f) POL-OX@NiFe, (g-i) PS-OX@NiFe, and (j-l) MIX-OX@NiFe.

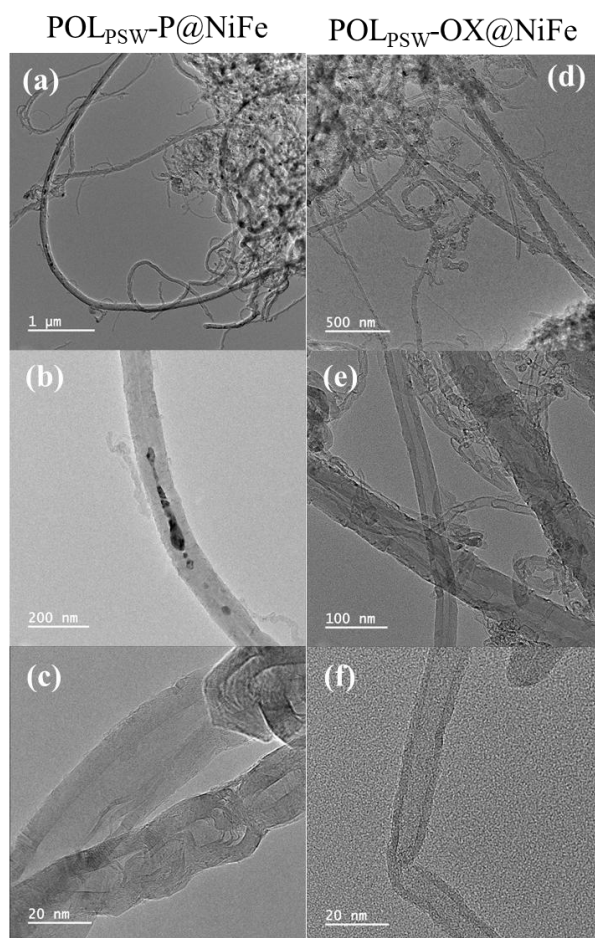


Figure 4.8. TEM images of (a-c) $\text{POL}_{\text{PSW}}\text{-P@NiFe}$ and (d-f) $\text{POL}_{\text{PSW}}\text{-OX@NiFe}$.

The mechanism of CNTs formation depends on a series of factors, and two main steps are generally assumed: (i) the adsorption of the carbon-rich gas in the catalyst and (ii) a competition between the diffusion of the carbon to the edge of the catalyst particle to form the hollow CNT or the accumulation of carbon on the catalyst to form amorphous carbon [38]. The diffusion or not of the carbon will depend on the catalytic particles (Fe, Ni, or other) [28] and the temperature of the process [38]. For Fe-based catalysts, it has been observed that lower temperatures (below 700 °C) favor the formation of amorphous carbon on the catalyst particle, hindering the growth of CNTs, whereas temperatures in the range of 750–800 °C favor diffusion and CNT growth [38]. NiFe-based catalysts have been shown to produce CNTs at lower temperatures compared to Fe-based catalysts [39] due to the higher diffusion coefficient of carbon in Ni particles [28], as previously mentioned.

The elemental analysis of the samples is described in Table 4.1. In general, NiFe-derived samples resulted in CNTs with higher carbon content (>89% for purified CNTs), whereas Fe-derived samples resulted in carbon content in the 70–86% range. This difference is related to the yield obtained during CVD using bimetallic catalysts (Figure 4.5), as previously seen, and the higher dissolution of alumina and CVD catalyst during acid washing, decreasing the content of ashes.

Among CNTs grown over Fe/Al₂O₃, LDPE-600-P@Fe resulted in the lowest carbon content among the samples and the highest incorporation of hydrogen and oxygen due to the acid treatment. The higher incorporation of oxygen and hydrogen by LDPE-600-P@Fe can be ascribed to its less crystalline structure compared to the other samples: amorphous carbon phases, which were observed for LDPE-600-P@Fe and not for the remaining CNTs, can be more easily oxidized during acid treatment [40]. Among the samples synthesized at 800 °C, there is also a tendency: LDPE results in the highest C content, followed by HDPE, PP, and the mixture of polymers (POL).

For NiFe-derived samples, oxygen content in the carbon nanotube structure varied significantly according to both acid treatment and polymer source. PS-containing materials (PS-OX@NiFe and MIX-OX@NiFe) resulted in more significant incorporation of oxygen (*ca.* 8-10%) compared to POL-OX@NiFe (4.4%), and nitric acid treatment also allowed more oxygen into the sample (1% for POL-P@NiFe). Oxygen content in POL@NiFe likely arises from oxygen transfer from the metallic particle during its reduction in a carbon-rich atmosphere, as shown elsewhere [41]. The heat treatment at 400 °C (POL-400@NiFe) greatly reduced the oxygen content of the sample (*ca.* 0.2 wt.%).

The elemental composition of POL_{PSW}@NiFe is very much like its counterpart synthesized with pure POL (POL@NiFe), with variations below 0.3%, 0.15%, 1.5% and 0.1% for C, O, ashes and Ni/Fe content, respectively.

Table 4.2. Elemental composition of the CNT samples.

Material	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Ashes ^c (wt.%)	Fe (wt.%)	Ni (wt.%)
LDPE-600-P@Fe	70.6±2.1	1.77±<0.01	0.07±<0.01	0.12±<0.01	4.50±0.01	29	9.7±<0.01	-
LDPE-800-P@Fe	86.2±1.1	0.32±0.04	0.10±0.01	0.08±0.01	0.88±0.07	19	11.3±0.2	-
HDPE-P@Fe	85.3±0.5	0.27±0.02	0.09±<0.01	0.14±0.01	0.83±0.03	20	14.0±0.7	-
PP-P@Fe	84.1±2.6	0.41±0.01	0.11±<0.01	0.18±0.03	1.18±0.01	19	11.9±0.7	-
POL-P@Fe	80.5±3.6	0.34±0.03	0.00±<0.01	0.36±0.09	1.83±<0.01	25	14.9±0.1	-
POL@NiFe	59.2±3.4	0.18±0.02	-	-	2.6±0.3	48	4.3±0.10	2.6±0.05
POL-P@NiFe	97.4±0.9	0.04±0.01	-	0.11±0.01	1.0±0.1	1.5	1.1±0.09	0.5±0.01
POL-OX@NiFe	91.9±0.3	0.15±0.01	0.11±<0.01	-	4.4±0.1	4.5	0.7±0.11	0.3±<0.01
PS-OX@NiFe	89.2±4.2	0.26±<0.01	0.12±<0.01	-	9.2 ^b	1.2	0.1±0.06	<0.01
MIX-OX@NiFe	92.3±0.1	0.25±0.01	0.12±<0.01	-	6.1 ^b	0.3	0.3±0.01	0.04±<0.01
POL-400@NiFe	97.4±0.1	0.17±0.01	-	-	0.2±<0.01	1.8	0.8±0.12	0.3±<0.01
POL _{PSW} @NiFe	58.6±3.5	0.18±0.01	-	-	2.3±0.2 ^a	51	4.1±0.30	2.8±0.08

^aDetermined directly. ^bEstimated as 100-C-H-N-S-ashes, ^cestimated from TG analysis.

It should be noted that the ashes content in Table 4.2 does not seem to corroborate with the organic content of the samples (as the sum between the C content and the ashes surpasses 100% in some cases), especially for samples with higher content of ashes, such as Fe-derived samples and non-purified NiFe-derived samples, POL@NiFe and POL_{PSW}@NiFe, which can be ascribed to a total or partial oxidation of the metallic particles during TGA under air atmosphere. Previous works have demonstrated that metal oxides could be reduced during CVD, resulting in reduced phases such as cementite (Fe₃-C) [1] and zero-valent phases (Fe⁰ [42] and Ni⁰ [43]). In fact, the reduction of iron at high temperatures (>230 °C) in the presence of carbon is a well-known process [44], so iron can be reduced during the process under

study in this work. Upon TGA in air, a mass increase of up to 143% can be expected for the oxidation of Fe^0 to Fe_2O_3 [45] for temperatures above 600 °C or up to 128% for the oxidation of Fe^0 to FeO . Previous works have also reported an average mass increase of 132% for Fe^0 starting at 450 °C up to 585 °C [46]. The oxidation state of Ni particles was also affected by carbon deposition during CH_4 reforming [43], and the oxidation of Ni^0 to NiO or NiO_3 could represent a mass gain in the 127-182% range.

The content of Fe and Ni is also reported in Table 4.2. The highest content of iron was found for POL-P@Fe (14.9 wt.%), whereas LDPE-600-P@Fe resulted in the lowest (9.7 wt.%), indicating that POL-P@Fe resulted in more encapsulation of metallic particles during CVD, whereas LDPE-600-P@Fe did not, allowing for the metallic content to be more easily removed during acid treatment. The remaining Fe-samples resulted in iron content in the 11–14 wt.% range. Functionalized NiFe-derived samples (POL-P@NiFe, POL-OX@NiFe, PS-OX@NiFe and MIX-OX@NiFe) all resulted in lower metal content compared to Fe-derived samples, indicating a higher removal of metallic particles during acid treatments, which is correlated with the higher yields obtained with NiFe-CNTs.

4.2.3 Raman spectra

The Raman spectra of the samples are displayed in Figure 4.9 and the calculated D/G ratio (based on the areas of the peaks [47]) is also shown. Except for LDPE-600-P@Fe, all materials displayed three bands: the D-band, associated with structural defects near *ca.* 1330-1345 cm^{-1} , and two bands associated with sp^2 -hybridized carbons in the CNTs; the G-band (*ca.* 1575-1585 cm^{-1}) and the G'-band (*ca.* 2675-2595 cm^{-1}). In the materials oxidized with nitric acid, a 4th band is also observed, located near *ca.* 1620 cm^{-1} (indicated with an arrow in Figure 4.9b), known as the D'-band, and typically associated with defects in the structure of the sample [48]. The D/G ratio indicates the degree of graphitization of a given sample, and lower values indicate higher graphitization. LDPE-600-P@Fe resulted in the highest value, indicating a high concentration of defects. This high concentration of defects in LDPE-600-P@Fe is also reinforced by the absence of the G'-band for this material. In general, Fe-derived samples obtained at $T = 800$ °C ($\text{D/G} = 0.49\text{-}0.96$) displayed lower D/G ratios compared to the equivalent sample derived from a bimetallic catalyst (POL-P@NiFe, with a D/G ratio of 0.91). This result agrees with previous TEM observations, in which $\text{Fe}/\text{Al}_2\text{O}_3$ resulted in CNTs with straight walls, whereas $\text{NiFe}/\text{Al}_2\text{O}_3$ also gave rise to cup-stacked walls. Among the NiFe-derived samples, the original sample (POL@NiFe) has the lowest D/G ratio, indicating a more graphitic structure. The acid treatment introduces surface groups on the materials, or it results in the destruction of graphitic layers [49], thus affecting the amount of sp^3 -hybridized carbons in the CNTs, resulting in a higher D/G ratio. Strong oxidizing conditions seem to result in more defects in the structure, as shown for POL-P@NiFe and POL-OX@NiFe (D/G ratios of 0.91 and 0.99, respectively). Nevertheless, the choice of the polymer sample has a higher impact on the graphitization of the sample, as MIX-OX@NiFe and PS-OX@NiFe

both resulted in an increased D/G ratio (1.19 and 1.71, respectively) compared to POL-OX@NiFe (0.99). A correlation between the percentual of PS in the precursor polymer and the D/G ratio of oxidized samples seems to exist (Figure 4.10). This result corroborates what has been observed in TEM images. Previous works also reported higher defects for PS-derived CNTs [35] compared to polyolefins-derived samples. Further thermal treatment (POL-400@NiFe, D/G = 0.92) removes part of the surface groups, reflecting a slightly lower D/G ratio than POL-OX@NiFe. Similar results have been reported for the D/G ratio of CNTs derived from polyethylene: 0.61 for a Ni-based catalyst [50] and 0.8-0.9 for a Fe-Al catalyst [51]. PP as a carbon source yielded CNTs with reported D/G ratios of 0.76 [14], 0.82-1.07 [52], and 0.52-1.13 [53] for NiFe-derived catalysts; 0.84 for a Fe-Mn catalyst [54]; and 0.45-0.83 over a Ni-based catalyst [55]. Other works also report D/G ratios of 0.8-1.11 for PET [56] and 0.45-0.47 for PS [57] over Fe catalysts.

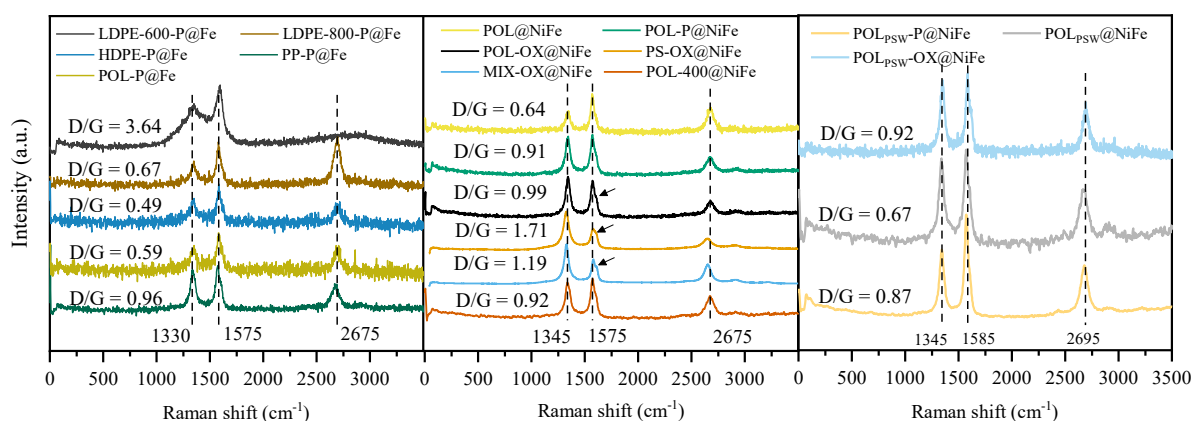


Figure 4.9. Raman spectra of the materials. (a) Fe-derived samples, (b) NiFe-derived samples and (c) samples synthesized using real PSW.

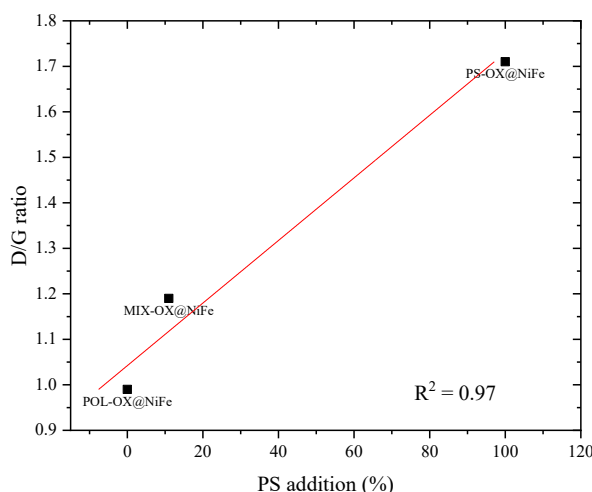


Figure 4.10. Correlation between PS addition in the feedstock and D/G ratio of oxidized NiFe-derived samples.

4.2.4 Thermogravimetric analysis

Figure 4.11 displays the results obtained for the TGA of samples in air atmosphere. In general, the materials synthesized in the presence of NiFe-based catalysts using polyolefin as a carbon source

resulted in samples more stable towards oxidation compared to Fe-derived materials. Fe-based CNTs have a mass loss centered at 590-600 °C, whereas NiFe-based CNTs with POL as a precursor result in a mass loss centered at 640-650 °C.

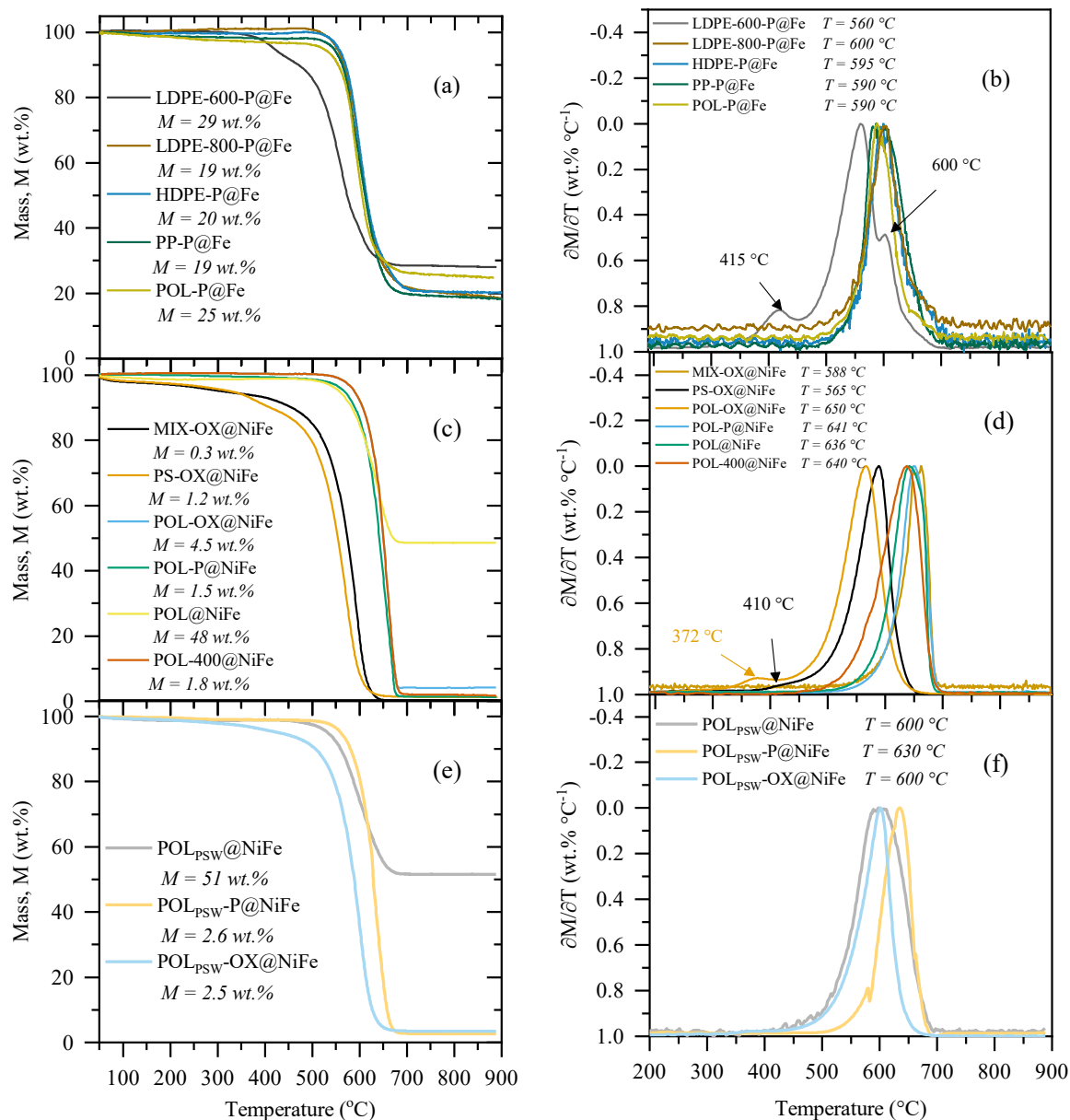


Figure 4.11. (a, c, e) TGA analysis and (b, d, f) DTG of (a, b) Fe-derived CNTs, (c, d) NiFe-derived CNTs, and (e, f) CNTs using real PSW as feedstock.

The thermogravimetric profile changes greatly depending on the temperature of the CVD process. For LDPE-600-P@Fe, three distinct regions of mass loss are evident: one centered at 410 °C, another one at 600 °C, and the main one centered at 550 °C. The region with the lower temperature, corresponding to approximately 8.1 wt.% of LDPE-600-P@Fe, is mostly related to the deposition of amorphous carbon on the catalyst, corroborating the results observed via TEM. In contrast, the region with higher temperatures is related to the deposition of highly graphitic carbon structures, such as graphene layers, which was also observed on TEM images. The CNTs synthesized at 800 °C do not demonstrate the

presence of amorphous carbonaceous structures, as the mass loss is mostly centered between 585 and 600 °C (Figure 4.11b), which also indicates that the use of different polyolefins does not seem to impact the center of mass loss. Other authors have also observed that increasing the synthesis temperature increases the degree of graphitization of the CNTs, affecting its resistance to oxidation [17, 58]. Similar profiles for TGA/DTG curves have been previously reported [1, 59]. Furthermore, as oxidative conditions were used, the mass at the end of the process is typically associated with the inorganic matter (ashes) of the materials. In this case, this quantity may be ascribed to the encapsulated iron nanoparticles along carbon structures, which were resistant to the purification conducted via acid attack and residual alumina support. As can be seen, the ashes of the carbonaceous materials are within the same range (18–20 wt.%) for the materials synthesized at the same temperature with single polymers (LDPE-800-P@Fe, HDPE-P@Fe, and PP-P@Fe). POL-P@Fe resulted in 25 wt.% of ashes and LDPE-600-P@Fe in 28 wt.%. These higher ashes content for LDPE-600-P@Fe and POL-P@Fe may also explain the lower mass loss centers (550 and 587 °C, respectively), as metal particles can catalyze the oxidation of carbon materials [60]. As previously mentioned, these ash values do not match the remaining weight calculated by elemental analysis, likely due to oxidation of those metallic particles during the TGA run.

The TGA and DTG profiles of the NiFe-derived CNTs are also displayed in Figure 4.11c. PS-OX@NiFe and MIX-OX@NiFe start to decompose at lower temperatures (*ca.* 250–300 °C) compared to the samples derived from polyolefins only (>450 °C). Similarly, the main mass loss event for PS-derived materials is located at a lower temperature (565–588 °C) compared to polyolefin-derived materials (636–650 °C). This behavior is correlated with the lower-quality CNT obtained with PS as a carbon precursor (as previously seen in TEM and Raman). Both PS-containing samples have a mass loss in the range of 150–450 °C (representing *ca.* 10.4 wt.% and 6.9 wt.%, respectively, for PS-OX@NiFe and MIX-OX@NiFe). POL@NiFe resulted in a slightly lower mass loss center (636 °C) compared to POL-P@NiFe and POL-OX@NiFe due to the catalytic effect from the metal particles within the CNTs [60]. Any mass loss below 150 °C is associated with moisture.

TGA/DTG analysis of the samples synthesized using mixtures of real PSW are shown in Figure 4.11e,f. As can be seen, the main event of mass loss is centered around 600–630 °C, which is slightly lower than the reported range for the samples synthesized using simulated polymers (POL@NiFe, POL-P@NiFe, and POL-OX@NiFe). Ashes content was also slightly higher, which may explain the slightly lower temperature decomposition [60]. Nevertheless, no formation of amorphous particles was found.

4.2.5 Textural properties

The N₂ adsorption-desorption isotherms at -196 °C and the calculated textural properties are reported in Figure 4.12 and Table 4.3. The BET surface area (S_{BET}) has varied from 159 to 242 m² g⁻¹ for Fe-based CNTs, 144 to 219 m² g⁻¹ for NiFe-derived CNTs and 146–187 m² g⁻¹ for PSW-derived samples.

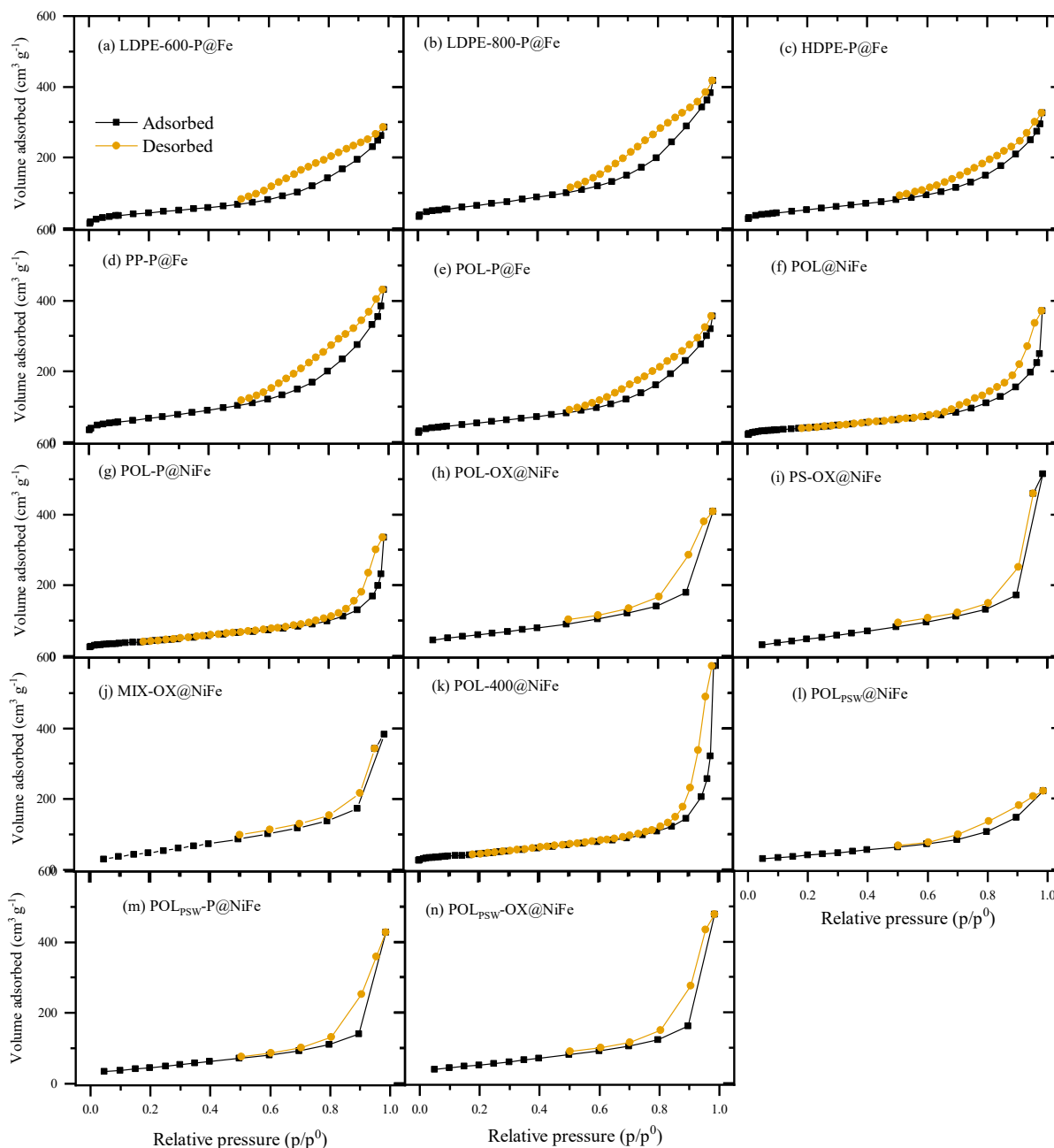


Figure 4.12. N₂ adsorption-desorption isotherms at -196 °C of (a) LDPE-600-P@Fe, (b) LDPE-800-P@Fe, (c) HDPE-P@Fe, (d) PP-P@Fe, (e) POL-P@Fe, (f) POL@NiFe, (g) POL-P@NiFe, (h) POL-OX@NiFe, (i) PS-OX@NiFe, (j) MIX-OX@NiFe, (k) POL-400@NiFe, (l) POL_{PSW}@NiFe, (m) POL_{PSW}-P@NiFe, and (n) POL_{PSW}-OX@NiFe.

The temperature of the synthesis seems to influence the surface area, as LDPE-600-P@Fe (159 m² g⁻¹) resulted in a lower surface area than LDPE-800-P@Fe (235 m² g⁻¹) and all other Fe-derived CNTs synthesized at 800 °C (≥189 m² g⁻¹). The total volume of pores followed a similar pattern, varying from 406 to 595 mm³ g⁻¹ with LDPE-600-P@Fe (406 mm³ g⁻¹), resulting in the lowest volume of pores compared to LDPE-800-P@Fe (594 mm³ g⁻¹). The CVD catalyst used to grow the CNTs also affected the surface area, as POL-P@Fe resulted in a higher surface area (194 m² g⁻¹) than POL-P@NiFe (148 m² g⁻¹). Acid washing affected the surface area of NiFe-derived samples, with nitric acid improving the textural properties (*ca.* 50% increase when comparing POL@NiFe with POL-OX@NiFe). The removal of oxygenated moieties also resulted in a slight increase in surface area (from 214 m² g⁻¹ for POL-

OX@NiFe to $219 \text{ m}^2 \text{ g}^{-1}$ for POL-400@NiFe) and a significant increase in the total volume of pores (*ca.* 40%). Similar results were previously reported for CNT samples [59]. The samples derived from real PSW (Figure 4.12 and Table 4.3) resulted in similar S_{BET} areas compared to the simulated PSW, although the increase in surface area after HNO_3 treatment was not as high (*ca.* 30% increase for PSW-derived samples versus 50% for simulated PSW). For NiFe-derived samples, the total volume of pores (V_{total}) is inversely proportional to the mean diameter of the CNT particles (Figure 4.13)

Table 4.3. Textural properties of the CNT samples.

Material	$S_{BET} (\text{m}^2 \text{ g}^{-1})$	$V_{total} (\text{mm}^3 \text{ g}^{-1})$
LDPE-600-P@Fe	159	406
LDPE-800-P@Fe	235	594
HDPE-P@Fe	189	456
PP-P@Fe	242	595
POL-P@Fe	194	496
POL@NiFe	144	575
POL-P@NiFe	148	359
POL-OX@NiFe	214	632
PS-OX@NiFe	226	794
MIX-OX@NiFe	219	592
POL-400@NiFe	219	894
POL _{PSW} @NiFe	146	342
POL _{PSW} -P@NiFe	166	663
POL _{PSW} -OX@NiFe	187	740

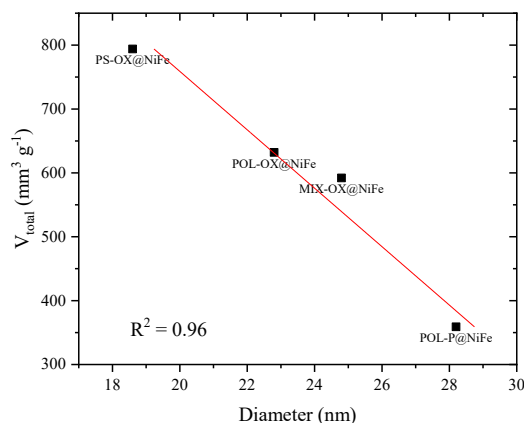


Figure 4.13. Correlation between CNT diameter and total volume of pores for NiFe-derived CNTs.

4.2.6 Surface chemistry

The infrared spectrum of the materials is reported in Figure 4.14. A band located at $1570\text{--}1582 \text{ cm}^{-1}$ was identified for all samples, which was ascribed to the stretching vibration of $\text{C}=\text{C}$ bonds of either CNT structures or graphene layers [61]. Two other bands were also identified at $2920\text{--}2926$ and $2851\text{--}2853 \text{ cm}^{-1}$, which were ascribed to the asymmetric and symmetric, respectively, stretching vibration of C-H bonds in $-\text{CH}_2$ groups [61], which could be attributed to defects [62]. The bands at $1381\text{--}1386 \text{ cm}^{-1}$ can be ascribed to the symmetrical bending of $-\text{CH}_2$ or $-\text{CH}_3$ groups, and $1630\text{--}1636 \text{ cm}^{-1}$ is ascribed to O-H bending from surface groups [61].

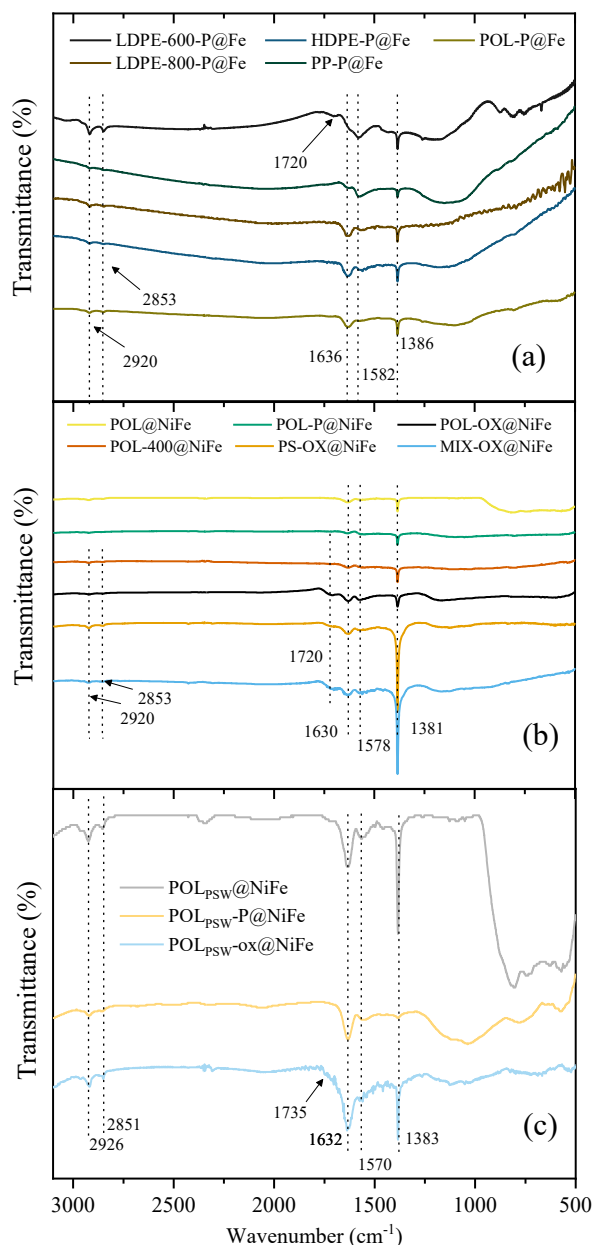


Figure 4.14. FTIR analysis of the samples. (a) Fe-derived CNTs, (b) NiFe-derived CNTs, and (c) CNTs obtained using real PSW.

POL@NiFe and POL_{PSW}@NiFe also displayed bands in the range 900-500 cm^{-1} associated with the catalyst used to grow the CNTs, as reported in Figure 4.1b. The band located at 1720-1735 cm^{-1} , mainly identified in POL-OX@NiFe, PS-OX@NiFe, MIX-OX@NiFe, POL_{PSW}-OX@NiFe and LDPE-600-P@Fe samples, can be ascribed to the C=O stretching from surface groups [61], indicating the incorporation of oxygenated moieties in those samples.

The contact angles of water are reported in Table 4.4. Most of the carbon samples synthesized in this work displayed a hydrophobic character, with water contact angles in the 117-138° range, except for oxidized samples containing PS as a precursor (PS-OX@NiFe and MIX-OX@NiFe). Higher incorporations of oxygenated moieties result in slightly lower water contact angles (117-126°), as seen

for LDPE-600-P@Fe, POL-P@Fe and POL-OX@NiFe. Similar results have been reported for acid-treated CNTs [63, 64]. It should be noted that the samples obtained from NiFe/Al₂O₃ either from simulated or real PSW resulted in a similar contact angle, except for POL_{PSW}-OX@NiFe, which resulted in a much lower value than expected (*ca.* 75° as opposed to 117° for POL-OX@NiFe).

Table 4.4. Water contact angles and acidic/basic groups for the materials used in this work.

Material	Contact angle (°)	Image	Acidic groups (μmol g ⁻¹)	Basic groups (μmol g ⁻¹)
LDPE-600-P@Fe	124±2°		1277	194
LDPE-800-P@Fe	136±2°		197	301
HDPE-P@Fe	137±1°		137	262
PP-P@Fe	129±3°		276	271
POL-P@Fe	123±7°		632	184
POL@NiFe	138±2°		1551	138
POL-P@NiFe	126±2°		982	25
POL-OX@NiFe	117±3°		1695	368
PS-OX@NiFe	51±5°		1897	465
MIX-OX@NiFe	101±4°		1758	365
POL-400@NiFe	134±1°		656	63
POL _{PSW} @NiFe	136±2°		1684	126
POL _{PSW} -P@NiFe	122±1°		991	201
POL _{PSW} -OX@NiFe	75±5°		1636	684

Table 4.4 also reports the values obtained for acidic and basic groups in the different samples. HNO₃-treated samples (POL-OX@NiFe, PS-OX@NiFe, MIX-OX@NiFe and POL_{PSW}-OX@NiFe) resulted in the highest amount of acidic groups (1636-1897 μmol g⁻¹, respectively) and basic groups (368-684 μmol g⁻¹, respectively), indicating that HNO₃ introduces both acidic and basic groups, as reported elsewhere [65]. LDPE-600-P@Fe, POL-P@NiFe and POL_{PSW}-P@NiFe displayed high content of acidic groups (1277, 982 and 991 μmol g⁻¹, respectively), yet the content of basic groups was lower (194, 25 and 201 μmol g⁻¹, respectively) than the previous oxidized materials. The as-synthesized CNT samples (POL@NiFe and POL_{PSW}@NiFe) resulted in a high content of acidic groups (1551 and 1684 μmol g⁻¹, respectively). However, this acidity is likely ascribed to the presence of alumina (1836 μmol g⁻¹ of acidic groups, Table 4.1) and/or CVD-catalyst (1840 μmol g⁻¹ of acidic groups, Table 4.1).

4.3 Conclusions

The study successfully demonstrated the synthesis of graphitic carbon nanomaterials, including carbon nanotubes (CNTs), using catalytic chemical vapor deposition (CVD) from simulated and real plastic solid waste (PSW) grown over Fe- and NiFe-based catalysts.

Both the synthesis temperature and the choice of catalyst influenced the yield and morphology of carbon nanomaterials. Increasing the temperature from 600 °C to 800 °C using Fe/Al₂O₃ not only resulted in increased yield (from 5% to 12%) but also allowed the formation of the hollow tubes characteristic of CNTs. The use of a bimetallic catalyst also resulted in increased yield (up to 2 times, from 12% using Fe/Al₂O₃ to 25% for NiFe/Al₂O₃) and distinct morphologies: while Fe-derived CNTs demonstrated mainly straight walls, NiFe-derived CNTs did result in more CNTs with distinct morphologies, such as cup-stacked or coiled CNTs. The formation of varied morphologies for NiFe-derived CNTs resulted in higher D/G ratios (>0.92) for NiFe-derived purified CNTs compared to Fe-derived CNTs (0.49-0.96).

Post-synthesis treatment using distinct acids introduced surface groups, especially oxygenated ones, while partially removing impurities. Acid washing also affected hydrophilicity, BET surface areas, and pore volumes. However, harsher oxidative conditions also increase structural defects, reflected in higher D/G ratios, and it also resulted in the removal of outer layers of the CNTs, resulting in lower CNT outer diameters.

The thermogravimetric analysis revealed higher oxidation stability for CNTs derived from NiFe/Al₂O₃ compared to Fe-based catalysts, with decomposition temperatures around 640–650 °C for NiFe-CNTs versus 590–600 °C for Fe-CNTs. This accelerated decomposition of CNTs derived from Fe/Al₂O₃ is likely associated with the catalytic effect during TGA arising from encapsulated metallic particles (10–15% for Fe-CNTs versus <5% for NiFe-CNTs). Furthermore, the addition of PS in the feedstock during CNT synthesis was associated with lower resistance to oxidation, resulting in decomposition starting at lower temperatures (250–300 °C) for PS-derived samples compared to samples obtained from POL (>450 °C).

This work highlights the potential of CVD to transform PSW into CNTs with tunable properties through the optimization of catalyst composition, synthesis conditions, and post-treatment steps. By replacing traditional non-renewable carbon sources with plastic waste, this approach helps mitigate plastic accumulation in landfills while reducing dependence on fossil resources. Moreover, it promotes a more sustainable and circular strategy for plastic waste upcycling. In this context, the development of CNTs from PSW not only contributes to waste valorization but also advances the creation of sustainable materials for environmental and energy applications.

4.4 References

- [1] J.L. Diaz de Tuesta, A.S. Silva, F.F. Roman, L.F. Sanches, F.A. da Silva, A.I. Pereira, A.M.T. Silva, J.L. Faria, H.T. Gomes, Polyolefin-derived carbon nanotubes as magnetic catalysts for wet peroxide oxidation of paracetamol in aqueous solutions, *Catalysis Today* 419 (2023) 114162. <https://doi.org/10.1016/j.cattod.2023.114162>.
- [2] Z.T. Khodair, N.M. Ibrahim, T.J. Kadhim, A.M. Mohammad, Synthesis and characterization of nickel oxide (NiO) nanoparticles using an environmentally friendly method, and their biomedical applications, *Chemical Physics Letters* 797 (2022) 139564. <https://doi.org/10.1016/j.cplett.2022.139564>.
- [3] X. Wang, Z. Zhao, J. Qu, Z. Wang, J. Qiu, Fabrication and characterization of magnetic Fe₃O₄-CNT composites, *Journal of Physics and Chemistry of Solids* 71(4) (2010) 673-676. <https://doi.org/10.1016/j.jpcs.2009.12.063>.
- [4] S. Sagadevan, Z.Z. Chowdhury, R.F. Rafique, Preparation and characterization of nickel ferrite nanoparticles via co-precipitation method, *Materials Research* 21(2) (2018) e20160533. <https://doi.org/10.1590/1980-5373-mr-2016-0533>.
- [5] S. Kazemifard, H. Nayeibzadeh, N. Saghatoleslami, E. Safakish, Assessment the activity of magnetic KOH/Fe₃O₄@Al₂O₃ core-shell nanocatalyst in transesterification reaction: effect of Fe/Al ratio on structural and performance, *Environmental Science and Pollution Research* 25(32) (2018) 32811-32821. <https://doi.org/10.1007/s11356-018-3249-7>.
- [6] A.S.S. Nila, Synthesis and XRD, FTIR Studies of Alumina Nanoparticle using Co-precipitation Method, *International Journal for Research in Applied Science and Engineering Technology* 6(3) (2018) 2493-2496. <https://doi.org/10.22214/ijraset.2018.3402>.
- [7] K. Djebaili, Z. Mekhalif, A. Boumaza, A. Djelloul, XPS, FTIR, EDX, and XRD analysis of Al₂O₃ scales grown on PM2000 Alloy, *Journal of Spectroscopy* 2015 (2015) 1-16. <https://doi.org/10.1155/2015/868109>.
- [8] S.M. Iveson, S. Holt, S. Biggs, Advancing contact angle of iron ores as a function of their hematite and goethite content: implications for pelletising and sintering, *International Journal of Mineral Processing* 74(1-4) (2004) 281-287. <https://doi.org/10.1016/j.minpro.2004.01.007>.
- [9] R.S. Ribeiro, O. Vieira, R. Fernandes, F.F. Roman, J.L. Diaz de Tuesta, A.M.T. Silva, H.T. Gomes, Synthesis of low-density polyethylene derived carbon nanotubes for activation of persulfate and degradation of water organic micropollutants in continuous mode, *Journal of Environmental Management* 308 (2022) 114622. <https://doi.org/10.1016/j.jenvman.2022.114622>.
- [10] K. Li, H. Zhang, Y. Zheng, G. Yuan, Q. Jia, S. Zhang, Catalytic Preparation of Carbon Nanotubes from Waste Polyethylene Using FeNi Bimetallic Nanocatalyst, *Nanomaterials* 10(8) (2020) 1517. <https://doi.org/10.3390/nano10081517>.
- [11] S. He, Y. Xu, Y. Zhang, S. Bell, C. Wu, Waste plastics recycling for producing high-value carbon nanotubes: Investigation of the influence of Manganese content in Fe-based catalysts, *Journal of Hazardous Materials* 402 (2021) 123726. <https://doi.org/10.1016/j.jhazmat.2020.123726>.
- [12] D. Yao, Y. Zhang, P.T. Williams, H. Yang, H. Chen, Co-production of hydrogen and carbon nanotubes from real-world waste plastics: Influence of catalyst composition and operational parameters, *Applied Catalysis B: Environmental* 221 (2018) 584-597. <https://doi.org/10.1016/j.apcatb.2017.09.035>.
- [13] X. Liu, B. Shen, Z. Wu, C.M.A. Parlett, Z. Han, A. George, P. Yuan, D. Patel, C. Wu, Producing carbon nanotubes from thermochemical conversion of waste plastics using Ni/ceramic based catalyst, *Chemical Engineering Science* 192 (2018) 882-891. <https://doi.org/10.1016/j.ces.2018.07.047>.
- [14] K.A. Graves, L.J.R. Higgins, M.A. Nahil, B. Mishra, P.T. Williams, Structural comparison of multi-walled carbon nanotubes produced from polypropylene and polystyrene waste plastics, *Journal of Analytical and Applied Pyrolysis* 161 (2022) 105396. <https://doi.org/10.1016/j.jaap.2021.105396>.
- [15] K. Raji, S. Thomas, C.B. Sobhan, A chemical kinetic model for chemical vapor deposition of carbon nanotubes, *Applied Surface Science* 257(24) (2011) 10562-10570. <https://doi.org/10.1016/j.apsusc.2011.07.051>.
- [16] S. M. Toussi, A. Fakhru'l-Razi, A. Luqman Chuah, A.R. Suraya, Effect of Synthesis Condition on the Growth of SWCNTs via Catalytic Chemical Vapour Deposition, *Sains Malaysiana* 40 (2011) 197-201.

- [17] Z. Niu, Y. Fang, Effect of temperature for synthesizing single-walled carbon nanotubes by catalytic chemical vapor deposition over Mo-Co-MgO catalyst, *Materials Research Bulletin* 43(6) (2008) 1393-1400. <https://doi.org/10.1016/j.materresbull.2007.06.040>.
- [18] P.T. Williams, Hydrogen and Carbon Nanotubes from Pyrolysis-Catalysis of Waste Plastics: A Review, *Waste and Biomass Valorization* 12(1) (2020) 1-28. <https://doi.org/10.1007/s12649-020-01054-w>.
- [19] J. Aguado, D.P. Serrano, J.M. Escola, E. Garagorri, J.A. Fernández, Catalytic conversion of polyolefins into fuels over zeolite beta, *Polymer Degradation and Stability* 69(1) (2000) 11-16. [https://doi.org/10.1016/s0141-3910\(00\)00023-9](https://doi.org/10.1016/s0141-3910(00)00023-9).
- [20] Q. Zhou, L. Zheng, Y.-Z. Wang, G.-M. Zhao, B. Wang, Catalytic degradation of low-density polyethylene and polypropylene using modified ZSM-5 zeolites, *Polymer Degradation and Stability* 84(3) (2004) 493-497. <https://doi.org/10.1016/j.polymdegradstab.2004.01.007>.
- [21] G. Yan, X. Jing, H. Wen, S. Xiang, Thermal Cracking of Virgin and Waste Plastics of PP and LDPE in a Semibatch Reactor under Atmospheric Pressure, *Energy & Fuels* 29(4) (2015) 2289-2298. <https://doi.org/10.1021/ef502919f>.
- [22] R. Rattanaamkulchai, T. Kludpantanapan, A. Srifa, W. Koo-Amornpattana, W. Chaiwat, C. Sakdaronnarong, T. Charinpanitkul, S. Assabumrungrat, S. Wongsakulphasatch, P.-L. Show, R. Watanabe, C. Fukuhara, S. Ratchahat, Simultaneous production of hydrogen and carbon nanotubes from biogas over mono- and bimetallic catalyst, *Journal of Environmental Chemical Engineering* 10(4) (2022) 107910. <https://doi.org/10.1016/j.jece.2022.107910>.
- [23] M. Diarra, H. Amara, F. Ducastelle, C. Bichara, Carbon solubility in nickel nanoparticles: A grand canonical Monte Carlo study, *physica status solidi (b)* 249(12) (2012) 2629-2634. <https://doi.org/10.1002/pssb.201200147>.
- [24] A.R. Harutyunyan, N. Awasthi, A. Jiang, W. Setyawan, E. Mora, T. Tokune, K. Bolton, S. Curtarolo, Reduced carbon solubility in Fe nanoclusters and implications for the growth of single-walled carbon nanotubes, *Physical Review Letters* 100(19) (2008) 195502. <https://doi.org/10.1103/PhysRevLett.100.195502>.
- [25] M. He, Y. Magnin, H. Amara, H. Jiang, H. Cui, F. Fossard, A. Castan, E. Kauppinen, A. Loiseau, C. Bichara, Linking growth mode to lengths of single-walled carbon nanotubes, *Carbon* 113 (2017) 231-236. <https://doi.org/10.1016/j.carbon.2016.11.057>.
- [26] A. Moisala, A.G. Nasibulin, E.I. Kauppinen, The role of metal nanoparticles in the catalytic production of single-walled carbon nanotubes—a review, *Journal of Physics: Condensed Matter* 15(42) (2003) S3011-S3035. <https://doi.org/10.1088/0953-8984/15/42/003>.
- [27] X. Liu, Y. Zhang, M.A. Nahil, P.T. Williams, C. Wu, Development of Ni- and Fe- based catalysts with different metal particle sizes for the production of carbon nanotubes and hydrogen from thermo-chemical conversion of waste plastics, *Journal of Analytical and Applied Pyrolysis* 125 (2017) 32-39. <https://doi.org/10.1016/j.jaap.2017.05.001>.
- [28] C.J. Lee, J. Park, J.A. Yu, Catalyst effect on carbon nanotubes synthesized by thermal chemical vapor deposition, *Chemical Physics Letters* 360(3-4) (2002) 250-255. [https://doi.org/10.1016/s0009-2614\(02\)00831-x](https://doi.org/10.1016/s0009-2614(02)00831-x).
- [29] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, Chemical oxidation of multiwalled carbon nanotubes, *Carbon* 46(6) (2008) 833-840. <https://doi.org/10.1016/j.carbon.2008.02.012>.
- [30] Q.-h. Yuan, H.-q. Huang, W.-c. Wang, G.-h. Zhou, L. Luo, X.-s. Zeng, Y. Liu, Achieving high stability of MgO/carbon nanotube interface via the co-deposition technique, *Journal of Alloys and Compounds* 824 (2020) 153889. <https://doi.org/10.1016/j.jallcom.2020.153889>.
- [31] A.R. Harutyunyan, B.K. Pradhan, U.J. Kim, G. Chen, P.C. Eklund, CVD Synthesis of Single Wall Carbon Nanotubes under “Soft” Conditions, *Nano Letters* 2(5) (2002) 525-530. <https://doi.org/10.1021/nl0255101>.
- [32] W. Qian, T. Liu, Z. Wang, H. Yu, Z. Li, F. Wei, G. Luo, Effect of adding nickel to iron–alumina catalysts on the morphology of as-grown carbon nanotubes, *Carbon* 41(13) (2003) 2487-2493. [https://doi.org/10.1016/s0008-6223\(03\)00324-5](https://doi.org/10.1016/s0008-6223(03)00324-5).
- [33] H. Khani, O. Moradi, Influence of surface oxidation on the morphological and crystallographic structure of multi-walled carbon nanotubes via different oxidants, *Journal of Nanostructure in Chemistry* 3(1) (2013) 73. <https://doi.org/10.1186/2193-8865-3-73>.
- [34] V.J. González, S.M. Vega-Díaz, A. Morelos-Gómez, K. Fujisawa, M. Endo, O.M. Cadiz, J.B. Llido, M. Terrones, H₂O₂/UV layer-by-layer oxidation of multiwall carbon nanotubes: The “onion effect” and the control of

- the degree of surface crystallinity and diameter, *Carbon* 139 (2018) 1027-1034. <https://doi.org/10.1016/j.carbon.2018.07.062>.
- [35] A.A. Aboul-Encin, A.E. Awadallah, A.A.H. Abdel-Rahman, A.M. Haggag, Synthesis of multi-walled carbon nanotubes via pyrolysis of plastic waste using a two-stage process, *Fullerenes, Nanotubes and Carbon Nanostructures* 26(7) (2018) 443-450. <https://doi.org/10.1080/1536383x.2018.1447929>.
- [36] A. Veksha, W. Chen, L. Liang, G. Lisak, Converting polyolefin plastics into few-walled carbon nanotubes via a tandem catalytic process: Importance of gas composition and system configuration, *Journal of Hazardous Materials* 435 (2022) 128949. <https://doi.org/10.1016/j.jhazmat.2022.128949>.
- [37] J. Cui, S. Tan, R. Song, Universal Ni-Mo-Mg catalysts combined with carbon blacks for the preparation of carbon nanotubes from polyolefins, *Journal of Applied Polymer Science* 134(14) (2016). <https://doi.org/10.1002/app.44647>.
- [38] G.P. Gakis, S. Termine, A.-F.A. Trompeta, I.G. Aviziotis, C.A. Charitidis, Unraveling the mechanisms of carbon nanotube growth by chemical vapor deposition, *Chemical Engineering Journal* 445 (2022) 136807. <https://doi.org/10.1016/j.cej.2022.136807>.
- [39] M.S. Mamat, G.S. Walker, D.M. Grant, Y. Yaakob, N.A. Shaharun, Effect of the reaction temperature and ethene/hydrogen composition on the nanostructured carbon produced by CVD using supported NiFe_2O_4 as a catalyst, *Results in Physics* 19 (2020) 103497. <https://doi.org/10.1016/j.rinp.2020.103497>.
- [40] B. Zhong, R. Huang, D.S. Su, H. Liu, Effect of graphitization of oxygen-modified carbon nanotubes in selective oxidation of acrolein, *Catalysis Today* 330 (2019) 142-148. <https://doi.org/10.1016/j.cattod.2018.02.057>.
- [41] Y.-L. Kuo, W.-M. Hsu, P.-C. Chiu, Y.-H. Tseng, Y. Ku, Assessment of redox behavior of nickel ferrite as oxygen carriers for chemical looping process, *Ceramics International* 39(5) (2013) 5459-5465. <https://doi.org/10.1016/j.ceramint.2012.12.055>.
- [42] A.A.S. Oliveira, I.F. Teixeira, T. Christofani, J.C. Tristão, I.R. Guimarães, F.C.C. Moura, Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue, *Applied Catalysis B: Environmental* 144 (2014) 144-151. <https://doi.org/10.1016/j.apcatb.2013.07.015>.
- [43] Y. Zhan, K. Song, Z. Shi, C. Wan, J. Pan, D. Li, C. Au, L. Jiang, Influence of reduction temperature on Ni particle size and catalytic performance of Ni/Mg(Al)O catalyst for CO_2 reforming of CH_4 , *International Journal of Hydrogen Energy* 45(4) (2020) 2794-2807. <https://doi.org/10.1016/j.ijhydene.2019.11.181>.
- [44] Q. Zhang, Y. Sun, Y. Han, Y. Li, P. Gao, Review on coal-based reduction and magnetic separation for refractory iron-bearing resources, *International Journal of Minerals, Metallurgy and Materials* 29(12) (2022) 2087-2105. <https://doi.org/10.1007/s12613-021-2408-x>.
- [45] N. Leventis, S. Donthula, C. Mandal, M.S. Ding, C. Sotiriou-Leventis, Explosive versus Thermite Behavior in Iron(0) Aerogels Infiltrated with Perchlorates, *Chemistry of Materials* 27(23) (2015) 8126-8137. <https://doi.org/10.1021/acs.chemmater.5b03898>.
- [46] L.F. Greenlee, S.A. Hooker, Development of stabilized zero valent iron nanoparticles, *Desalination and Water Treatment* 37(1-3) (2012) 114-121. <https://doi.org/10.1080/19443994.2012.661262>.
- [47] G.J.H. Melvin, Q.-Q. Ni, Y. Suzuki, T. Natsuki, Microwave-absorbing properties of silver nanoparticle/carbon nanotube hybrid nanocomposites, *Journal of Materials Science* 49(14) (2014) 5199-5207. <https://doi.org/10.1007/s10853-014-8229-9>.
- [48] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Physics Reports* 473(5-6) (2009) 51-87. <https://doi.org/10.1016/j.physrep.2009.02.003>.
- [49] H. Nakajima, K. Kobashi, Y. Zhou, M. Zhang, T. Okazaki, Quantitative analysis of the correlation between sp^3 bonds and functional groups in covalently functionalized single-walled carbon nanotubes, *Carbon* 216 (2024) 118495. <https://doi.org/10.1016/j.carbon.2023.118495>.
- [50] Q.-L. Li, R. Shan, S.-X. Wang, H.-R. Yuan, Y. Chen, Carbon nanotubes production from catalytic pyrolysis of polyethylene over nickel-based catalysts: The influence of support materials, *Fuel* 343 (2023) 127966. <https://doi.org/10.1016/j.fuel.2023.127966>.
- [51] H. Qiao, R. Xu, X. Hou, H. Zhou, C. Song, L. Yin, J. Huang, E. Yuan, T. Cui, Synthesis of Fe-Al catalysts to boost CNTs formation from polymer wastes via the improved two-stage system, *Journal of Environmental Chemical Engineering* 11(6) (2023) 111449. <https://doi.org/10.1016/j.jece.2023.111449>.

- [52] D. Yao, H. Li, Y. Dai, C.-H. Wang, Impact of temperature on the activity of Fe-Ni catalysts for pyrolysis and decomposition processing of plastic waste, *Chemical Engineering Journal* 408 (2021) 127268. <https://doi.org/10.1016/j.cej.2020.127268>.
- [53] W. Meng, B. Xing, S. Cheng, Y. Nie, H. Zeng, X. Qu, B. Xu, C. Zhang, J. Yu, S. Won Hong, Preparation of high quality carbon nanotubes by catalytic pyrolysis of waste plastics using FeNi-based catalyst, *Waste Management* 189 (2024) 11-22. <https://doi.org/10.1016/j.wasman.2024.08.005>.
- [54] S. Dlova, O. Olaitan Ayeleru, F. Victoria Adams, M.A. Mamo, P. Apata Olubambi, Development of multi-walled carbon nanotubes obtained from recycled plastics by single stage pyrolysis process, *Materials Today: Proceedings* 38 (2021) 1170-1173. <https://doi.org/10.1016/j.matpr.2020.07.460>.
- [55] J. Wang, B. Shen, M. Lan, D. Kang, C. Wu, Carbon nanotubes (CNTs) production from catalytic pyrolysis of waste plastics: The influence of catalyst and reaction pressure, *Catalysis Today* 351 (2020) 50-57. <https://doi.org/10.1016/j.cattod.2019.01.058>.
- [56] E. Oh, J. Lee, S.H. Jung, S. Cho, H.J. Kim, S.H. Lee, K.H. Lee, K.H. Song, C.H. Choi, D.S. Han, Turning refuse plastic into multi-walled carbon nanotube forest, *Science and Technology of Advanced Materials* 13(2) (2012) 025004. <https://doi.org/10.1088/1468-6996/13/2/025004>.
- [57] A. Hedayati, C. Barnett, G. Swan, A. Orback White, Chemical Recycling of Consumer-Grade Black Plastic into Electrically Conductive Carbon Nanotubes, *C* 5(2) (2019) 32. <https://doi.org/10.3390/c5020032>.
- [58] J. Sengupta, C. Jacob, Growth temperature dependence of partially Fe filled MWCNT using chemical vapor deposition, *Journal of Crystal Growth* 311(23-24) (2009) 4692-4697. <https://doi.org/10.1016/j.jcrysgro.2009.09.029>.
- [59] F.F. Roman, J.L. Diaz de Tuesta, F.K.K. Sanches, A.S. Silva, P. Marin, B.F. Machado, P. Serp, M. Pedrosa, A.M.T. Silva, J.L. Faria, H.T. Gomes, Selective denitrification of simulated oily wastewater by oxidation using Janus-structured carbon nanotubes, *Catalysis Today* (2023) 114001. <https://doi.org/10.1016/j.cattod.2023.01.008>.
- [60] H. Li, N. Zhao, C. He, C. Shi, X. Du, J. Li, Thermogravimetric analysis and TEM characterization of the oxidation and defect sites of carbon nanotubes synthesized by CVD of methane, *Materials Science and Engineering: A* 473(1-2) (2008) 355-359. <https://doi.org/10.1016/j.msea.2007.04.003>.
- [61] V. Tucureanu, A. Matei, A.M. Avram, FTIR Spectroscopy for Carbon Family Study, *Critical Reviews in Analytical Chemistry* 46(6) (2016) 502-20. <https://doi.org/10.1080/10408347.2016.1157013>.
- [62] B. Scheibe, E. Borowiak-Palen, R.J. Kalenczuk, Oxidation and reduction of multiwalled carbon nanotubes — preparation and characterization, *Materials Characterization* 61(2) (2010) 185-191. <https://doi.org/10.1016/j.matchar.2009.11.008>.
- [63] C. Herrera, L. Barrientos, A. Rosenkranz, C. Sepulveda, J.L. García-Fierro, M.A. Laguna-Bercero, N. Escalona, Tuning amphiphilic properties of Ni/Carbon nanotubes functionalized catalysts and their effect as emulsion stabilizer for biomass-derived furfural upgrading, *Fuel* 276 (2020) 118032. <https://doi.org/10.1016/j.fuel.2020.118032>.
- [64] N. Briggs, A.K.Y. Raman, L. Barrett, C. Brown, B. Li, D. Leavitt, C.P. Aichele, S. Crossley, Stable pickering emulsions using multi-walled carbon nanotubes of varying wettability, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 537 (2018) 227-235. <https://doi.org/10.1016/j.colsurfa.2017.10.010>.
- [65] J. Zhou, P. Yang, P.A. Kots, M. Cohen, Y. Chen, C.M. Quinn, M.D. de Mello, J. Anibal Boscoboinik, W.J. Shaw, S. Caratzoulas, W. Zheng, D.G. Vlachos, Tuning the reactivity of carbon surfaces with oxygen-containing functional groups, *Nature Communications* 14(1) (2023) 2293. <https://doi.org/10.1038/s41467-023-37962-3>.

CHAPTER 5. REMOVAL OF QUINOLINE USING FE-BASED CARBON NANOTUBES

Chapter 5

Removal of Quinoline using Fe-based carbon nanotubes

This chapter explores the utilization of carbon nanotubes (CNTs), synthesized over the iron-based catalysts reported in Chapter 4, in the removal of quinoline. The chapter begins by examining the catalytic activity of CNTs in quinoline degradation by catalytic wet peroxide oxidation (CWPO). Building upon the positive experimental results observed in CWPO reactions, the catalysts are then applied for the oxidative denitrogenation (ODN) of quinoline, resulting in the proposal of a detailed reaction mechanism for the ODN of quinoline using CNT-based catalysts. To further substantiate the proposed mechanism, a mathematical model is developed, simulating the kinetics of the ODN process in the presence of CNT catalysts.

This chapter is constructed based on two peer-reviewed articles:

- Fernanda F. Roman, Larissa de G. Piccinin, Adriano S. Silva, Jose L. Diaz de Tuesta, Isabella V. K. Freitas, Admilson Vieira, Giane G. Lenzi, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Carbon Nanomaterials from Polyolefin Waste: Effective Catalysts for Quinoline Degradation through Catalytic Wet Peroxide Oxidation. *Catalysts* 13 (2023) 1259. <https://doi.org/10.3390/catal13091259>
- Fernanda F. Roman, Larissa de G. Piccinin, Adriano S. Silva, Jose L. Diaz de Tuesta, Admilson Vieira, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Oxidative denitrogenation of fuel contaminants using polyolefin-derived carbon nanotubes as versatile catalysts. *Journal of Environmental Chemical Engineering* 13(1) (2025) 115128. <https://doi.org/10.1016/j.jece.2024.115128>

5.1 Catalytic Wet Peroxide Oxidation of Quinoline

The results for the CWPO of QN are shown in Figure 5.1. The initial concentration of QN (100 mg L^{-1}) was chosen due to its limited solubility in aqueous phase. As seen, the degradation of QN in the presence of the CNTs synthesized in this work is very fast, resulting in over 90% of QN abatement in 30–60 min of reaction, depending on the CNTs tested (Figure 5.1a). In comparison, the non-catalytic run (N.C.) required over 240 min for a similar result, and the commercial CNT sample (CNT-C) required around 120 min. In fact, in less than 30 min of reaction, most of the CNTs synthesized in this work resulted in over 80% of QN abatement, except for LDPE-600-P@Fe, with 50% degradation. In the same timeframe, the N.C. run resulted in less than 1% removal and the commercial CNT sample (CNT-C) in about 60% abatement, indicating that the CNTs synthesized in this work are more active than the commercial sample.

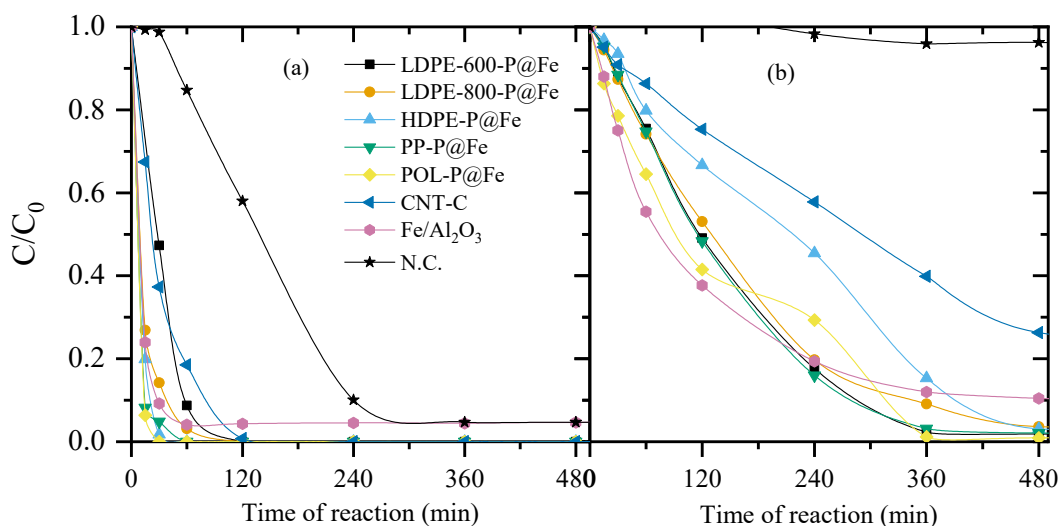


Figure 5.1. Normalized concentration of (a) QN and (b) H_2O_2 during CWPO runs in the presence of the catalysts. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ \text{C}$, and $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$.

The catalyst for CVD ($\text{Fe}/\text{Al}_2\text{O}_3$) also resulted in a fast abatement of QN; however, it could not completely oxidize the pollutant, ending the reaction with around 5% of the initial concentration of QN still present. There seems to be a synergistic effect for CNTs bearing metallic phases compared to pure $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and this enhanced effect when carbon layers are present has been previously reported for the CWPO of a range of pollutants [1-3]. The synergistic effect between metal phases and carbon layers results from the contribution of both parts to the electron transfer due to their electron-donor ability [3].

For the N.C. run, detecting three oxidized compounds in HPLC was also possible (detected in each oxidation experiment at the retention times of 1.86, 2.15, and 3.89 min, for compounds #1, #2, and #3, respectively, at the analytical conditions used for QN analysis), although they were not identified (Figure 5.2). All those compounds show a maximum concentration between 120 and 360 min, meaning that the reaction intermediates are also oxidized. Two intermediates (#1 and #3) persisted until the end of the experiment, whereas intermediate #2 was fully degraded in 6 h of reaction. Literature reports that a

series of reaction products can arise from QN oxidation via AOPs. The reaction products seem to depend on the radical, with sites with higher electron density being mainly attacked by the electrophilic $\text{HO}^\bullet$ [4]; thus, in this system, QN is expected to be initially attacked in the benzene ring, leading to 8-hydroxyquinoline [4, 5] further being oxidized into other intermediates still containing the aromatic ring [4, 6]. By the end of the reaction, low-molecular-weight carboxylic acids, such as oxalic, acetic, and formic acids [6, 7], as well as propionic and fumaric acids [7], are mostly identified and can be further mineralized. In catalyzed reactions, no intermediates were detected, probably due to their fast formation and subsequent degradation, leading to, most likely, low-molecular-weight carboxylic acids, water, and carbon dioxide.

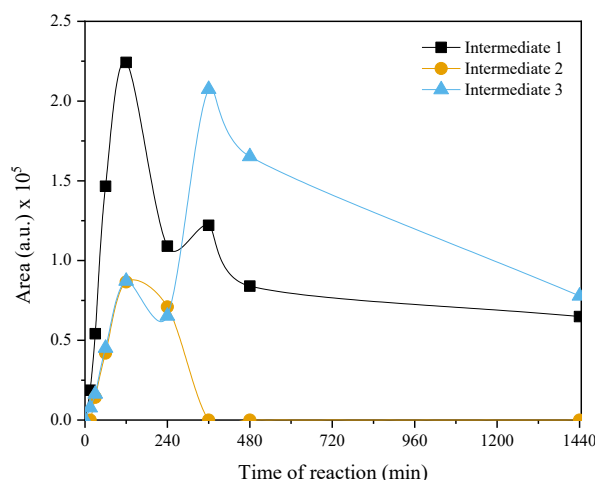


Figure 5.2. Formation and degradation of intermediate compounds detected by HPLC during the non-catalytic wet peroxide oxidation of QN. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$, $T = 80^\circ\text{C}$.

The behavior toward H_2O_2 consumption varied significantly among the CNTs (Figure 5.1b). The activity towards H_2O_2 decomposition follows the order $\text{Fe}/\text{Al}_2\text{O}_3 > \text{POL-P@Fe} > \text{PP-P@Fe} \sim \text{LDPE-600-P@Fe} \sim \text{LDPE-800-P@Fe} > \text{HDPE-P@Fe} > \text{CNT-C}$ (data from 1 h of reaction), and complete decomposition of the oxidant was observed in 2–8 h, depending on the catalyst, except for CNT-C and the CVD substrate ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$). In the same timeframe, N.C. resulted in less than 10% decomposition of H_2O_2 . The distinct behavior in the decomposition of H_2O_2 vs. abatement of QN can be explained by the fact that the chosen H_2O_2 concentration surpasses the stoichiometric concentration needed for QN mineralization; thus, not all oxidant needs to be consumed to ensure QN degradation. Furthermore, we can observe that the fastest consumption of H_2O_2 was obtained in the presence of $\text{Fe}/\text{Al}_2\text{O}_3$, indicating that the metallic particles may influence the rate of H_2O_2 decomposition. Nevertheless, the rate of decomposition of the oxidant is not the only factor needed for ensuring pollutant degradation, and often, the presence of carbon results in a synergistic effect [8]: in fact, in this work, most CNT particles allowed complete H_2O_2 decomposition in 360–480 min of reaction, whereas $\text{Fe}/\text{Al}_2\text{O}_3$ required over 8 h of reaction for 100% H_2O_2 decomposition.

The TOC abatement after 24 h of reaction is seen in Figure 5.3. As observed, the mineralization of QN ranged between 19% for N.C. to 75% in the presence of POL-P@Fe , followed closely by LDPE-800-

P@Fe (73%). The other catalysts resulted in abatements in the range of 33–63%, with LDPE-600-P@Fe and CNT-C being highlighted for their low removals.

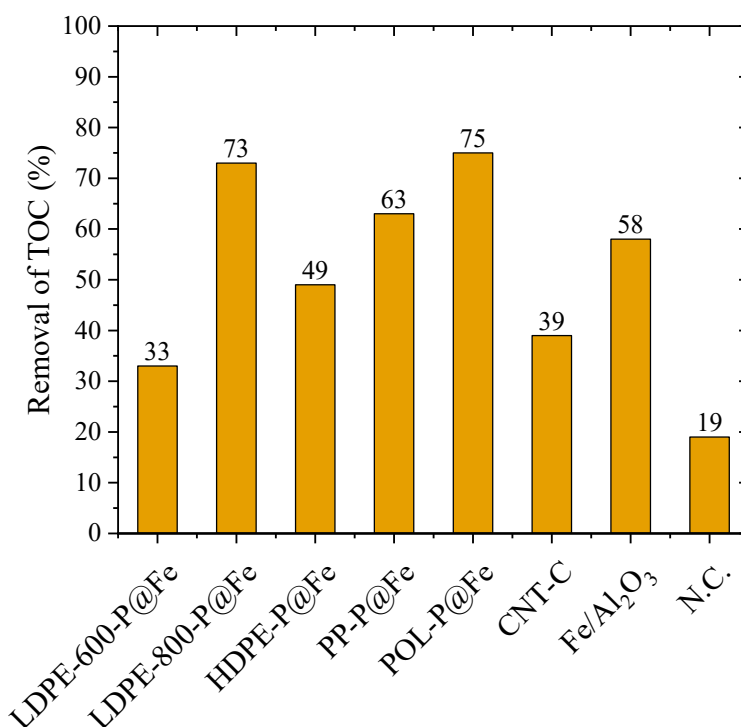


Figure 5.3. Removal of TOC after 24 h of reaction in the presence of the catalysts. Conditions: $\text{pH}_0 = 3.0$, $[\text{QN}]_0 = 100 \text{ mg L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ \text{C}$, and $[\text{H}_2\text{O}_2]_0 = 6.2 \text{ g L}^{-1}$.

The pH at the end of the reaction (Figure 5.4a) was below the initial pH for all runs except for the run conducted in the presence of LDPE-600-P@Fe and with Fe/Al₂O₃. Compared to the initial value, the pH reduction may be ascribed to the formation of low-molecular-weight carboxylic acids not detected via HPLC. This conclusion is also reinforced when analyzing the concentration of other aromatic compounds (ARMs) in the reaction medium by the end of the reaction: over 70% of the ARMs were removed in the presence of CNTs (Figure 5.4b), whereas in the presence of Fe/Al₂O₃, the removal of the ARMs was slightly above 50%. The iron leaching was very low (<0.05 wt.%, regardless of the catalyst). It is worthwhile to highlight that most of the materials synthesized in this work have displayed suitable activities toward the degradation of QN, indicating the feasibility of using polymers as feedstock for producing active CNTs. Not one material can be immediately emphasized as the best-performing one. Nevertheless, POL-P@Fe can be highlighted as a promising material due to its precursor (a mixture of polyolefins, more closely resembling real PSW) and good performance.

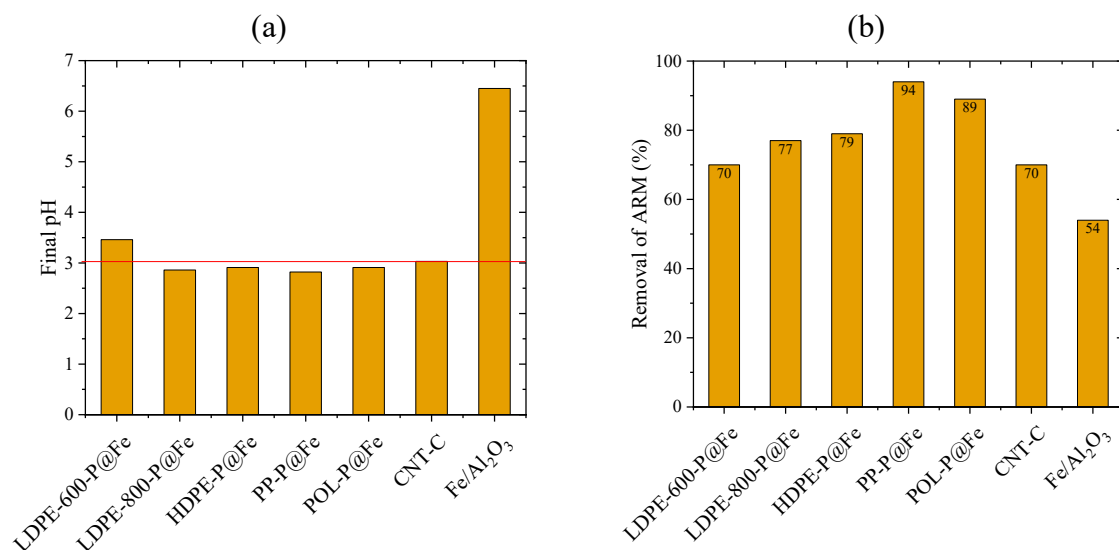


Figure 5.4. (a) pH after CWPO in the presence of the catalysts (Red line indicates initial pH); and (b) abatement of ARM after CWPO in the presence of the catalysts. Conditions: $pH_0 = 3.0$, $[QN]_0 = 100 \text{ mg L}^{-1}$, $[H_2O_2]_0 = 6.2 \text{ g L}^{-1}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$.

The results reported here for QN degradation in an aqueous medium are similar to those reported in the literature for catalytic ozonation [6, 9, 10], photolysis [5], and Fenton-like systems [11].

5.2 Selective biphasic oxidation: an oxidative denitrogenation (ODN) case study

5.2.1 Extraction and adsorption as blank runs

The extraction of QN from 2,2,4-trimethylpentane, considering ultrapure water at a pH of 3.0 as the extractant phase and different initial QN concentrations (250-1000 mg L^{-1}), is depicted in Figure 5.5a. As observed, the extraction effect is more relevant for lower initial concentrations regardless of the contact time. For an initial concentration of 250 mg L^{-1} , up to 25% of QN is removed purely by extraction in 8 h. In contrast, when increasing the concentration to 500 mg L^{-1} , the effect reduces to 16%. For concentrations over 750 mg L^{-1} , only 7% of QN is removed by pure extraction in 8 h under the studied conditions. It is also possible to observe that the removal of QN reaches a maximum at around 30 min of contact time, slightly decreasing after up to 8 h, as it reaches an equilibrium. The extractions were not carried out for longer than 8 h, as we did not aim to establish the equilibrium between the phases. Rather, we wanted data to compare with the results obtained on oxidation reactions. Similarly, the removal of QN by pure adsorption after 8 h of contact time, given in Figure 5.5b (solid filling), ranges between 1-11%, with the highest removal obtained in the presence of HDPE-P@Fe and Fe/Al₂O₃ (11% for both). No other reports were found regarding the adsorption of QN by CNTs. Typical values for the adsorption of other N-compounds by CNTs under similar conditions have been reported, such as 14-25% [12] and 7-13% [13] for 4-nitrophenol and 2-nitrophenol, respectively, and 11-30% [14] for paracetamol. The combined effects of both techniques, *i.e.*, simultaneous extraction and adsorption,

were also evaluated, and the obtained results are shown in Figure 5.5b (patterned filling). It is possible to observe a slight increment in the removal of QN: in all cases, the removal exceeds 10%; however, neither approach is suitable to remove QN from the fuel, especially for higher concentrations ($>750 \text{ mg L}^{-1}$). For comparison purposes, the pure extraction effect after 8 h of contact time for an initial concentration of QN of 1000 mg L^{-1} is also given in Figure 5.5b.

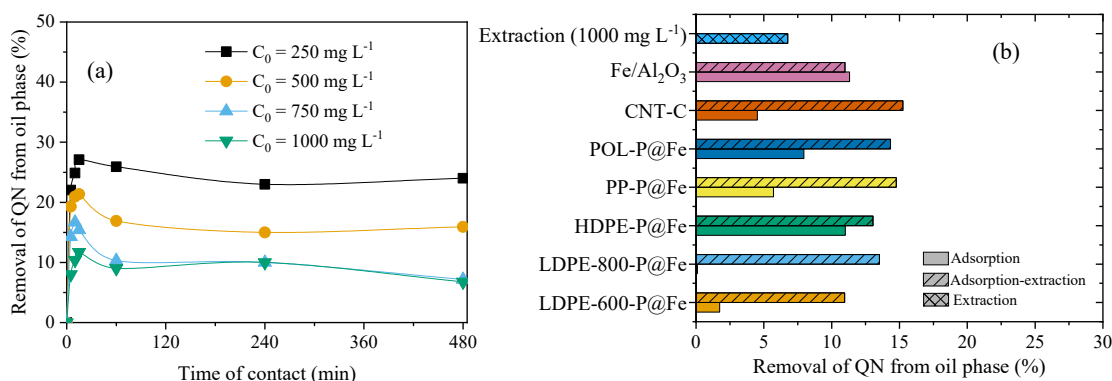


Figure 5.5. QN removed from oil phase (a) by pure extraction effect (without catalysts), considering varying initial concentrations of QN; and (b) by pure adsorption (solid filling) and combined adsorption-extraction (patterned filling) in the presence of CNTs and CVD substrate after 8 h of contact time (Conditions: $[\text{QN}]_0 = 250\text{--}1000 \text{ mg L}^{-1}$, O/W volume ratio = 80:20 (where applicable), $\text{pH}_0 = 3.0$, $T = 80^\circ\text{C}$; and for adsorption runs: $[\text{QN}]_0 = 1000 \text{ mg L}^{-1}$, $C_{\text{adsorbent}} = 2.5 \text{ g L}^{-1}$).

5.2.2 Oxidative denitrogenation (ODN) of QN

The results related to the removal of QN at an initial concentration of 1000 mg L^{-1} (in the oil phase) under a biphasic system are reported in Figure 5.6. For the biphasic reactions, a higher initial concentration of QN was chosen to reduce the effect of the liquid-liquid extraction (as reported in Figure 5.5a) and better observe the catalytic activity of the materials. The non-catalytic run (N.C.) did not result in significant removal of QN from the fuel, with around 11% removal in 24 h, similar to the values observed in pure extraction experiments (Figure 5.5a). On the other hand, all CNTs displayed high catalytic activity towards the removal of QN by ODN; complete removals from the fuel are obtained in 60 - 240 min of reaction, depending on the catalyst, at the selected operating conditions. In the presence of POL-P@Fe and LDPE-600-P@Fe, complete removal of QN was observed in only 60 min of reaction, followed closely by HDPE-P@Fe and PP-P@Fe (*ca.* 90% in 60 min, and complete removal in less than 4 h), and by Fe/ Al_2O_3 , CNT-C and LDPE-800-P@Fe. Interestingly, it is possible to observe that for all reactions, the reported values start at around 7% of removal (at time $t = 0 \text{ min}$). The addition of the extractant phase took place before the addition of the CNTs; thus, this initial removal is solely due to the extraction effect, and the values agree with those reported earlier for the pure extraction effect for an initial concentration of 1000 mg L^{-1} (Figure 5.5a). The results reported here (37-100% of QN removal in 60 min of reaction) for the removal of QN from a simulated fuel are similar to other reports in the literature (Table 5.1) [12, 13, 15-19], with QN removals being reported in the range between 30-100%, obtained in 30-60 min of reaction. Nevertheless, it should be emphasized that the present work has reported a lower catalyst and hydrogen peroxide concentration than the remaining works dealing with

QN. Furthermore, the use of polyolefin-derived CNTs is advantageous from an environmental point of view.

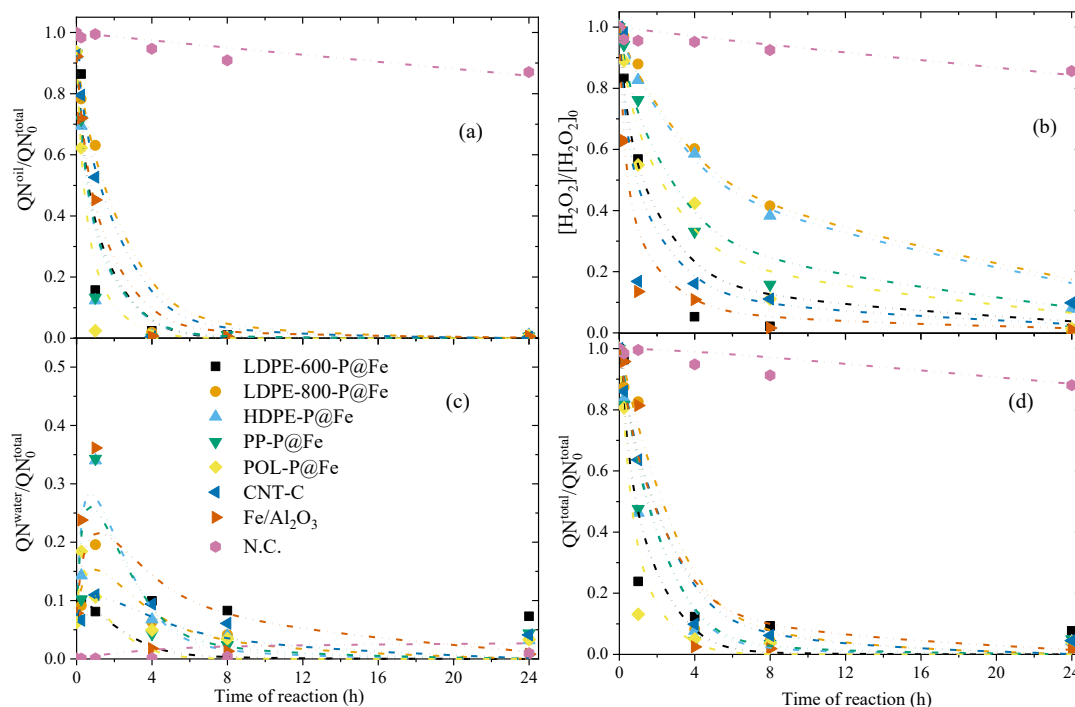


Figure 5.6. (a) Normalized number of mols of QN in the oily phase, (b) normalized concentration of H_2O_2 during ODN, (c) normalized number of mols of QN in the water phase, and (d) normalized conversion of total amount of QN during ODN in the presence of the catalysts tested in this work. Conditions: O/W volume ratio = 80:20, $\text{pH}_0 = 3.0$, $[\text{QN}]_{\text{oil}}^0 = 1000 \text{ mg L}^{-1}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $T = 80^\circ \text{C}$, $[\text{H}_2\text{O}_2]_0 = 247 \text{ g L}^{-1}$. Dashed lines are from the kinetic model described in section 5.2.3.

Table 5.1. Reported biphasic selective oxidation reactions using water as extractant, H_2O_2 as oxidant source, and carbon nanotubes as catalysts.

Target molecule	Carbon source	Catalyst	Conditions	Results	Ref.
QN	Ethylene and acetonitrile	N-doped CNT grown over a red mud-based catalyst	$[\text{QN}]_0 = 278 \text{ ppm}$ ($[\text{N}]_0 = 30 \text{ ppm}$) in cyclohexane; $T = 25^\circ \text{C}$, $\text{pH} = \text{natural pH}$ of H_2O_2 , $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $O/W = 5:1$, $[\text{H}_2\text{O}_2] = 300 \text{ g L}^{-1}$.	80% removal in 45 min of reaction	[16]
QN	Ethanol	CNT grown over a FeMo catalyst	$[\text{QN}]_0 = 4630 \text{ ppm}$ ($[\text{N}]_0 = 500 \text{ ppm}$) in cyclohexane; $T = 25^\circ \text{C}$, $\text{pH} = \text{natural pH}$ of H_2O_2 , $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $O/W = 5:1$, $[\text{H}_2\text{O}_2] = 300 \text{ g L}^{-1}$.	100% oxidation in 30 min of reaction	[17]
QN	Ethanol	Carbon deposits over a red mud-based catalyst	$[\text{QN}]_0 = 500 \text{ ppm}$ in cyclohexane; $T = 25^\circ \text{C}$, $\text{pH} = \text{natural pH}$ of H_2O_2 , $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $O/W = 5:1$, $[\text{H}_2\text{O}_2] = 300 \text{ g L}^{-1}$.	100% oxidation in 60 min of reaction.	[15]
QN	Ethylene and acetonitrile	Fe^{+2} + Janus-structured CNTs grown over $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$	$[\text{QN}]_0 = 500 \text{ ppm}$ in cyclohexane, 5.6 mmol L^{-1} of Fe^{+2} + 1 wt.% of CNTs, $O/W = 5:1.3$, $[\text{H}_2\text{O}_2] = 90 \text{ g L}^{-1}$; 300 μL of formic acid	30-100% removal in 40 min of reaction	[20]
4-nitrophenol	Ethylene and acetonitrile	Janus-structured CNTs grown over AlCoFeO_4	$[\text{4-NP}]_0 = 1000 \text{ ppm}$ in 2,2,4-trimethylpentane; $T = 80^\circ \text{C}$, $\text{pH} = 3.5$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $O/W = 1:9$, $[\text{H}_2\text{O}_2] = 3.6 \text{ g L}^{-1}$.	50-100% removal in 4 h of reaction	[12]
2-nitrophenol	Ethylene and acetonitrile	Janus-structured CNTs grown over $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$	$[\text{2-NP}]_0 = 5000 \text{ ppm}$ in cyclohexane; $T = 50^\circ \text{C}$, $\text{pH} = 3.0$, $C_{\text{cat}} = 2.27 \text{ g L}^{-1}$, $O/W = 50:16$, $[\text{H}_2\text{O}_2] = 18 \text{ g L}^{-1}$.	20-80% in 24 h of reaction	[13]
QN	Methane	CNTs grown over $\text{FeMo}/\text{Al}_2\text{O}_3$	$[\text{N}]_0 = 500 \text{ ppm}$ in cyclohexane; $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $O/W = 5:1$, $[\text{H}_2\text{O}_2] = 300 \text{ g L}^{-1}$.	100% in 30 min of reaction	[19]

QN	Polyolefins	CNTs grown over a Fe/Al ₂ O ₃	[QN] ₀ = 1000 ppm ([N] ₀ = 108 ppm) in 2,2,4-trimethylpentane; <i>T</i> = 80 °C, pH = 3.0, <i>C_{cat}</i> = 2.5 g L ⁻¹ , <i>O/W</i> = 80:20, [H ₂ O ₂] = 247 g L ⁻¹ .	100% of removal of QN in 60 min of reaction	This work
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The decomposition of the oxidant during ODN is shown in Figure 5.6b. As can be observed, Fe/Al₂O₃ and CNT-C resulted in very fast decomposition of the oxidant, especially in the first 1 h of reaction, achieving over 80% of oxidant consumption. The fast decomposition of hydrogen peroxide allied to the poor ability to adsorb QN in the presence of these materials indicates that there is likely recombination of hydroxyl radicals into non-active species [3], hindering the abatement of QN. On the other hand, the materials LDPE-600-P@Fe, POL-P@Fe, PP-P@Fe and HDPE-P@Fe all resulted in around 10% consumption of the oxidant in 1 h of reaction, which is a sufficient amount of oxidant for QN degradation. The controlled decomposition of H₂O₂ allows for more efficient oxidant usage, translating into higher QN removal. Notably, an active catalyst, which is also capable of consuming only the required H₂O₂, is crucial for peroxide oxidation systems since H₂O₂ can be the highest operational cost of the process [21]. As far as we are aware, no other works report the consumption of oxidant sources during ODN reactions; however, we believe it is crucial to understand better and design the ODN reaction.

QN in the water phase was followed by HPLC, and the results are given in Figure 5.6c. In the presence of HDPE-P@Fe, PP-P@Fe, LDPE-800-P@Fe and Fe/Al₂O₃, QN accumulates in the water phase, reaching a maximum at 1 h of reaction, followed by a fast decrease in the next 2 h. In the presence of POL-P@Fe, QN reaches its maximum in the water phase at a shorter reaction time (15 min). For the remaining materials (LDPE-600-P@Fe and CNT-C), not much accumulation of QN is observed. By the end of the reaction, QN is still present in the water phase in most cases, accounting for 1-12% of QN initially loaded in the system.

The normalized concentration of QN, accounting for QN present both in the oil and water phases, is displayed in Figure 5.6d and follows a similar pattern to that observed for the removal of QN from the oil phase. LDPE-600-P@Fe and POL-P@Fe both resulted in the fastest total conversion of QN, reaching more than 80% of conversion in just 1 h of reaction. PP-P@Fe and HDPE-P@Fe both resulted in over 50% of QN degradation in 1 h of reaction, followed by CNT-C (35% in 1 h), Fe/Al₂O₃ and LDPE-800-P@Fe (15% in 1 h). The N.C. run resulted in less than 1% of QN degradation. In general, for catalyzed reactions, more than 90% of QN initially loaded was completely degraded in just 2 h of reaction.

The TOC conversion is shown in Figure 5.7. As can be observed, most of the materials synthesized in this work display a similar TOC conversion (24-26%). The CVD-catalyst performs slightly worse (16%), followed by the CNT-C sample (11%). The N.C. run did not allow any significant removal (<1%), similar to the removals observed for QN itself. The results reported here for TOC conversion are lower than the removals reported for aqueous-phase QN oxidation [6, 11, 22]. No other works report

the TOC conversion for ODN reactions. The TOC removal results are within the range observed for the TOC removal of similar reactions under biphasic systems using 4-nitrophenol as model compound [12].

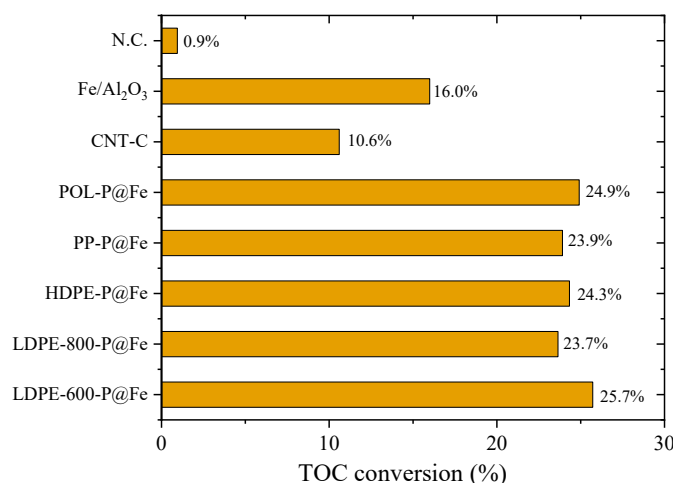
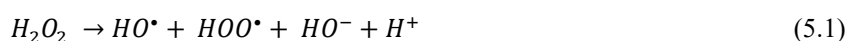


Figure 5.7. TOC conversion in the presence of the materials tested in this work. (O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$, 24 h of reaction).

Considering the interesting results reported with POL-P@Fe and the fact that it is a material obtained from a polymer mixture representative of real mixed PSW, POL-P@Fe was chosen for further testing.

5.2.3 Kinetic modeling and mechanism

The consumption of hydrogen peroxide was modeled according to other works in the literature reporting catalytic wet peroxide oxidation using carbon-based materials [23, 24]. The concentration of the catalyst (W_{cat}) was assumed to remain constant, and it was omitted from the equations. Hydrogen peroxide was assumed to decompose into hydroxyl and hydroperoxyl radicals when it comes in contact with the catalyst surface, according to Equation (5.1).



The hydrogen peroxide disappearance rate ($-\frac{dn_{H_2O_2}}{dt}$) can be modeled according to Equation (5.2), as it is expected that all hydrogen peroxide remains within the aqueous fraction.

$$-\frac{dn_{H_2O_2}}{dt} = k'_{H_2O_2} \cdot n_{H_2O_2}^2 \quad (5.2)$$

in which $k'_{H_2O_2}$ is the rate constant for H_2O_2 (in $\text{mol}^{-1} \text{ h}^{-1}$) and $n_{H_2O_2}$ is the number of mols of H_2O_2 .

The disappearance of QN from the oil phase ($-\frac{dn_{QN,oil}}{dt}$) is mainly ascribed to mass transfer due to the difference in the concentration of QN in the oil and water phases. This mass transfer depends on: (i) the interfacial area between the phases ($A_{interface}$), which was assumed to be constant and equal for all reactions, and (ii) in a driving force. This driving force can be defined as the difference between the amount of QN in the oil phase ($n_{QN,oil}$) and the concentration of QN in the oil phase when the equilibrium

has been reached ($n_{QN,oil,eq}$). Thus, its rate of disappearance from the oil phase was modeled according to Equation (5.3) and (5.4):

$$-\frac{dn_{QN,oil}}{dt} = k'_{QN,mt} \cdot (n_{QN,oil} - n_{QN,oil,eq}) \quad (5.3)$$

$$k'_{QN,mt} = A_{interfacial} \cdot k_{QN,mt} \quad (5.4)$$

in which $k_{QN,mt}$ is the rate constant for the disappearance of QN from the oil phase (in $m^{-2} h^{-1}$). The concentration of QN in the oil phase when the equilibrium has been reached depends on the partition coefficient of QN in the system (POW), and thus, Equation (5.3) can be rewritten as Equation (5.5).

$$-\frac{dn_{QN,oil}}{dt} = k'_{QN,mt} \cdot (n_{QN,oil} - POW \cdot n_{QN,aqueous}) \quad (5.5)$$

in which $n_{QN,aqueous}$ is the number of mols of QN in the aqueous phase. The value considered for POW (0.18) was chosen based on previous studies that reported values of QN partition coefficients for 2,2,4-trimethylpentane-water systems with varying pH [25].

Then, the presence of QN in the aqueous phase ($\frac{dn_{QN,aqueous}}{dt}$) was modeled considering the inflow of QN from the oil phase (which is equal to Equation (5.5)) and the oxidation of QN in the aqueous phase. The oxidation of QN in the aqueous phase was modeled following reports regarding the aqueous phase oxidation reaction of other micropollutants [24]. Thus, the overall rate of disappearance of QN from the aqueous phase can be described by Equation (5.6).

$$\frac{dn_{QN,aqueous}}{dt} = k'_{QN,mt} \cdot (n_{QN,oil} - POW \cdot n_{QN,aqueous}) - k'_{QN,ox} \cdot n_{QN,aqueous} \cdot n_{H_2O_2} \quad (5.6)$$

in which $k'_{QN,ox}$ is the rate constant for the oxidation of QN in the aqueous phase (in $mol^{-1} h^{-1}$). Equations (5.1), (5.5) and (5.6) were fitted to the experimental data, resulting in the kinetics and statistical parameters shown in Table 5.2. All models adjusted well to the data, as shown by the high coefficient of correlation ($R^2 > 0.94$) and parity plot (Figure 5.8). The model can also accurately reproduce the experimental data, as shown in Figure 5.6a-d.

Table 5.2. Kinetic and statistical coefficients obtained from the fit of the kinetic model during ODN.

Coefficient	LDPE-600-P@Fe	LDPE-800-P@Fe	HDPE-P@Fe	PP-P@Fe	POL-P@Fe	CNT-C	Fe/Al ₂ O ₃	N.C.
$k'_{H_2O_2}$ ($mol^{-1} h^{-1}$)	7.23	1.33	1.57	3.04	3.97	10.18	18.58	0.05
$k'_{QN,mt}$ (h^{-1})	1.21	0.55	1.44	1.39	2.08	0.63	1.03	0.01
$k'_{QN,ox}$ ($mol^{-1} h^{-1}$)	66.54	14.22	12.71	14.43	47.46	45.39	33.08	1.40
POW				0.18				
SSE_{model}	0.103	0.057	0.055	0.067	0.050	0.138	0.066	0.007
R^2	0.958	0.980	0.977	0.974	0.977	0.942	0.967	0.999

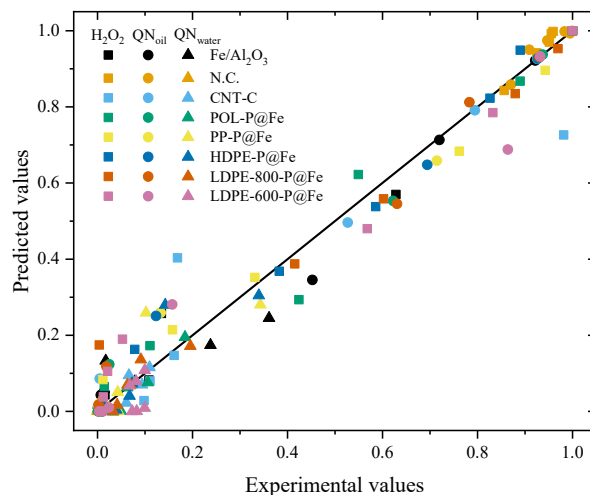
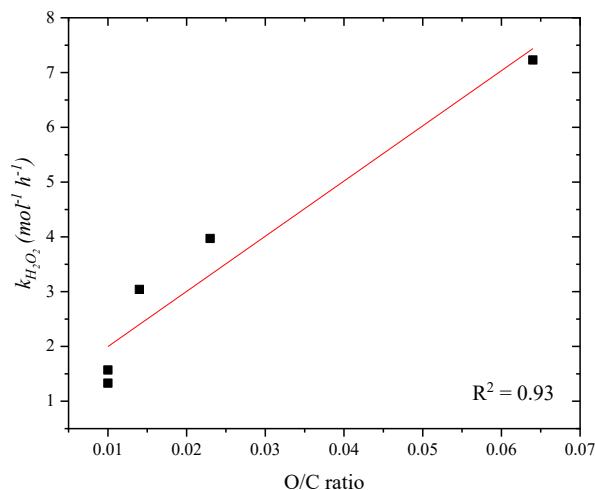


Figure 5.8. Parity plot.

The highest kinetic coefficient for the decomposition of hydrogen peroxide was found for Fe/Al₂O₃, followed by CNT-C, LDPE-600@Fe, POL-P@Fe, PP-P@Fe, HDPE-P@Fe and LDPE-800@Fe. The coefficient for the decomposition of hydrogen peroxide ($k'_{H_2O_2}$) was found to positively correlate with the O/C ratio for polyolefin-derived CNTs (Figure 5.9), indicating that the presence of oxygenated groups accelerates the decomposition of H₂O₂. The kinetic constant for QN oxidation follows a different order, with LDPE-600@Fe (66.54 mol⁻¹ h⁻¹), POL-P@Fe (47.46 mol⁻¹ h⁻¹) and CNT-C (45.39 mol⁻¹ h⁻¹) displaying significantly higher coefficients compared to the remaining CNTs (<14 mol⁻¹ h⁻¹). In all cases, $k'_{QN,ox}$ was higher than $k'_{QN,mt}$, indicating that the mass transfer of QN from the oil phase to the aqueous phase is the limiting step. It should be noted that the materials allowed an increase in $k'_{QN,mt}$ (> 0.55 h⁻¹) compared to the non-catalytic run ($k'_{QN,mt}$ = 0.01 h⁻¹), indicating that their presence facilitates the mass transfer of QN and they indeed act as phase transfer catalysts and are crucial for ODN purposes. The highest $k'_{QN,mt}$ was found for POL-P@Fe, explaining its more suitable behavior for the process compared to the other samples synthesized at 800 °C. No clear correlation between the materials' characteristics and their ability to act as phase transfer catalysts was found, so this behavior can be attributed to a combination of different characteristics (such as contact angle and oxygenated groups).

Figure 5.9. Correlation between O/C ratio and $k'_{H_2O_2}$

Given the results obtained and the adjusted kinetic model, we propose an expected reaction mechanism, shown in Figure 5.10.

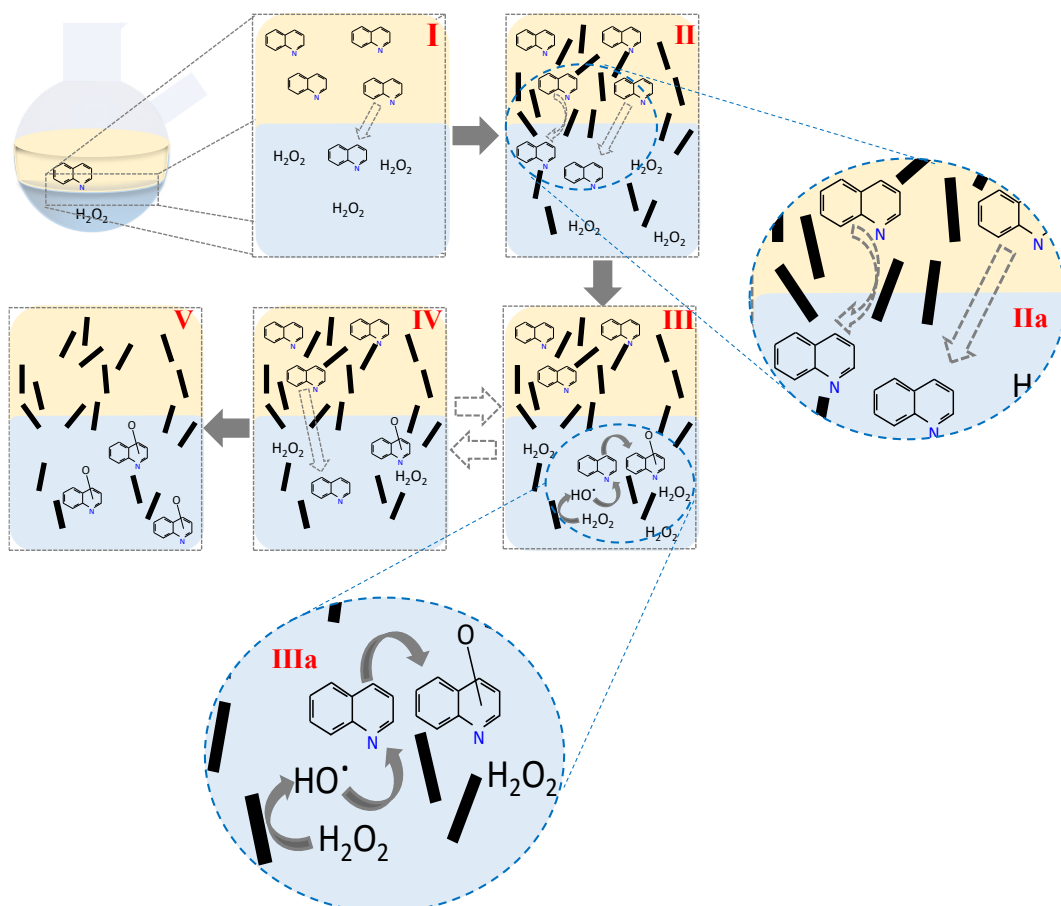


Figure 5.10. Schematics of the proposed route for ODN.

QN is a molecule with a partition coefficient ($\log P$) that is highly affected by the pH of the aqueous phase [25], as pH affects the dissociation of QN. At pHs lower than its pK_a (approximately 4.9), more QN is expected to migrate to the water phase [25], and its solubility in water increases [26]. Under the conditions studied in this work, we expect that QN initially migrates to the water phase (as observed in extraction experiments and represented in Figure 5.10, **I**), especially since the reactions were carried out under an acidic pH. The addition of the CNTs (Figure 5.10, **II**) can further enhance the mass transfer of QN to the water phase (Figure 5.10, **IIa**), given that the CNTs can act as phase transfer catalysts, as shown by the increased $k'_{QN,mt}$ ($> 0.55 \text{ h}^{-1}$) in comparison to the non-catalytic run ($k'_{QN,mt} = 0.01 \text{ h}^{-1}$). The CNTs are also responsible for yielding hydroxyl radicals (Figure 5.10, **IIIa**), leading to the oxidation of QN (Figure 5.10, **III** and **IIIa**); we expect that QN both in water and at the interface between phases to be oxidized, although the QN present in the aqueous phase is the most likely to be oxidized. Given that the mass transfer of QN was found to be the limiting step, more effective materials, such as POL-P@Fe, should address this issue. The degradation of QN in the water phase disrupts the equilibrium of QN between the oil and aqueous phase, resulting in more QN migrating towards the water phase (Figure 5.10, **IV**). This extraction-oxidation-extraction cycle (Figure 5.10, **III** $\leftrightarrow$ **IV**) will continue until all QN

is removed from the oil phase (Figure 5.10, V). Since the products formed are more hydrophilic, they are expected to remain in the water phase (Figure 5.10, V). It is also important to note that oxidized intermediates can be further degraded into other oxidized compounds until reaching refractory compounds (such as low-molecular-weight carboxylic acids [27]) and ultimately full mineralization products (CO_2 and H_2O). It should be noted that the selectivity towards degradation of QN or intermediates depends on several factors, especially on the materials' adsorptive interactions with each intermediate.

5.2.4 ODN of PYR and QN with sample POL-P@Fe

POL-P@Fe was tested as a catalyst in the ODN of PYR or QN (as individual compounds) and benchmarked against CNT-C. The concentration of PYR was chosen in order to maintain an equivalent N concentration as those used for QN ($[\text{N}]_0 = 108 \text{ mg L}^{-1}$). The results are reported in Figure 5.11. The removal of PYR was superior in the presence of the CNT prepared from a mix of polyolefins (POL-P@Fe) compared to CNT-C. In 1 h of reaction, nearly 87% of PYR was removed from the fuel phase in the presence of POL-P@Fe compared to 69% for CNT-C. Comparing with the QN abatement, QN removal achieved 98% and 47% with POL-P@Fe and CNT-C under the same timeframe, respectively. The higher activity of POL-P@Fe compared to the commercial CNT sample for the selective oxidation of PYR may be ascribed to its ability to act as a phase transfer catalyst (Table 5.2). As previously performed for QN removal, pure extraction by water and adsorption of PYR on the catalyst were studied under the same operating conditions. In the case of PYR, pure extraction accounts for a high proportion of PYR (nearly 50%, Figure 5.11). The higher extraction effect for PYR is related to its lower logP compared to QN (0.65 for PYR [28] and 2.03 for QN [29] at neutral pH). Pure adsorption accounts for 3.2% and 2.8% with POL-P@Fe and CNT-C, respectively. Combined adsorption and extraction represent 30% and 45% of removal in 1 h with CNT-C and POL-P@Fe, respectively, which may indicate some resistance to mass transfer, mainly in the presence of the CNT-C. In the case of ODN of a mixed fuel ($\text{ODN}_{\text{mixed}}$ in Figure 5.11) containing simultaneously QN and PYR, 87% and 86%, respectively, are removed from the fuel phase with POL-P@Fe. The catalytic activity for the ODN of QN seems to decrease slightly in the presence of PYR. In contrast, PYR removal is unaffected, possibly due to the higher contribution of extraction for PYR. Nevertheless, the overall removal of N from the fuel remains high (87%), indicating that the material is versatile for removing N-compounds.

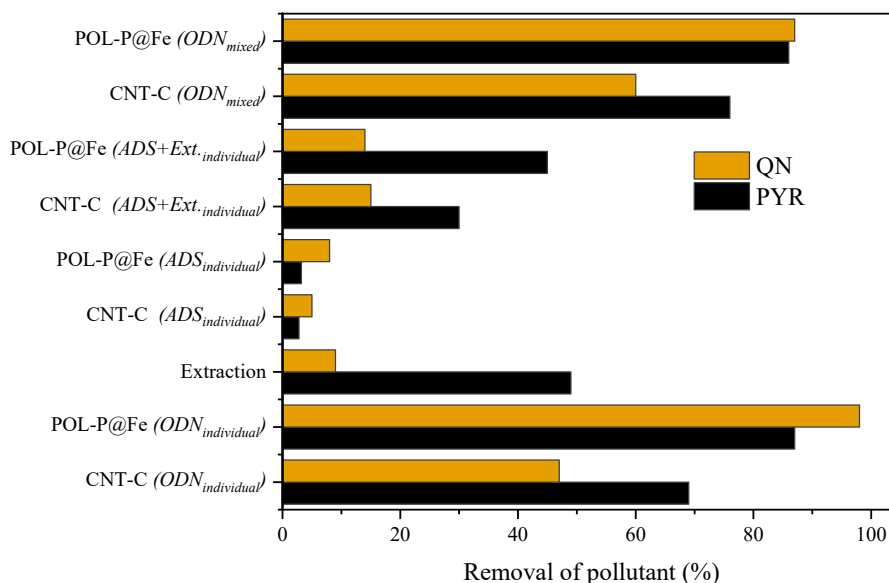


Figure 5.11. Removal of QN or PYR from the oily phase during ODN in the presence of CNT-C and POL-P@Fe after 60 min of reaction considering the components individually ($ODN_{individual}$) and in a mixture (ODN_{mixed}). (O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$ or $[PYR]^{oil}_0 = 610 \text{ mg L}^{-1}$ (in runs with mixed fuel: $[QN]^{oil}_0 = 500 \text{ mg L}^{-1}$ and $[PYR]^{oil}_0 = 305 \text{ mg L}^{-1}$), $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$, 1 h).

5.2.5 Catalyst reuse

The results obtained for the reutilization runs of POL-P@Fe are reported in Figure 5.12.

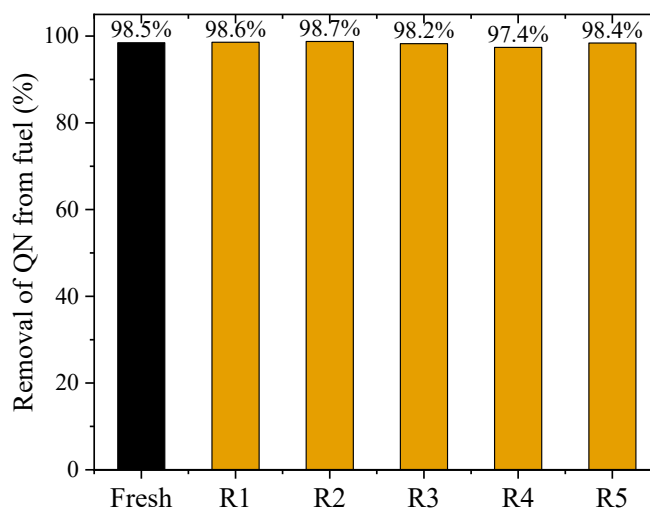


Figure 5.12. Removal of QN from the fuel phase in the presence of POL-P@Fe after 60 min of reaction for fresh catalyst and reutilization runs. Conditions: O/W volume ratio = 80:20, $pH_0 = 3.0$, $[QN]^{oil}_0 = 1000 \text{ mg L}^{-1}$ (equivalent to $[N]^{oil}_0 = 108 \text{ mg L}^{-1}$), $C_{cat} = 2.5 \text{ g L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $[H_2O_2]_0 = 247 \text{ g L}^{-1}$.

As can be observed, no obvious loss of catalytic activity was observed for the 6 cycles reported here, maintaining an average removal of QN from the fuel of 98% in just 1 h of reaction, indicating that the catalyst is highly stable for the proposed system. Metal leaching was assessed during experiments by atomic absorption, and negligible metal leaching from the catalyst into aqueous media was observed ($<0.05 \text{ wt.}\%$ of POL-P@Fe). Similarly, carbon loss was assessed by measuring the TOC for pure hydrogen peroxide decomposition for reactions carried out under aqueous-phase only (following similar

ODN conditions: $T = 80\text{ }^{\circ}\text{C}$, $\text{pH} = 3.0$, $[\text{H}_2\text{O}_2] = 247\text{ g L}^{-1}$ and $C_{\text{cat}} = 2.5\text{ g L}^{-1}$, and no carbon was measured in the aqueous phase ($<0.5\text{ mg}_\text{C}\text{ L}^{-1}$).

5.3 Conclusions

All samples were active in the abatement of QN via CWPO, resulting in complete QN degradation in 30 min under the best scenario and 120 min under the worst scenario. Up to 75% of mineralization was observed, with the remaining TOC content being likely ascribed to the formation of low-molecular-weight carboxylic acids, corroborated by the reduction in the pH of the effluent and the high removals of other aromatic compounds.

The CNTs were applied for the oxidation of QN considering 2,2,4-trimethylpentane-water to simulate the selective ODN of liquid fuels. The complete removal of QN after 60-240 min was achieved, depending on the CNT catalyst, at the operating conditions of $80\text{ }^{\circ}\text{C}$, pH of the aqueous phase of 3.0, $C_{\text{cat}} = 2.5\text{ g L}^{-1}$, O/W volume ratio of 80:20 and $[\text{H}_2\text{O}_2]_0 = 247\text{ g L}^{-1}$. The catalytic activity shown by the materials synthesized in the ODN of QN far surpassed that of the commercial CNT sample. Additionally, the removal of QN by ODN was compared to the removal obtained by water extraction and adsorption with the materials at the same operating conditions, evidencing that QN removals obtained are mainly due to oxidation. In fact, kinetic modeling indicated that the mass transference from the oil to the aqueous phase is the limiting step in the reaction, and higher removals in the catalyzed runs were ascribed to the ability of the CNTs to act as phase transfer catalysts. For the ODN of QN, over 98% of the initial content was completely removed for a simulated fuel in 1 h of reaction, and this activity was maintained for up to 5 additional cycles in the presence of the catalyst prepared from a mixture of 35:25:40 of LDPE:HDPE:PP (POL-P@Fe). POL-P@Fe could also remove significant amounts of PYR from 2,2,4-trimethylpentane in just 1 h of reaction and PYR and QN when they were simultaneously present. The results reported here suggest that polyolefins are suitable precursors for the synthesis of highly active CNTs for oxidation purposes.

5.4 References

- [1] R.S. Ribeiro, Z. Frontistis, D. Mantzavinos, D. Venieri, M. Antonopoulou, I. Konstantinou, A.M.T. Silva, J.L. Faria, H.T. Gomes, Magnetic carbon xerogels for the catalytic wet peroxide oxidation of sulfamethoxazole in environmentally relevant water matrices, *Applied Catalysis B: Environmental* 199 (2016) 170-186. <https://doi.org/10.1016/j.apcatb.2016.06.021>.
- [2] R. Zhu, Y. Zhu, H. Xian, L. Yan, H. Fu, G. Zhu, Y. Xi, J. Zhu, H. He, CNTs/ferrihydrite as a highly efficient heterogeneous Fenton catalyst for the degradation of bisphenol A: The important role of CNTs in accelerating Fe(III)/Fe(II) cycling, *Applied Catalysis B: Environmental* 270 (2020) 118891. <https://doi.org/10.1016/j.apcatb.2020.118891>.
- [3] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review, *Applied Catalysis B: Environmental* 187 (2016) 428-460. <https://doi.org/10.1016/j.apcatb.2016.01.033>.
- [4] S. Wang, L. Zhou, M. Zheng, J. Han, R. Liu, J. Yun, Catalytic Ozonation over $\text{Ca}_2\text{Fe}_2\text{O}_5$ for the Degradation of Quinoline in an Aqueous Solution, *Industrial & Engineering Chemistry Research* 61(19) (2022) 6343-6353. <https://doi.org/10.1021/acs.iecr.2c00464>.
- [5] W.B. Zhang, T.C. An, X.M. Xiao, J.M. Fu, G.Y. Sheng, M.C. Cui, Photochemical degradation performance of quinoline aqueous solution in the presence of hydrogen peroxide, *Journal of Environmental Science and Health, Part A. Toxic/hazardous substances and environmental engineering* 38(11) (2003) 2599-611. <https://doi.org/10.1081/ese-120024442>.
- [6] D. Liu, C. Wang, Y. Song, Y. Wei, L. He, B. Lan, X. He, J. Wang, Effective mineralization of quinoline and bio-treated coking wastewater by catalytic ozonation using $\text{CuFe}_{(2)}\text{O}_{(4)}$ /Sepiolite catalyst: Efficiency and mechanism, *Chemosphere* 227 (2019) 647-656. <https://doi.org/10.1016/j.chemosphere.2019.04.040>.
- [7] X. Ma, L. Bian, J. Ding, Y. Wu, H. Xia, J. Li, Electrochemical oxidation of quinoline aqueous solution on beta- PbO_2 anode and the evolution of phytotoxicity on duckweed, *Water Science & Technology* 75(7-8) (2017) 1820-1829. <https://doi.org/10.2166/wst.2017.053>.
- [8] R.S. Ribeiro, J. Gallo, M. Bañobre-López, A.M.T. Silva, J.L. Faria, H.T. Gomes, Enhanced performance of cobalt ferrite encapsulated in graphitic shell by means of AC magnetically activated catalytic wet peroxide oxidation of 4-nitrophenol, *Chemical Engineering Journal* 376 (2019) 120012. <https://doi.org/10.1016/j.cej.2018.09.173>.
- [9] X. Huang, X.M. Wang, Toxicity change patterns and its mechanism during the degradation of nitrogen-heterocyclic compounds by O_3 /UV, *Chemosphere* 69(5) (2007) 747-54. <https://doi.org/10.1016/j.chemosphere.2007.05.014>.
- [10] Q. Wei, S. Qiao, B. Sun, H. Zou, J. Chen, L. Shao, Study on the treatment of simulated coking wastewater by O_3 and O_3 /Fenton processes in a rotating packed bed, *RSC Advances* 5(113) (2015) 93386-93393. <https://doi.org/10.1039/c5ra14198b>.
- [11] L. Chu, J. Wang, J. Dong, H. Liu, X. Sun, Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide, *Chemosphere* 86(4) (2012) 409-14. <https://doi.org/10.1016/j.chemosphere.2011.09.007>.
- [12] F.F. Roman, J.L. Diaz de Tuesta, F.K.K. Sanches, A.S. Silva, P. Marin, B.F. Machado, P. Serp, M. Pedrosa, A.M.T. Silva, J.L. Faria, H.T. Gomes, Selective denitrification of simulated oily wastewater by oxidation using Janus-structured carbon nanotubes, *Catalysis Today* (2023) 114001. <https://doi.org/10.1016/j.cattod.2023.01.008>.
- [13] J.L. Diaz de Tuesta, B. F. Machado, P. Serp, A.M. T. Silva, J.L. Faria, H. T. Gomes, Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide, *Catalysis Today* 356 (2020) 205-215. <https://doi.org/10.1016/j.cattod.2019.07.012>.
- [14] J.L. Diaz de Tuesta, A.S. Silva, F.F. Roman, L.F. Sanches, F.A. da Silva, A.I. Pereira, A.M.T. Silva, J.L. Faria, H.T. Gomes, Polyolefin-derived carbon nanotubes as magnetic catalysts for wet peroxide oxidation of paracetamol in aqueous solutions, *Catalysis Today* 419 (2023) 114162. <https://doi.org/10.1016/j.cattod.2023.114162>.
- [15] A.A.S. Oliveira, I.F. Teixeira, T. Christofani, J.C. Tristão, I.R. Guimarães, F.C.C. Moura, Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue, *Applied Catalysis B: Environmental* 144 (2014) 144-151. <https://doi.org/10.1016/j.apcatb.2013.07.015>.

- [16] A.A.S. Oliveira, A.R. Martins, R.V. Ferreira, I.T. Cunha, P. Serp, J.P. de Mesquita, F.C.C. Moura, N-doped carbon nanotubes grown on red mud residue: Hybrid nanocomposites for technological applications, *Catalysis Today* 344 (2020) 247-258. <https://doi.org/10.1016/j.cattod.2019.04.060>.
- [17] R.V. Mambrini, C.Z. Maia, J.D. Ardisson, P.P. de Souza, F.C.C. Moura, Fe/C and FeMo/C hybrid materials for the biphasic oxidation of fuel contaminants, *New Journal of Chemistry* 41(1) (2017) 142-150. <https://doi.org/10.1039/c6nj02718k>.
- [18] I.R. Guimarães, A.S. Giroto, W.F. de Souza, M.C. Guerreiro, Highly reactive magnetite covered with islands of carbon: Oxidation of N and S-containing compounds in a biphasic system, *Applied Catalysis A: General* 450 (2013) 106-113. <https://doi.org/10.1016/j.apcata.2012.10.017>.
- [19] I.F. Teixeira, A.A.d.S. Oliveira, T. Christofani, F.C.C. Moura, Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process, *Journal of Materials Chemistry A* 1(35) (2013) 10203-10208. <https://doi.org/10.1039/c3ta11535f>.
- [20] A.D. Purceno, B.F. Machado, A.P. Teixeira, T.V. Medeiros, A. Benyounes, J. Beausoleil, H.C. Menezes, Z.L. Cardeal, R.M. Lago, P. Serp, Magnetic amphiphilic hybrid carbon nanotubes containing N-doped and undoped sections: powerful tensioactive nanostructures, *Nanoscale* 7(1) (2015) 294-300. <https://doi.org/10.1039/c4nr04005h>.
- [21] J.L. Diaz de Tuesta, A. Quintanilla, D. Moreno, V.R. Ferro, J.A. Casas, Simulation and Optimization of the CWPO Process by Combination of Aspen Plus and 6-Factor Doehlert Matrix: Towards Autothermal Operation, *Catalysts* 10(5) (2020) 548. <https://doi.org/10.3390/catal10050548>.
- [22] F.F. Roman, L. De Grande Piccinin, A. Santos Silva, J.L. Diaz de Tuesta, I.V.K. Freitas, A. Vieira, G. Gonçalves Lenzi, A.M.T. Silva, J.L. Faria, H.T. Gomes, Carbon nanomaterials from polyolefin waste: effective catalysts for quinoline degradation through catalytic wet peroxide oxidation, *Catalysts* 13(9) (2023) 1259. <https://doi.org/10.3390/catal13091259>.
- [23] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez, P-, B- and N-doped carbon black for the catalytic wet peroxide oxidation of phenol: Activity, stability and kinetic studies, *Catalysis Communications* 102 (2017) 131-135. <https://doi.org/10.1016/j.catcom.2017.09.012>.
- [24] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez, Kinetic modeling of wet peroxide oxidation with a carbon black catalyst, *Applied Catalysis B: Environmental* 209 (2017) 701-710. <https://doi.org/10.1016/j.apcatb.2017.03.031>.
- [25] S.H. Standal, A.M. Blokhus, J. Haavik, A. Skauge, T. Barth, Partition Coefficients and Interfacial Activity for Polar Components in Oil/Water Model Systems, *Journal of Colloid and Interface Science* 212(1) (1999) 33-41. <https://doi.org/10.1006/jcis.1998.5988>.
- [26] M.T. Carvajal, S. Yalkowsky, Effect of pH and Ionic Strength on the Solubility of Quinoline: Back-to-Basics, *AAPS PharmSciTech* 20(3) (2019) 124. <https://doi.org/10.1208/s12249-019-1336-9>.
- [27] M. Huber, M.J. Poller, J. Tochtermann, W. Korth, A. Jess, J. Albert, Revealing the nitrogen reaction pathway for the catalytic oxidative denitrification of fuels, *Chemical Communications* 59(27) (2023) 4079-4082. <https://doi.org/10.1039/d3cc00648d>.
- [28] National Center for Biotechnology Information, PubChem Annotation Record for PYRIDINE, Source: Hazardous Substances Data Bank (HSDB), 2023. Available at <https://pubchem.ncbi.nlm.nih.gov/source/hsdb/118>. (Accessed November 28th, 2023).
- [29] National Center for Biotechnology Information, PubChem Annotation Record for QUINOLINE, Source: Hazardous Substances Data Bank (HSDB), 2023. Available at <https://pubchem.ncbi.nlm.nih.gov/source/hsdb/121>. (Accessed November 28th, 2023).

CHAPTER 6 – OXIDATIVE DENITROGENATION USING NiFe-BASED CARBON NANOTUBES

Chapter 6

Oxidative denitrogenation using NiFe-based carbon nanotubes

This chapter focuses on the application of carbon nanotubes (CNTs) derived from a mixture of polyolefins synthesized over the nickel-iron catalysts (reported in Chapter 4) for the oxidative denitrogenation (ODN) of quinoline. The initial selection of the catalyst follows the same reaction conditions used in Chapter 5. Then, the influence of key operating parameters, including catalyst concentration, hydrogen peroxide dosage, and reaction temperature, on quinoline degradation, total organic carbon (TOC) abatement, and hydrogen peroxide utilization were systematically evaluated. The kinetic model developed in Chapter 5 for the ODN of QN is also adjusted to the data generated in this chapter, allowing to estimate the activation energy required for the degradation of QN and the consumption of hydrogen peroxide. Comparative analysis with literature benchmarks is conducted to contextualize the performance of the synthesized CNT catalysts (both from Chapters 5 and 6) relative to previously reported materials.

6.1 Screening of materials

The initial screening of the NiFe-derived CNTs are displayed in Figure 6.1. The conditions employed for screening were similar to those used in Chapter 5. As it can be seen, the removal of QN (>50% in 2 h of reaction) was more pronounced for the CNTs if compared to the non-catalytic run (N.C.) and with NiFe/Al₂O₃ (*ca.* 10% in 2 h of reaction for both) (Figure 6.1a). For all CNTs, a removal of over 90% was achieved in 4 h of reaction. Similarly, all CNTs resulted in a higher decomposition of hydrogen peroxide (>20% in 2 h of reaction) compared to the N.C. run (*ca.* 5% in 2 h of reaction) (Figure 6.1b).

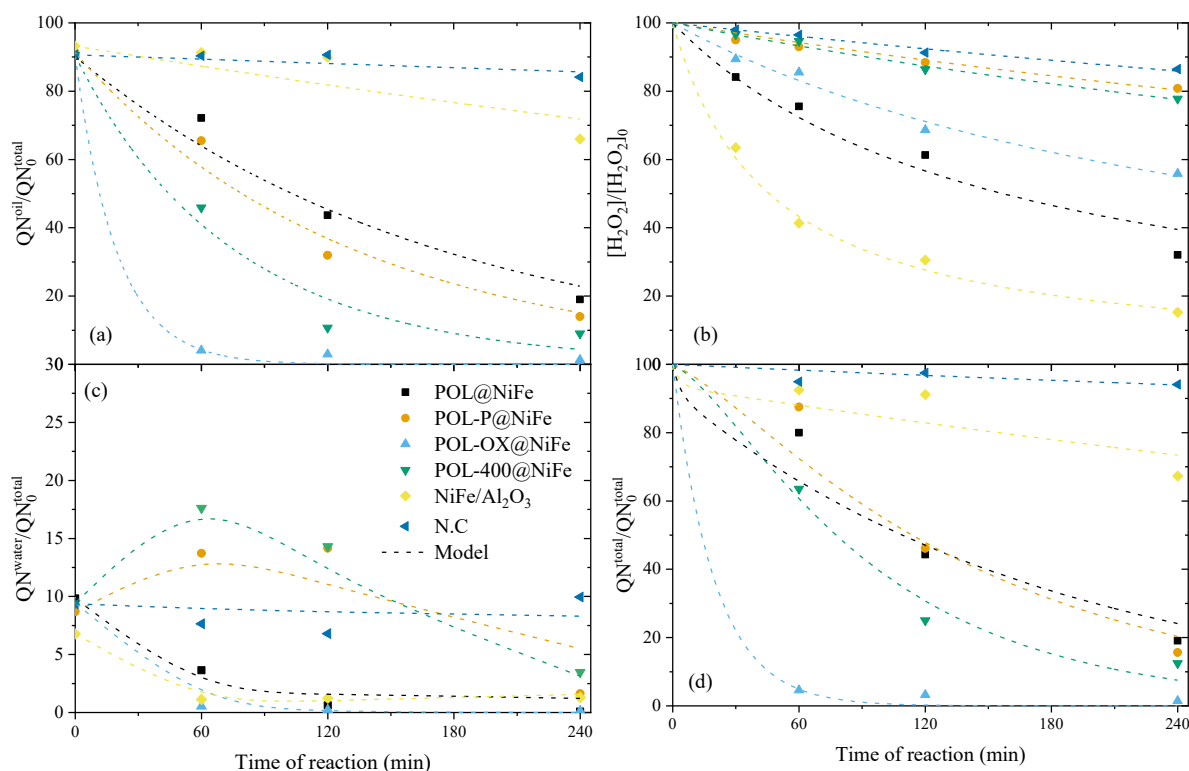


Figure 6.1. Screening of materials. (a) Removal of QN from the fuel phase, (b) decomposition of hydrogen peroxide in the aqueous phase, (c) QN in the water phase, and (d) overall QN abatement. (Conditions: $[Q_N]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 123 \text{ g L}^{-1}$ (H_2O_2/N molar ratio = 230), O/W volume ratio = 80:20, $T = 80^\circ \text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0). Dashed lines represent the kinetic model described in section 5.2.3.

Among the catalysts tested, POL-OX@NiFe resulted in the fastest removal of QN from the oil phase (*ca.* 95%), followed by POL-400@NiFe (54%), POL@NiFe (24%), POL-P@NiFe (13%) and NiFe/Al₂O₃ (10%) in 1 h of reaction (Figure 6.1a). The results here are within the same range as those reported in Chapter 5: a QN removal of 37-100% in 60 min of reaction for Fe-based catalysts, although some of the Fe-based catalysts resulted in a slightly higher activity (100% removal in 1 h) likely due to the catalytic effect promoted by the iron particles within the CNT. The NiFe-based CNTs display a lower content of iron compared to the Fe-based CNTs (Table 4.2, Chapter 4). A different reactivity for the H₂O₂ decomposition was observed in the order NiFe/Al₂O₃ (87%) > POL@NiFe (35%) > POL-OX@NiFe (25%) > POL-400@NiFe (14%) > POL-P@NiFe (9%) in 1 h of reaction. The difference observed between H₂O₂ decomposition, and QN removal is because the starting concentration of H₂O₂

greatly surpasses the stoichiometric concentration needed for QN mineralization; thus, not all H_2O_2 needs to be decomposed to ensure proper QN removal. Another important consideration is that the decomposition of the oxidant source is not the sole factor affecting an oxidation process. It is well established that the adsorptive interaction between the material and the pollutant is a crucial factor in allowing proper utilization of the generated hydroxyl radicals in oxidation reactions [1]. As can be seen in Figure 6.2, POL-OX@NiFe displays a much higher adsorption capacity (*ca.* 28%) for QN (in 2,2,4-trimethylpentane) compared to all remaining materials (5-9%). The higher adsorption capacity allied to a more controlled H_2O_2 decomposition (Figure 6.1b) is likely the reason behind its much higher activity towards the process. Another important aspect of reactions conducted under the biphasic system is related to the capacity of the material to interact with both oil and aqueous phases, acting as a phase-transfer catalyst. The results depicted here have shown that the CVD-catalyst has a very outstanding ability towards the decomposition of hydrogen peroxide. On the other hand, it behaves poorly in the removal of QN from the fuel phase. This low ability to remove QN (despite its high catalytic activity for H_2O_2 consumption) can be ascribed to its more hydrophilic behavior (Table 4.1, Chapter 4) compared to the CNTs (Table 4.4, Chapter 4), leaving it mostly located in the aqueous phase, and to its higher content of Fe moieties, which is a known promotor of Fenton-like reactions.

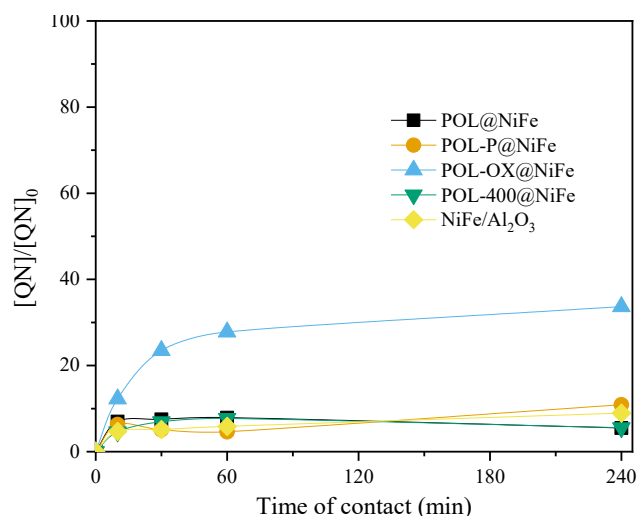


Figure 6.2. Adsorption capacity. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $T = 80^\circ \text{C}$, $C_{\text{adsorbent}} = 2.5 \text{ g L}^{-1}$. Solid lines are only intended to guide the eyes.

The concentration of QN in the water phase was also followed, and the results are depicted in Figure 6.1c. In the presence of POL-OX@NiFe, QN is initially extracted from the oil phase and degraded in the water phase, not leading to any accumulation. The two materials with lower H_2O_2 decomposition ability (POL-P@NiFe and POL-400@NiFe) both result in an accumulation of QN in the water phase in the first 1 h of the reaction, followed by its oxidation in the next 3 h of reaction. Nevertheless, neither allows complete QN conversion by the end of the 4 h of reaction. The N.C. run results in a slight decomposition of QN in the first 1 h of reaction, followed by an increased concentration of QN in the water phase up to the end of the reaction due purely to an extraction effect. The total abatement of QN,

accounting for QN from both the oil and water phases, is shown in Figure 6.1d. The profile is similar to the one observed for removing QN from the oil phase.

TOC conversion is displayed in Figure 6.3, and it remains in the range of 16–31%, with POL-OX@NiFe also resulting in a higher TOC removal compared to the remaining materials. The efficiency of hydrogen peroxide consumption ($\eta_{H_2O_2}^{ODN}$) was calculated according to Equation (3.11), Chapter 3. A higher rate of hydrogen peroxide decomposition (as seen for NiFe/Al₂O₃ and POL@NiFe) resulted in lower efficiencies (4% and 5.5%, respectively). In contrast, the materials with a more controlled decomposition resulted in higher efficiencies (16%, 14%, and 17% for POL-P@NiFe, POL-OX@NiFe, and POL-400@NiFe, respectively). The N.C. resulted in a *ca.* 4% efficiency. However, the efficiencies are very low, which is expected given that the hydrogen peroxide concentration selected for catalyst screening was quite high (ten times the needed concentration for QN mineralization, leading to an H_2O_2/N molar ratio of 230) to ensure QN degradation. POL-OX@NiFe was chosen to optimize the reaction conditions due to a higher activity towards the removal of QN via ODN in most parameters considered (removal and abatement of QN, TOC removal, and efficiency of hydrogen peroxide consumption).

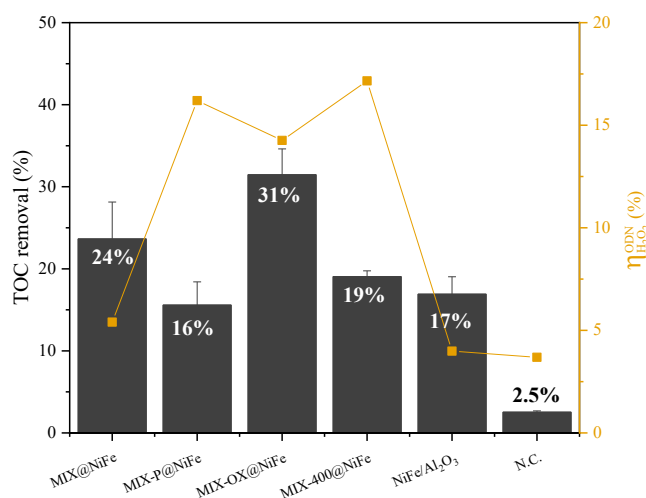


Figure 6.3. TOC removal and efficiency of hydrogen peroxide consumption. (Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 123 \text{ g L}^{-1}$ (H_2O_2/N molar ratio = 230), O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0).

6.1.1 Kinetic modeling

Equations (5.1), (5.5) and (5.6) described in section 5.2.3, Chapter 5, were fitted to the experimental data, resulting in the kinetic constants displayed in Table 6.1. The model fits the data well, as seen in the parity plot shown in Figure 6.4, and the high determination coefficient ($R^2 > 0.98$) and low residual errors ($SSE_{model} < 0.018$). The model is also able to accurately predict the experimental data, as seen in the dashed lines in Figure 6.1. The coefficients for the decomposition of hydrogen peroxide ($k'_{H_2O_2}$) followed the order $NiFe/Al_2O_3 > POL@NiFe > POL-OX@NiFe > POL-400@NiFe \sim POL-P@NiFe >$

N.C. For the mass transference ($k'_{QN,mt}$), it should be highlighted that all CNTs positively affected the mass transfer of QN from the oil to the water phase, as $k'_{QN,mt}$ was considerably higher for the CNTs (0.34-3.09 h⁻¹) compared to the non-catalytic run ($k'_{QN,mt} = 0.01$ h⁻¹). In contrast, the CVD-catalyst did not affect it significantly ($k'_{QN,mt} = 0.07$ h⁻¹). POL-OX@NiFe resulted in the highest $k'_{QN,mt}$ likely because it does not have a so marked lipophilic character compared to the remaining CNTs. POL-OX@NiFe also resulted in a considerably higher $k'_{QN,ox}$ compared to all remaining samples; and this is very much correlated with the content of basic groups ($R^2 = 0.94$, Figure 6.5b) and its oxygen content ($R^2 = 0.97$, Figure 6.5a). The $k'_{QN,ox}$ was considerably higher than $k'_{QN,mt}$ for all samples, indicating that mass transference is the rate-determining step.

The values reported here were lower compared to the Fe/Al₂O₃-derived CNTs reported in Chapter 5 for hydrogen peroxide decomposition ($k'_{H_2O_2}$ in the range 1.3-7.2 mol⁻¹ h⁻¹ for Fe-derived CNTs *versus* 0.9-2.8 mol⁻¹ h⁻¹ for NiFe-derived CNTs), but they were in the same range for the mass transference coefficient ($k'_{QN,mt}$ in the range 0.5-2.1 h⁻¹ for Fe-derived CNTs *versus* 0.3-3.1 h⁻¹ for NiFe-derived CNTs), with POL-OX@NiFe resulting in the highest value among all CNTs. The values for the QN oxidation ($k'_{QN,ox}$ in the range 28.8-435.8 mol⁻¹ h⁻¹) were significantly higher than those reported in Chapter 5 ($k'_{QN,ox}$ in the range 12.7-66.5 mol⁻¹ h⁻¹).

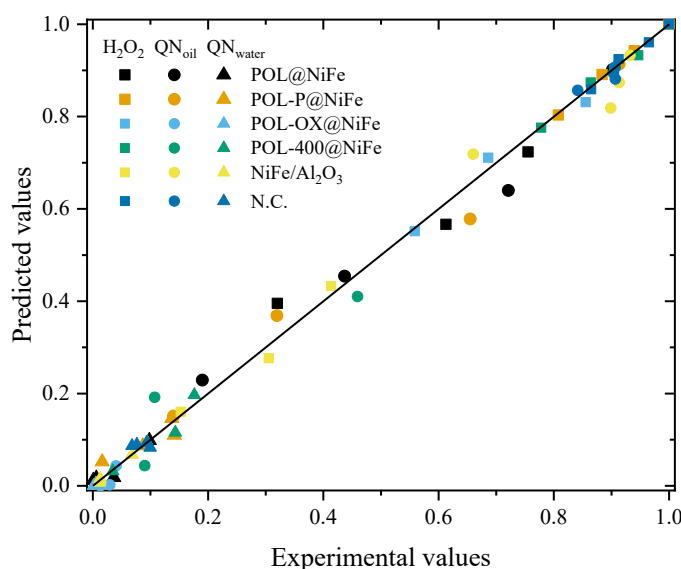


Figure 6.4. Parity plot

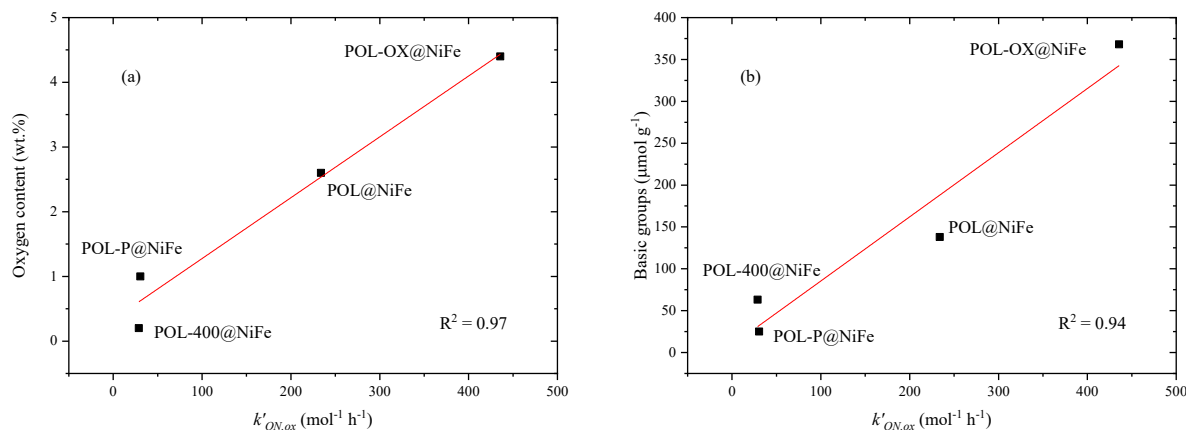


Figure 6.5. Correlation between $k'_{QN,ox}$ and (a) oxygen content and (b) basic groups.

Only one similar model that considers the consumption of hydrogen peroxide, mass transference and pollutant oxidation for a biphasic reaction was found [2], and the results obtained here for the apparent coefficient of hydrogen peroxide decomposition ($k'_{H_2O_2}$), pollutant mass transference ($k'_{QN,mt}$) and oxidation ($k'_{QN,ox}$) were superior to previously reported values for the selective biphasic oxidation of 2-nitrophenol using Janus-like CNTs (0-0.258 M⁻¹ h⁻¹ for H₂O₂, 0.63-1.68 M⁻¹ h⁻¹ for 2-nitrophenol oxidation and 0.008-0.054 M⁻¹ h⁻¹ for the mass transference of 2-nitrophenol) [2]. Other works have proposed different modeling approaches for the ODN of nitrogenated compounds [3-5], reporting pseudo-first-order rate constants for nitrogenated compounds in biphasic systems in the range of 1.9×10^{-3} to 8.8×10^{-2} min⁻¹ [3], 1.07×10^{-2} – 2.67×10^{-2} min⁻¹ [4], and 1.2×10^{-2} – 1.5×10^{-1} min⁻¹ [5], depending on the nitrogenated compound. Models based on the Eley-Rideal model were also proposed [6].

The kinetic coefficient determined for H₂O₂ was inferior to those reported for AOPs in water phase: 180-6000 M⁻¹ h⁻¹ for Fenton reaction for dyes decolorization [7], 24 M⁻¹ h⁻¹ for CWPO of paracetamol using carbon-coated cobalt ferrite [8] and 1.2-85 M⁻¹ h⁻¹ for CWPO of 4-nitrophenol using clays as catalysts [9]. However, the kinetic coefficient for the oxidation of QN was similar to other reported values for aqueous phase oxidation reactions: 420 M⁻¹ h⁻¹ for CWPO of PCM using carbon-coated cobalt ferrite [8] and 5-390 M⁻¹ h⁻¹ for CWPO of 4-nitrophenol using clays as catalysts [9].

Table 6.1. Kinetic and statistical coefficients obtained for each material during ODN.

Coefficient	POL@NiFe	POL-P@NiFe	POL-OX@NiFe	POL-400@NiFe	NiFe/Al ₂ O ₃	N.C.
$k'_{H_2O_2}$ (mol ⁻¹ h ⁻¹)	5.29	0.90	2.84	0.98	12.30	0.58
$k'_{QN,mt}$ (h ⁻¹)	0.34	0.47	3.09	0.83	0.07	0.01
$k'_{QN,ox}$ (mol ⁻¹ h ⁻¹)	233.94	30.54	435.79	28.80	166.56	2.64
<i>POW</i>			0.18			
<i>SSE_{model}</i>	0.018	0.011	0.002	0.013	0.013	0.002
<i>R²</i>	0.989	0.994	0.999	0.992	0.993	0.999

6.2 Optimization of reaction conditions

6.2.1 Effect of hydrogen peroxide concentration

One of the main factors affecting the reaction is the concentration of the oxidant source. It is also one of the main operational costs associated with oxidation-based processes [10]. Thus, the concentration of hydrogen peroxide was studied, ranging from 10 to $0.1\times$ the stoichiometric concentration needed for QN mineralization or from $[\text{H}_2\text{O}_2]_0 = 123$ to 1.2 g L^{-1} ($\text{H}_2\text{O}_2/\text{N}$ molar ratio 223 to 2.3). The results are shown in Figure 6.6. In most cases, QN removal from fuel surpassed 90% in 4 h of reaction, except when the run was carried out with the lowest concentration ($[\text{H}_2\text{O}_2]_0 = 1.2 \text{ g L}^{-1}$), where the maximum removal achieved was 60% at 4 h of reaction. There is an evident correlation between hydrogen peroxide concentration and QN removal. The higher the oxidant concentration, the faster quinoline is removed from the fuel. In 30 minutes of reaction, over 90% and 80% of QN had already been removed for initial concentrations of $[\text{H}_2\text{O}_2]_0 = 123$ and 62 g L^{-1} , respectively. A stoichiometric concentration for QN mineralization ($[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$) resulted in *ca.* 75% and 89% removal in 30 and 60 min of reaction, respectively. Initial concentration in the range of $0.25\text{--}0.5\times$ the stoichiometric amount ($[\text{H}_2\text{O}_2]_0 = 3\text{--}6 \text{ g L}^{-1}$) resulted in removals in the range of 40–55% in 30 min of reaction. For concentrations below $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, most of the oxidant source is converted ($>75\%$ in 4 h of reaction). Although higher hydrogen peroxide concentrations lead to faster QN removals, most of this hydrogen peroxide is not fully utilized (40% and 50% conversion for $[\text{H}_2\text{O}_2]_0 = 123$ and 62 g L^{-1} , respectively), as seen in Figure 6.6b.

The concentration of QN in the water phase can be seen in Figure 6.6c. As discussed in Chapter 5 (Figure 5.10), QN initially migrates to the water phase. All reactions resulted in its rapid degradation (up to 30 min). For concentrations higher than $[\text{H}_2\text{O}_2]_0 = 6 \text{ g L}^{-1}$, QN does not accumulate in the water phase; however, for lower H_2O_2 concentrations ($[\text{H}_2\text{O}_2]_0 = 3$ and 1.2 g L^{-1}), QN accumulates in the water phase, ending the reaction with 0.06 and $0.13 \mu\text{mol}$ of QN, respectively (corresponding to 7.5% and 16% of the initial concentration loaded). QN abatement (Figure 6.6d) also depends on the concentration of the oxidant, with lower concentration ($[\text{H}_2\text{O}_2]_0 = 1.2, 3$ and 6 g L^{-1}) resulting in incomplete conversion (50%, 85%, and 95% conversions, respectively).

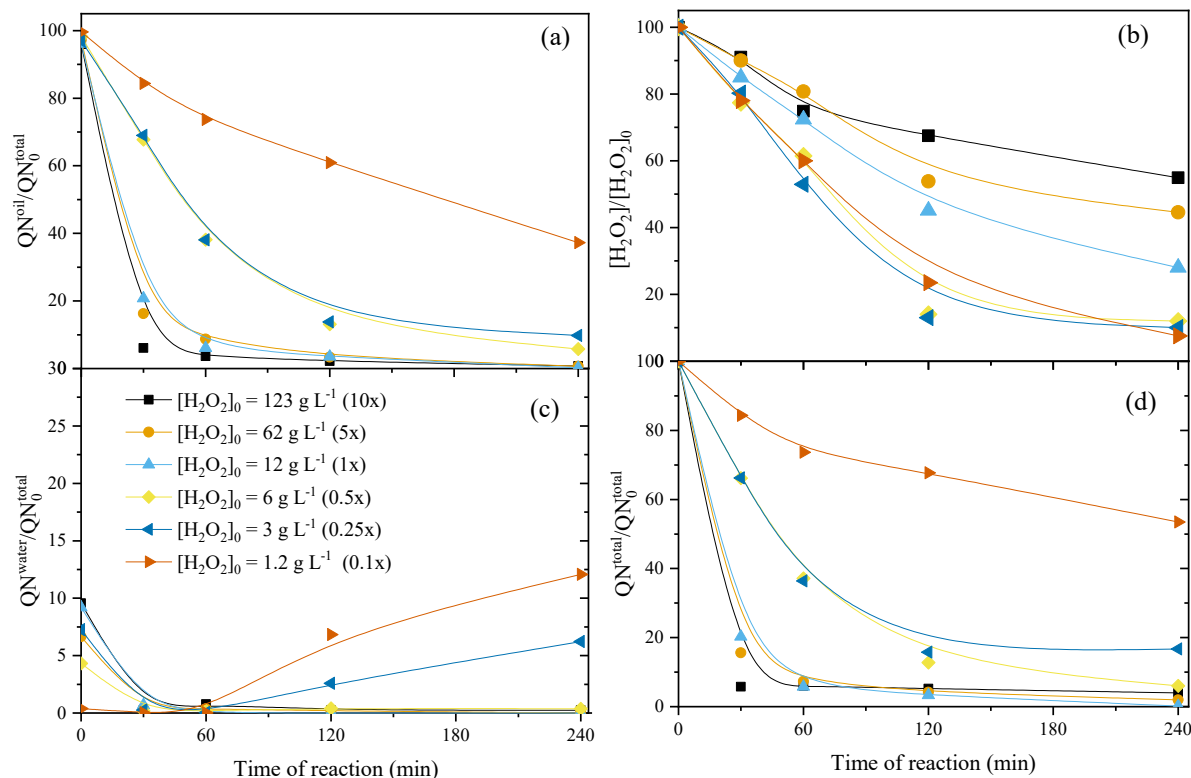


Figure 6.6. ODN of QN with varying hydrogen peroxide concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 1.2\text{--}123 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80^\circ \text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. Solid lines are only intended to guide the eyes.

The TOC removal is also highly affected by the concentration of hydrogen peroxide (Figure 6.7a). From $[H_2O_2]_0 = 1.2$ to 12 g L^{-1} , there is a positive correlation between the increase in concentration and increase in TOC removal ($R^2 = 0.99$, Figure 6.7b); however, further increasing the concentration of hydrogen peroxide ($[H_2O_2]_0 > 12 \text{ g L}^{-1}$) does not impact TOC removal significantly.

The efficiency of hydrogen peroxide consumption was calculated for all reaction conditions and is depicted in Figure 6.7a. Too high concentration ($[H_2O_2]_0 = 123$ and 62 g L^{-1}) results in poor efficiency of hydrogen peroxide consumption (*ca.* 13% and 20%, respectively). Similarly, too low concentration ($[H_2O_2]_0 = 1.2 \text{ g L}^{-1}$) resulted in *ca.* $\eta_{H_2O_2}^{ODN} = 20\%$. Intermediate concentrations ($[H_2O_2]_0 = 3, 6$ and 12 g L^{-1}) resulted in efficiencies in the range of 40–50%, with $[H_2O_2]_0 = 6 \text{ g L}^{-1}$ resulting in the highest efficiency.

Given the results reported here, a concentration of hydrogen peroxide of 12 g L^{-1} was assumed as the optimum condition, as QN removal and abatement is high in just 1 h of reaction (*ca.* 90% and 85%, respectively), H_2O_2 degradation, $\eta_{H_2O_2}^{ODN}$ and TOC removals are adequate (*ca.* 75%, 40% and 29%, respectively) compared to the other conditions studied.

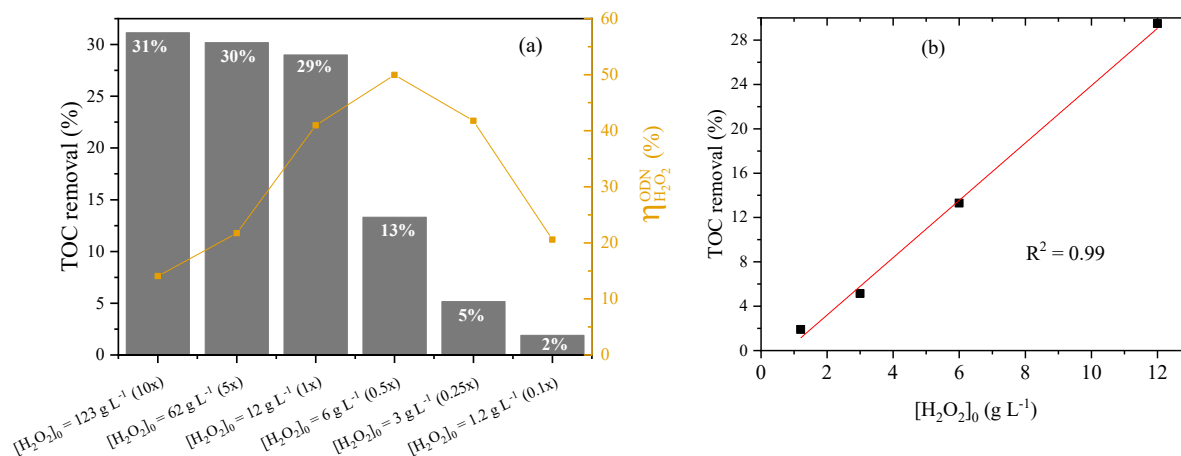


Figure 6.7. (a) TOC removal and efficiency of hydrogen peroxide consumption and (b) correlation between TOC removal and hydrogen peroxide concentration. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 1.2\text{--}123 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0.

6.2.2 Effect of catalyst concentration

The catalyst concentration was studied in the range of 5–0.25 g L⁻¹; the results are shown in Figure 6.8. Again, the higher the catalyst concentration, the faster the removal of QN (Figure 6.8a) and the faster its abatement (Figure 6.8d). It also significantly impacts hydrogen peroxide consumption (Figure 6.8b), where only the higher catalyst concentration (5 g L⁻¹) allowed over 90% H₂O₂ consumption. Only catalysts concentration higher than 2.5 g L⁻¹ resulted in QN removal higher than 90% in 1 h of reaction. Decreasing the catalyst concentration to 1 g L⁻¹ requires an extra hour to allow the same QN removal.

TOC removal (Figure 6.9) was very much influenced by the catalyst concentration, reaching a maximum removal at 5 g L⁻¹ (37%). Nevertheless, a catalyst concentration of 5 g L⁻¹ also impacts the efficiency of hydrogen peroxide consumption ($\eta_{H_2O_2}^{ODN}$), decreasing it slightly compared to a concentration of 2.5 g L⁻¹. A higher catalyst concentration favors the reaction, and thus, a catalyst concentration of 2.5 g L⁻¹ was chosen.

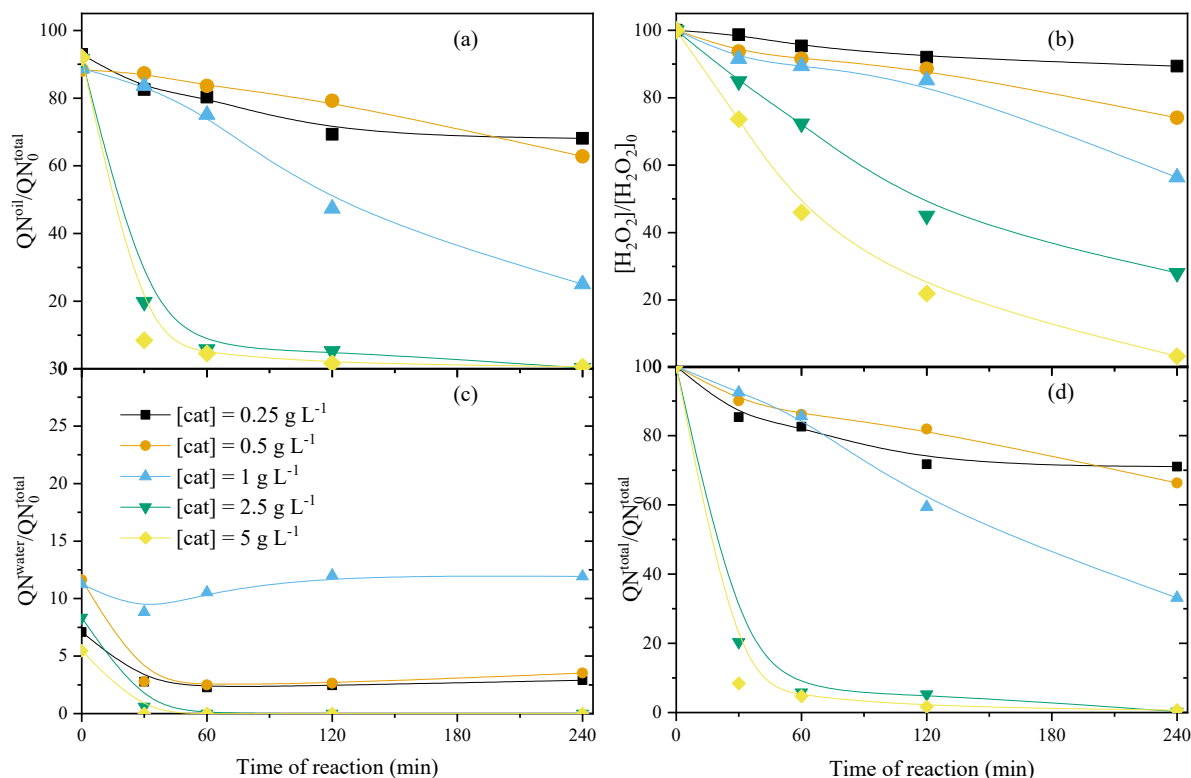


Figure 6.8. ODN of QN with varying catalyst concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 0.25\text{--}5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0. Solid lines are only intended to guide the eyes.

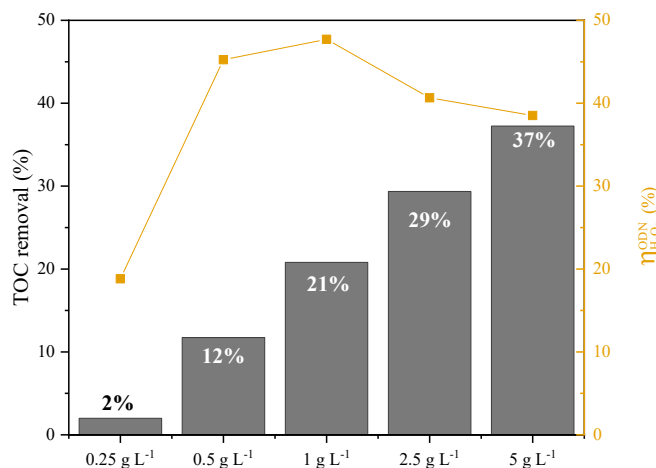


Figure 6.9. TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 80 \text{ }^\circ\text{C}$, $C_{cat} = 0.25\text{--}5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0.

6.2.3 Effect of the temperature

The effect of temperature was studied in the range of 50–80 °C considering a concentration of hydrogen peroxide ($[H_2O_2]_0 = 12 \text{ g L}^{-1}$) and catalyst ($C_{cat} = 2.5 \text{ g L}^{-1}$) as previously determined. The results are displayed in Figure 6.10. Again, the temperature plays a crucial role in removing QN from the fuel phase. A temperature of 50 °C did not allow complete removal of QN (Figure 6.10a) or complete abatement (Figure 6.10d) in 4 h of reaction, ending the reaction with *ca.* 200 mg L⁻¹ of QN in the fuel

phase and around 60 mg L⁻¹ of QN in the water phase (corresponding to 33% and 4% of QN initially loaded). At 60 °C, removal of QN from the fuel phase achieves approximately 90% after 4 h of reaction, with no significant accumulation in the water phase. For 70 °C and above, over 90% of QN removal is achieved in 2 h of reaction, and the higher the temperature, the faster the removal. Similar results have been reported for oxidation-based treatments both in aqueous [11] and biphasic systems [12].

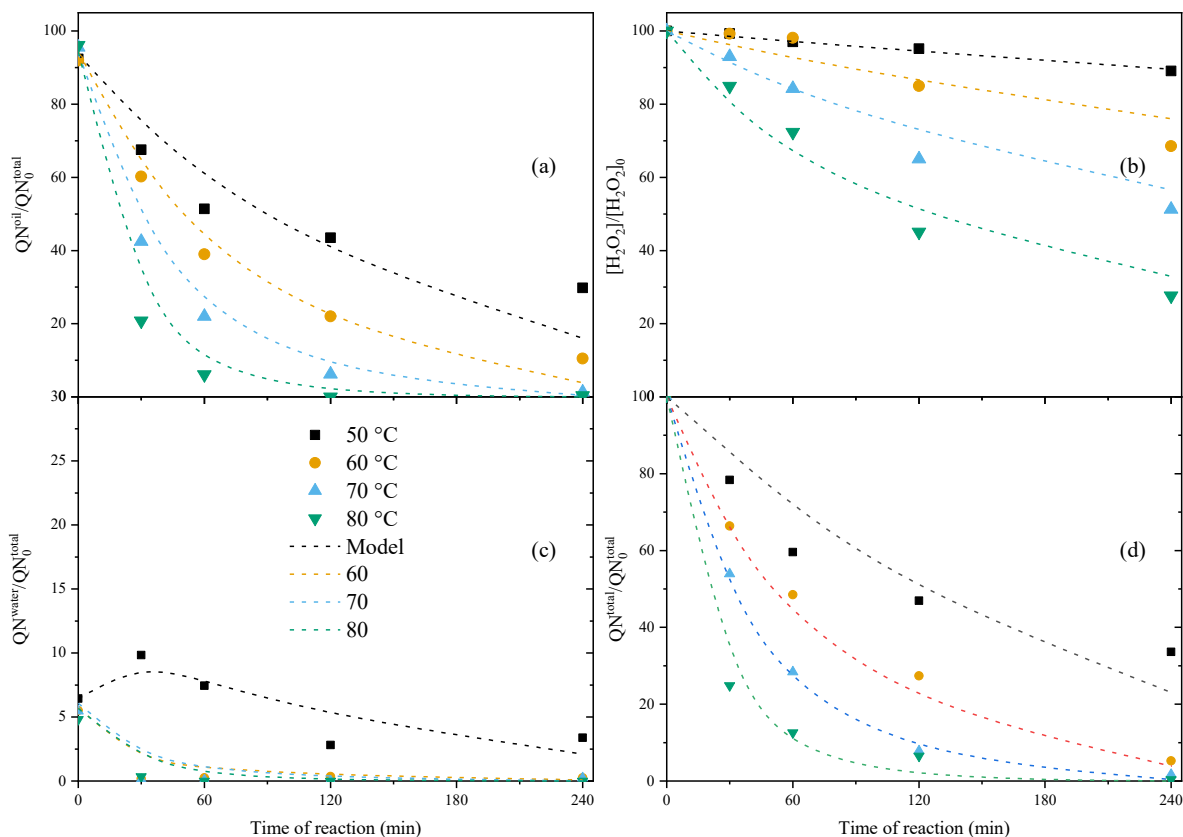


Figure 6.10. ODN of QN with varying temperatures. (a) Removal of QN from the fuel phase, (b) decomposition of H₂O₂, (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: [QN]₀ = 500 mg L⁻¹ in 2,2,4-trimethylpentane, [H₂O₂]₀ = 12 g L⁻¹, O/W volume ratio = 80:20, T = 50–80 °C, C_{cat} = 2.5 g L⁻¹, pH of aqueous phase = 3.0. Dashed lines represent the kinetic modeling described in section 5.2.3.

Increasing the temperature also increases TOC removal (Figure 6.11), with a maximum removal at 70 °C; further increasing to 80 °C results in a lower TOC removal, and it impacts the efficiency of hydrogen peroxide consumption (Figure 6.11), with a temperature of 70 °C allowing a $\eta_{H_2O_2}^{ODN}$ of ca. 77%.

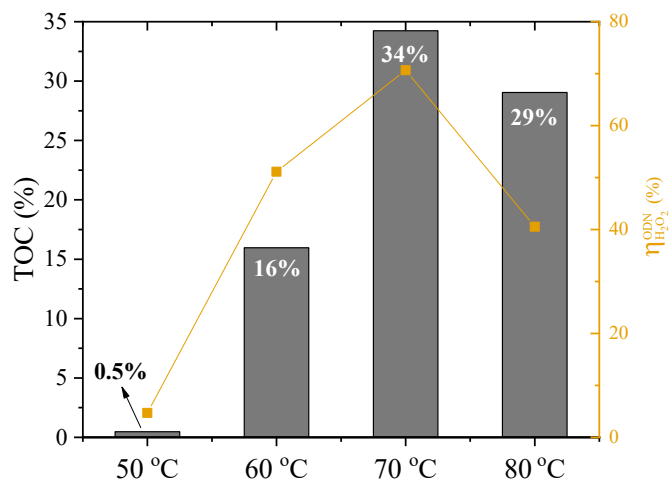


Figure 6.11. TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 50\text{--}80 \text{ }^\circ\text{C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 3.0.

The kinetic model developed in section 5.2.3 (Chapter 5) was fitted to the data, and the results are depicted in Table 6.2. A good fit was obtained, as seen in the parity plot (Figure 6.12) and by the high coefficient of determination ($R^2 > 0.99$). As can be seen, all parameters depend on temperature, especially the decomposition of hydrogen peroxide. On the other hand, the oxidation of QN, although it also depends on temperature, the effect is not so evident when the temperature increases $>70 \text{ }^\circ\text{C}$. As previously seen for the TOC removal and hydrogen peroxide oxidation, the abatement of QN seems to reach a maximum at $70 \text{ }^\circ\text{C}$, as the coefficient for its degradation ($k'_{QN,ox}$) is lower at $80 \text{ }^\circ\text{C}$ (14.8 kmol h^{-1}) compared to the one obtained at $70 \text{ }^\circ\text{C}$ (61.4 kmol h^{-1}). The main factor driving the oxidation of QN in the water phase is the presence of hydroxyl radicals. At higher temperatures, H_2O_2 decomposes at a faster rate [13] (Figure 6.10b), likely increasing the yield of hydroxyl radicals [14]. The increased concentration of hydroxyl radicals can result in its recombination, generating non-oxidizing species, such as water and oxygen, or into an auto-scavenging effect [15].

Table 6.2. Kinetic and statistical coefficients obtained for each temperature during ODN.

Coefficient	50 °C	60 °C	70 °C	80 °C
$k'_{H_2O_2} (\text{mol}^{-1} \text{ h}^{-1})$	12.31	25.83	52.00	77.49
$k'_{QN,mt} (\text{h}^{-1})$	0.40	0.80	1.36	2.50
$k'_{QN,ox} (\text{mol}^{-1} \text{ h}^{-1})$	585	12538	61411	14834
POW			0.18	
SSE_{model}	0.011	0.008	0.001	0.008
R^2	0.995	0.996	0.999	0.996

The Arrhenius plot (Figure 6.13) was used to estimate the pre-exponential factor and the activation energy for the reactions carried out at $50\text{--}80 \text{ }^\circ\text{C}$, and the results are given in Table 6.3. Two other works were found reporting activation energy for QN oxidation using hydrogen peroxide for aqueous phase reaction (not a biphasic system), with values of 22.4 kJ mol^{-1} [16] and 23.2 kJ mol^{-1} [17]. Other AOPs-based processes reported 55 kJ mol^{-1} using Ferrate(VI) as the oxidant for QN oxidation in water [18] and 29 kJ mol^{-1} and 93 kJ mol^{-1} for TOC removal during catalytic air oxidation of QN [19]. The kinetic

model of the supercritical water oxidation of QN was estimated as 226-234 kJ mol⁻¹ in a continuous plug-flow reactor [20] and 112 kJ mol⁻¹ in a batch reactor [21]. Only one report was found estimating the activation energy for the biphasic oxidation of nitrogenated compounds (in this case, indole), resulting in a value of 26.6 kJ mol⁻¹ using O₂ as oxidant and a P,O-co-doped carbon material; however, the authors did not take into account the mass transference [4].

The activation energy found for the decomposition of hydrogen peroxide is similar to other reports in the literature: 52-89 kJ mol⁻¹ [7] and 45-65 kJ mol⁻¹ [22] for aqueous Fenton reaction for dyes decolorization and 43±10 kJ mol⁻¹ for CWPO of phenol using carbon black as catalyst [23], and lower than those reported for aqueous phase CWPO of caffeine using compost-derived catalysts (78 kJ mol⁻¹ [24]) and 4-nitrophenol using clays as catalysts (103 kJ mol⁻¹ [25]).

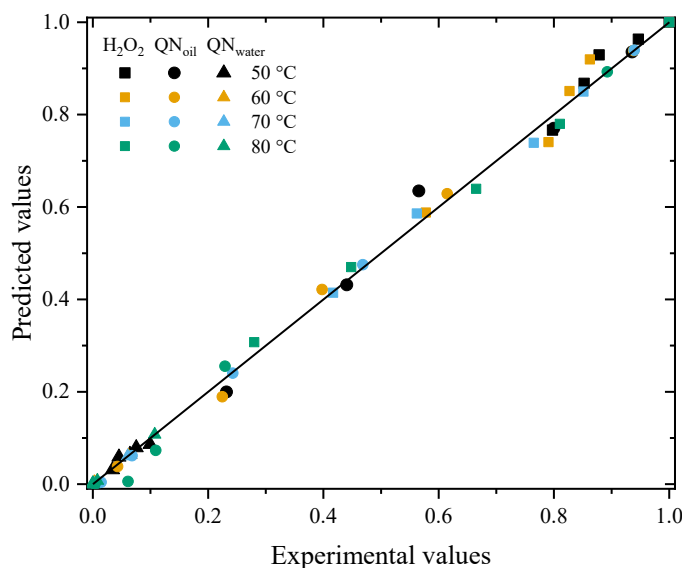


Figure 6.12. Parity plot.

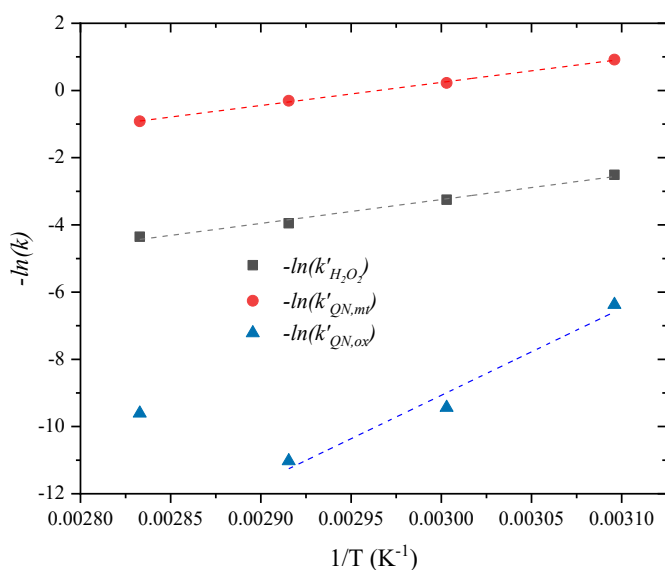


Figure 6.13. Arrhenius plot. The coefficient for $k'_{QN, ox}$ at 80 °C was not used for the linear regression.

Table 6.3. Activation energy and pre-exponential factor.

Coefficient	Pre-exponential factor (mol ⁻¹)	Ea (kJ mol ⁻¹)	R ²	Range
$k'_{H_2O_2}$ (mol ⁻¹ h ⁻¹)	2.13E-11	59.1	0.989	50-80 °C
$k'_{QN,mt}$ (h ⁻¹)	1.40E-09	57.2	0.997	50-80 °C
$k'_{QN,ox}$ (mol ⁻¹ h ⁻¹)	2.39E-38	214.9	0.973	50-70 °C

6.2.4 Effect of the pH of aqueous phase

The effect of pH was studied in the range 1-11 considering a concentration of hydrogen peroxide ($[H_2O_2]_0 = 12 \text{ g L}^{-1}$), catalyst ($C_{cat} = 2.5 \text{ g L}^{-1}$) and temperature ($T = 70 \text{ °C}$) as previously determined, and the results are reported in Figure 6.14. The removal of QN from the oil phase was accelerated for lower pHs; at $pH_0 = 1$, over 90% of QN was removed from the fuel phase in just 30 min of reaction, whereas a $pH_0 = 3.0$ required 120 min to achieve the same result, and higher pHs ($pH > 5$) required 240 min or longer to achieve a similar result.

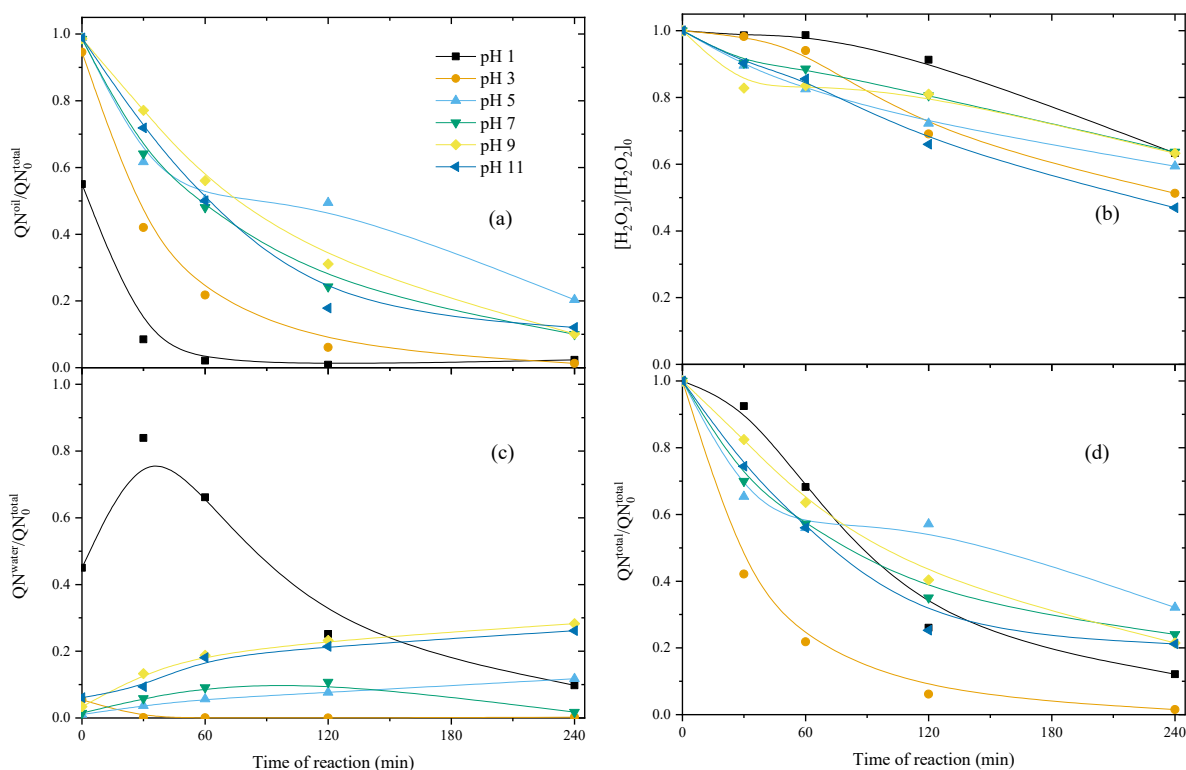


Figure 6.14. ODN of QN with varying pH. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[QN]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70 \text{ °C}$, $C_{cat} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 1.0-11.0. Solid lines are only intended to guide the eye.

This improved activity is directly correlated to the solubility [26] and partition coefficient [27] of QN upon changing the pH of the aqueous phase. Previous works have shown that the solubility of QN in water increases from 6.46 to 61.3 mg mL^{-1} when the pH decreases from 3.07 to 0.55 [26]. A similar effect over the partition coefficient has been observed: at pH of 4.9 (which is its pK_a) or higher, QN is mostly in its molecular form, resulting in more lipophilic behavior. When the pH drops to values below

4.90, QN dissociates, and it is increasingly hydrophilic as the pH decreases, reaching a partition coefficient that approaches 0 as the pH approaches 0 [27]; thus, working at lower pH is beneficial in QN biphasic oxidation as it increases the mass transference from oil to water. Despite faster removal of QN from the fuel phase, an initial pH of 1 resulted in the accumulation of QN in the water phase, reaching a peak in 30 min of reaction (Figure 6.14c). This result may be attributed to the lower H_2O_2 decomposition at pH 1 in the first 60 min of the reaction (Figure 6.14b). Since the formation of hydroxyl radicals is the main factor affecting QN oxidation, poor H_2O_2 decomposition will lead to poor QN oxidation, translating into a lower overall conversion of QN (Figure 6.14d), TOC removal and efficiency of hydrogen peroxide consumption (Figure 6.15).

Higher pH, especially basic pHs, resulted in poorer activity towards QN removal (Figure 6.14a) and an accumulation of QN in the oil phase of 10-20% of the initial mass of QN (30-100 mg L^{-1} of QN). The decomposition of hydrogen peroxide is less efficient at higher pH [28], likely yielding non-reactive species, such as oxygen and water [11]. QN accumulates in the water phase (Figure 6.14c) by the end of the reaction (12-28% of the initial mass, 180-340 mg L^{-1} of QN), resulting in a lower overall QN abatement (Figure 6.14d). A similar behavior was observed for the TOC removal, with better efficiencies on the use of hydrogen peroxide being achieved in the pH range of 3-5, with significant drops in TOC removal and efficiency of H_2O_2 use for pH 1 and pH >7.

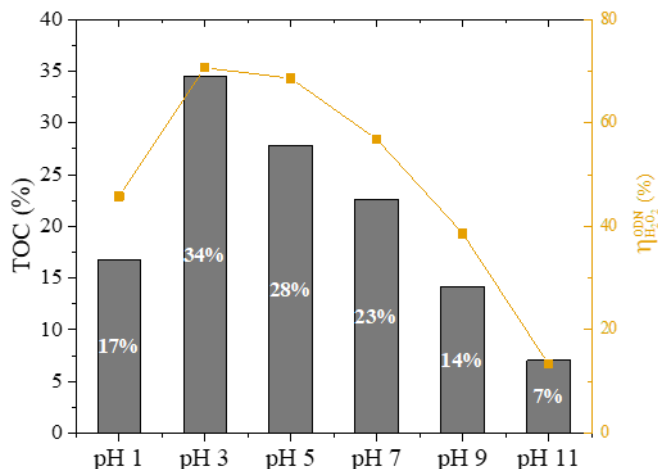


Figure 6.15. TOC removal and efficiency of hydrogen peroxide consumption. Conditions: $[\text{QN}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 12 \text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70 \text{ }^\circ\text{C}$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, pH of aqueous phase = 1.0-11.0.

6.2.5 Effect of initial concentration of QN

The effect of the initial concentration of QN was studied in the range 100-5000 mg L^{-1} considering a stoichiometric hydrogen peroxide concentration ($[\text{H}_2\text{O}_2]_0 = 2.4\text{-}120 \text{ g L}^{-1}$), catalyst concentration ($C_{\text{cat}} = 2.5 \text{ g L}^{-1}$), temperature ($T = 70 \text{ }^\circ\text{C}$) and initial pH of 3.0. The results are reported in Figure 6.16. For QN concentrations in the range of 100-1000 mg L^{-1} , a 60-minute reaction is sufficient to remove over 90% of QN from the fuel phase, whereas for higher QN concentrations (5 g L^{-1}), longer reaction times

are required (120 min). Nevertheless, the system is sufficiently flexible to deal with a wide range of QN concentrations.

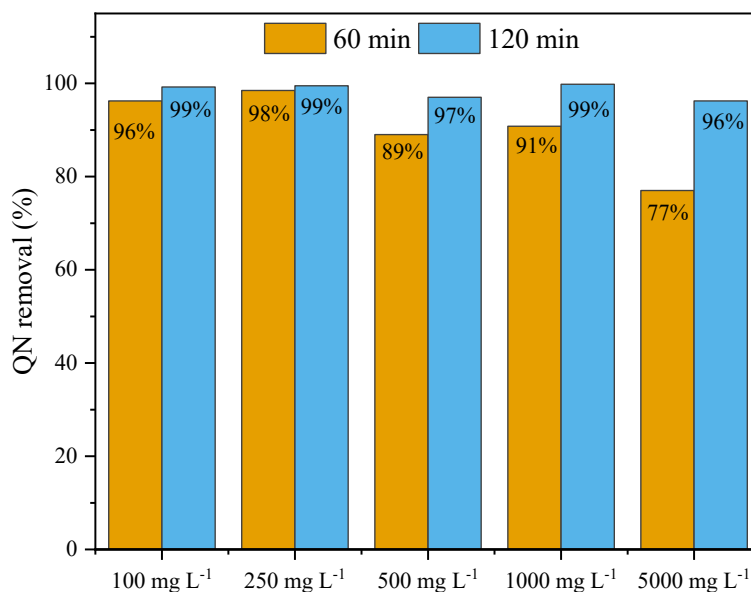


Figure 6.16. ODN of QN with varying initial QN concentration. (a) Removal of QN from the fuel phase, (b) decomposition of H_2O_2 , (c) QN in the aqueous phase and (d) overall abatement of QN. Conditions: $[QN]_0 = 100\text{--}5000\text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[H_2O_2]_0 = 12\text{ g L}^{-1}$, O/W volume ratio = 80:20, $T = 70\text{ }^\circ\text{C}$, $C_{cat} = 2.5\text{ g L}^{-1}$, pH of aqueous phase = 3.0, $t = 60\text{--}120\text{ min}$ of reaction.

6.3 Comparison with literature

Table 6.4 shows other papers that deal with the oxidation of nitrogenated compounds under biphasic systems using catalysts based on carbon materials. Denitrogenation has been reported in the range of 0–100% with temperatures ranging from 25–100 $^\circ\text{C}$, catalyst concentrations from 0.5–3.33 g L^{-1} , H_2O_2/N molar ratios from 0–820, acidic pH (3–6), and fuel-to-extractant volume ratios of 99:1 to 50:50. Only another work [4] was found for ODN purposes using carbon materials as a catalyst rather than as support or in a hybrid material, and only two other works reported the valorization of waste materials to produce the catalysts [29, 30]. In the present work, we were able to obtain an oxygen-doped CNT derived from simulated plastic waste, resulting in >89% denitrogenation in 1 h of reaction, using lower concentrations of hydrogen peroxide ($H_2O_2/N = 23$) compared to most reports (only two other works used H_2O_2/N molar ratios lower than 23 [3, 5]). The main limitation of this work is that it required slightly higher temperatures (70 $^\circ\text{C}$) than most reports using hydrogen peroxide (25–60 $^\circ\text{C}$).

Table 6.4. Reports in the literature for ODN using carbon-containing materials as catalysts.

Fuel	Catalyst	Extractant	Operational Conditions	Removal	Ref.
QN in Toluene ($C_0 = 50$ ppm)	$\text{Fe}_2\text{O}_3/\text{C}$	Aqueous H_2O_2 phase	$V_{\text{fuel}}/V_{\text{extractant}} = 99:1$, $C_{\text{cat}} = 1 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 112$, $T = 25^\circ\text{C}$, $\text{pH} = 4.0$, $t = 3 \text{ h}$.	60%	[31]
QN in Cyclohexane ($[\text{N}]_0 = 50$ ppm)	Fe/C and FeMo/C	Aqueous H_2O_2 phase	$V_{\text{fuel}}/V_{\text{extractant}} = 5:1$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 495$, $T = 25^\circ\text{C}$, $\text{pH} = 4.0$, $t = 2 \text{ h}$.	100%	[32]
QN in Cyclohexane ($[\text{N}]_0 = 30$ ppm)	N-Doped CNT/Red Mud	Aqueous H_2O_2 phase	$V_{\text{fuel}}/V_{\text{extractant}} = 5:1$, $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 820$, $t = 45 \text{ min}$.	80%	[29]
QN in Cyclohexane ($C_0 = 500$ ppm)	WEEE-clay hybrid material	ACN	$V_{\text{fuel}}/V_{\text{extractant}} = 10:2$, $\text{H}_2\text{O}_2/N = 72$, $T = 60^\circ\text{C}$, $t = 3 \text{ h}$.	73.5 $\text{mgQN g}_{\text{cat}}^{-1}$	[30]
QN in n-Octane* ($C_0 = 5000$ ppm)	$\text{TiO}_2@$ porous C	Acetic Acid	$V_{\text{fuel}}/V_{\text{extractant}} = 20:2$, $C_{\text{cat}} = 0-0.5 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 0-15$, $T = 30-50^\circ\text{C}$, $t = 5-120$ min, 100–1000 rpm, 5–10 wt.% water, $t = 2$ h.	0%	[3]
QN in Cyclohexane ($C_0 = 500$ ppm)	C/red mud	Aqueous H_2O_2 Phase	$V_{\text{fuel}}/V_{\text{extractant}} = 5:1$, $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 450$, $t = 1 \text{ h}$.	100%	[33]
QN in Toluene ($C_0 = 25$ ppm)	Fe/Onion-like Carbon	Aqueous H_2O_2 Phase	$V_{\text{fuel}} = 10 \text{ mL}$, $C_{\text{cat}} = 1 \text{ g L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.05$ mol L^{-1} , $T = 25^\circ\text{C}$, $\text{pH} = 6$.	93%	[34]
QN in Cyclohexane ($[\text{N}]_0 = 500$ ppm)	FeMo/CNT	Aqueous H_2O_2 Phase	$V_{\text{fuel}}/V_{\text{extractant}} = 5:1$, $C_{\text{cat}} = 3.33 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 50$, $t = 50 \text{ min}$.	100%	[35]
PYR or QN in n- Octane* ($C_0 = 1000$ ppm)	$\text{W}_2\text{N}@$ carbon	Acetic acid	$V_{\text{extractant}} = 2 \text{ mL}$, $m_{\text{cat}} = 5 \text{ mg}$, $\text{H}_2\text{O}_2/N = 10$, $T = 37^\circ\text{C}$, $t = 120 \text{ min}$, U.S. = 40%, $t = 2 \text{ h}$.	QN: 90% PYR: 76%	[5]
QN in n-Dodecane ($C_0 = 500$ ppm)	O, P-co-doped carbon	Acetic acid	$V_{\text{fuel}}/V_{\text{extractant}} = 10:10$, $C_{\text{cat}} = 3 \text{ g L}^{-1}$, 50 mL min^{-1} of O_2 , $T = 100^\circ\text{C}$, $t = 4 \text{ h}$	QN: 86%	[4]
QN and PYR in 2,2,4- Trimethylpentane ($C_0 = 1000$ ppm)	$\text{CNT}@$ Fe	Aqueous H_2O_2 Phase	$V_{\text{fuel}}/V_{\text{extractant}} = 80:20$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 230$, $T = 80^\circ\text{C}$, $\text{pH} = 3.0$, $t = 1 \text{ h}$.	QN: 98%, PYR: 89%	This work
QN in 2,2,4- Trimethylpentane ($C_0 = 100-5000$ ppm)	$\text{CNT}@$ NiFe	Aqueous H_2O_2 Phase	$V_{\text{fuel}}/V_{\text{extractant}} = 80:20$, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$, $\text{H}_2\text{O}_2/N = 23$, $T = 70^\circ\text{C}$, $\text{pH} = 3.0$, $t = 1 \text{ h}$.	QN: 89-97%	This work

6.4 Conclusions

This study investigated the oxidative denitrogenation of quinoline in biphasic systems using CNTs derived from a mixture of polyolefins grown over a NiFe/ Al_2O_3 catalyst, resulting in denitrogenation higher than 90% in 4 h of reaction. POL-OX@NiFe can be highlighted as an active catalyst, leading to >90% denitrogenation in just 1 h of reaction. POL-OX@NiFe also allowed a controlled hydrogen peroxide decomposition, superior adsorption capacity, and enhanced phase-transfer ability, which was thus further used to study the reaction conditions.

The ideal conditions identified were a hydrogen peroxide concentration of 12 g L^{-1} for a QN concentration of 500 mg L^{-1} (equivalent to an $\text{H}_2\text{O}_2/N$ molar ratio of 23), a catalyst concentration of 2.5 g L^{-1} , a reaction temperature of 70°C , and an initial pH of 3.0. Under these conditions, QN removal achieved 89% in 1 h of reaction, improved TOC reduction (34%), and effective utilization of hydrogen peroxide ($\eta_{\text{H}_2\text{O}_2}^{\text{ODN}} = 77\%$). Using the optimized conditions, it is possible to effectively and quickly (in *ca.*

1 h) remove a wide range of concentrations of quinoline (89-96% of QN removal for concentrations in the range of 100-1000 mg L⁻¹). In contrast, higher concentrations (5000 mg L⁻¹) require longer times to achieve a similar result (*ca.* 2 h).

Kinetic modeling revealed that mass transfer was the rate-limiting step and that the CNTs allow an increase in the mass transfer rate of QN ($k'_{QN,mt} > 0.34 \text{ h}^{-1}$ for catalyzed reactions *versus* 0.01 h^{-1} for the non-catalytic run), as previously observed for Fe-derived CNTs. POL-OX@NiFe allowed a higher kinetic coefficient for the mass transference ($k'_{QN,mt} = 3.09 \text{ h}^{-1}$) among all CNTs tested in this work ($k'_{QN,mt}$ in the range $0.34\text{-}2.08 \text{ h}^{-1}$, including Fe-derived CNTs reported in Chapter 5). The activation energy for QN oxidation (214 kJ mol^{-1}) and hydrogen peroxide decomposition (59 kJ mol^{-1}) was also estimated. The activation energy for the consumption of hydrogen peroxide aligned well with previous reports related to the CWPO of micropollutants in aqueous phase only ($43\text{-}103 \text{ kJ mol}^{-1}$). Polyolefin-derived CNTs represent a promising, sustainable, and efficient solution for biphasic ODN and fuel purification processes.

6.5 References

- [1] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review, *Applied Catalysis B: Environmental* 187 (2016) 428–460. <https://doi.org/10.1016/j.apcatb.2016.01.033>.
- [2] J.L. Diaz de Tuesta, B. F. Machado, P. Serp, A.M. T. Silva, J.L. Faria, H. T. Gomes, Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide, *Catalysis Today* 356 (2020) 205–215. <https://doi.org/10.1016/j.cattod.2019.07.012>.
- [3] B.N. Bhadra, J.Y. Song, N. Uddin, N.A. Khan, S. Kim, C.H. Choi, S.H. Jung, Oxidative denitrogenation with TiO_2 @porous carbon catalyst for purification of fuel: Chemical aspects, *Applied Catalysis B: Environmental* 240 (2019) 215–224. <https://doi.org/10.1016/j.apcatb.2018.09.004>.
- [4] I. Ahmed, S.H. Jung, Effective aerobic oxidative denitrogenation of model fuel with metal-free porous carbon derived from phytic acid-loaded polyaniline, *Chemical Engineering Journal* 479 (2024) 147679. <https://doi.org/10.1016/j.cej.2023.147679>.
- [5] B.N. Bhadra, Y.S. Baek, S. Kim, C.H. Choi, S.H. Jung, Oxidative denitrogenation of liquid fuel over W_2N @carbon catalyst derived from a phosphotungstic acid encapsulated metal–azolate framework, *Applied Catalysis B: Environmental* 285 (2021) 119842. <https://doi.org/10.1016/j.apcatb.2020.119842>.
- [6] S. Kumari, S. Sengupta, Kinetic modeling of dual-stage oxidative extractive denitrogenation of model fuel, *Chemical Engineering Communications* 211(10) (2024) 1572–1587. <https://doi.org/10.1080/00986445.2024.2362814>.
- [7] M.D. Nicodemos Ramos, L.A. Sousa, A. Aguiar, Effect of cysteine using Fenton processes on decolorizing different dyes: a kinetic study, *Environmental Technology* 43(1) (2022) 70–82. <https://doi.org/10.1080/09593330.2020.1776402>.
- [8] Magnetic CoFe_2O_4 @carbon yolk-shell nanoparticles as catalysts for the catalytic wet peroxide oxidation of paracetamol: kinetic insights, *Global NEST Journal* (2022) 57–66. <https://doi.org/10.30955/gnj.004309>.
- [9] M.S. Kalmakhanova, J.L. Diaz de Tuesta, B.K. Massalimova, H.T. Gomes, Pillared clays from natural resources as catalysts for catalytic wet peroxide oxidation: Characterization and kinetic insights, *Environmental Engineering Research* 25(2) (2019) 186–196. <https://doi.org/10.4491/eer.2018.402>.
- [10] J.L. Diaz de Tuesta, A. Quintanilla, D. Moreno, V.R. Ferro, J.A. Casas, Simulation and Optimization of the CWPO Process by Combination of Aspen Plus and 6-Factor Doehlert Matrix: Towards Autothermal Operation, *Catalysts* 10(5) (2020) 548. <https://doi.org/10.3390/catal10050548>.
- [11] J. Rueda Márquez, I. Levchuk, M. Sillanpää, Application of catalytic wet peroxide oxidation for industrial and urban wastewater treatment: A Review, *Catalysts* 8(12) (2018) 673. <https://doi.org/10.3390/catal8120673>.
- [12] Q. Gu, Y. Ding, Z. Liu, Y. Lin, R. Schlögl, S. Heumann, D. Su, Probing the intrinsic catalytic activity of carbon nanotubes for the metal-free oxidation of aromatic thiophene compounds in ionic liquids, *Journal of Energy Chemistry* 32 (2019) 131–137. <https://doi.org/10.1016/j.jechem.2018.07.004>.
- [13] J.A. Zazo, G. Pliego, S. Blasco, J.A. Casas, J.J. Rodriguez, Intensification of the Fenton Process by Increasing the Temperature, *Industrial & Engineering Chemistry Research* 50(2) (2011) 866–870. <https://doi.org/10.1021/ie101963k>.
- [14] C. Lee, J. Yoon, Temperature dependence of hydroxyl radical formation in the $\text{hv}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems, *Chemosphere* 56(10) (2004) 923–34. <https://doi.org/10.1016/j.chemosphere.2004.04.047>.
- [15] A. Rey, A. Bahamonde, J.A. Casas, J.J. Rodriguez, Selectivity of hydrogen peroxide decomposition towards hydroxyl radicals in catalytic wet peroxide oxidation (CWPO) over Fe/AC catalysts, *Water Science & Technology* 61(11) (2010) 2769–78. <https://doi.org/10.2166/wst.2010.077>.
- [16] V. Gosu, B.R. Gurjar, T.C. Zhang, R.Y. Surampalli, Oxidative Degradation of Quinoline Using Nanoscale Zero-Valent Iron Supported by Granular Activated Carbon, *Journal of Environmental Engineering* 142(1) (2016). [https://doi.org/10.1061/\(asce\)jee.1943-7870.0000981](https://doi.org/10.1061/(asce)jee.1943-7870.0000981).
- [17] L. Singh, P. Rekha, S. Chand, Comparative evaluation of synthesis routes of Cu/zeolite Y catalysts for catalytic wet peroxide oxidation of quinoline in fixed-bed reactor, *Journal of Environmental Management* 215 (2018) 1–12. <https://doi.org/10.1016/j.jenvman.2018.03.021>.

- [18] Z. Luo, X. Li, J. Zhai, Kinetic investigations of quinoline oxidation by ferrate(VI), *Environmental Technology* 37(10) (2016) 1249-56. <https://doi.org/10.1080/09593330.2015.1111424>.
- [19] N.J. Pachupate, P.D. Vaidya, Catalytic wet oxidation of quinoline over Ru/C catalyst, *Journal of Environmental Chemical Engineering* 6(1) (2018) 883-889. <https://doi.org/10.1016/j.jece.2017.12.014>.
- [20] L.D.S. Pinto, L.M.F. dos Santos, R.C.D. Santos, B. Al-Duri, Supercritical water oxidation of quinoline in a continuous plug flow reactor—part 2: kinetics, *Journal of Chemical Technology & Biotechnology* 81(6) (2006) 919-926. <https://doi.org/10.1002/jctb.1419>.
- [21] Z. Li, T.J. Houser, Kinetics of the catalyzed supercritical water-quinoline reaction, *Industrial & Engineering Chemistry Research* 31(11) (2002) 2456-2459. <https://doi.org/10.1021/ie00011a008>.
- [22] C.S. Santana, M.D. Nicodemus Ramos, C.C. Vieira Velloso, A. Aguiar, Kinetic Evaluation of Dye Decolorization by Fenton Processes in the Presence of 3-Hydroxyanthranilic Acid, *International Journal of Environmental Research and Public Health* 16(9) (2019) 1602. <https://doi.org/10.3390/ijerph16091602>.
- [23] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, J.J. Rodriguez, Kinetic modeling of wet peroxide oxidation with a carbon black catalyst, *Applied Catalysis B: Environmental* 209 (2017) 701-710. <https://doi.org/10.1016/j.apcatb.2017.03.031>.
- [24] J.L. Diaz de Tuesta, F.V.M. de Almeida, J.R.P. Oliveira, P. Praça, M.C. Guerreiro, H.T. Gomes, Kinetic insights on wet peroxide oxidation of caffeine using EDTA-functionalized low-cost catalysts prepared from compost generated in municipal solid waste treatment facilities, *Environmental Technology & Innovation* 24 (2021) 101984. <https://doi.org/10.1016/j.eti.2021.101984>.
- [25] J.L. Diaz de Tuesta, A. Quintanilla, J.A. Casas, S. Morales-Torres, J.L. Faria, A.M.T. Silva, H.T. Gomes, The pH effect on the kinetics of 4-nitrophenol removal by CWPO with doped carbon black catalysts, *Catalysis Today* 356 (2020) 216-225. <https://doi.org/10.1016/j.cattod.2019.08.033>.
- [26] M.T. Carvajal, S. Yalkowsky, Effect of pH and Ionic Strength on the Solubility of Quinoline: Back-to-Basics, *AAPS PharmSciTech* 20(3) (2019) 124. <https://doi.org/10.1208/s12249-019-1336-9>.
- [27] S.H. Standal, A.M. Blokhuis, J. Haavik, A. Skaug, T. Barth, Partition Coefficients and Interfacial Activity for Polar Components in Oil/Water Model Systems, *Journal of Colloid and Interface Science* 212(1) (1999) 33-41. <https://doi.org/10.1006/jcis.1998.5988>.
- [28] A. Fischbacher, C. von Sonntag, T.C. Schmidt, Hydroxyl radical yields in the Fenton process under various pH, ligand concentrations and hydrogen peroxide/Fe(II) ratios, *Chemosphere* 182 (2017) 738-744. <https://doi.org/10.1016/j.chemosphere.2017.05.039>.
- [29] A.A.S. Oliveira, A.R. Martins, R.V. Ferreira, I.T. Cunha, P. Serp, J.P. de Mesquita, F.C.C. Moura, N-doped carbon nanotubes grown on red mud residue: Hybrid nanocomposites for technological applications, *Catalysis Today* 344 (2020) 247-258. <https://doi.org/10.1016/j.cattod.2019.04.060>.
- [30] C.V. Diniz, J.V. Nascimento, I. Binatti, P.E. Freitas, R.V. Mambrini, Hybrid catalysts based on waste electrical and electronic equipment supported on bentonite for the removal of contaminants compounds in liquid phase, *Catalysis Today* 344 (2020) 75-83. <https://doi.org/10.1016/j.cattod.2018.10.030>.
- [31] I.R. Guimarães, A.S. Giroto, W.F. de Souza, M.C. Guerreiro, Highly reactive magnetite covered with islands of carbon: Oxidation of N and S-containing compounds in a biphasic system, *Applied Catalysis A: General* 450 (2013) 106-113. <https://doi.org/10.1016/j.apcata.2012.10.017>.
- [32] R.V. Mambrini, C.Z. Maia, J.D. Ardisson, P.P. de Souza, F.C.C. Moura, Fe/C and FeMo/C hybrid materials for the biphasic oxidation of fuel contaminants, *New Journal of Chemistry* 41(1) (2017) 142-150. <https://doi.org/10.1039/c6nj02718k>.
- [33] A.A.S. Oliveira, I.F. Teixeira, T. Christofani, J.C. Tristão, I.R. Guimarães, F.C.C. Moura, Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue, *Applied Catalysis B: Environmental* 144 (2014) 144-151. <https://doi.org/10.1016/j.apcatb.2013.07.015>.
- [34] W.F. Souza, M.C. Pereira, L.C. A. Oliveira, Amphiphilic catalysts based on onion-like carbon over magnetic iron oxide for petrochemical industry use, *Fuel* 96 (2012) 604-607. <https://doi.org/10.1016/j.fuel.2012.01.011>.
- [35] I.F. Teixeira, A.A.d.S. Oliveira, T. Christofani, F.C.C. Moura, Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process, *Journal of Materials Chemistry A* 1(35) (2013) 10203-10208. <https://doi.org/10.1039/c3ta11535f>.

CHAPTER 7 - OXIDATIVE DESULFURIZATION WITH NiFe-BASED CATALYSTS

Chapter 7

Oxidative desulfurization with NiFe-based catalysts

This chapter focuses on the application of carbon nanotubes (CNTs) synthesized from nickel-iron catalysts for the oxidative desulfurization (ODS) of dibenzothiophene (DBT) in a model fuel. The study explores the effect of different plastic-derived carbon sources and their physicochemical properties on their catalytic performance. The role of surface modifications, particularly acid treatments, is analyzed to understand how functional groups influence catalytic efficiency. The effect of different extraction phases, namely water and acetonitrile, is also examined, considering their influence on reaction kinetics and product distribution. Additionally, the chapter explores the role of co-catalysts, such as formic acid, in enhancing oxidative transformations. Finally, the chapter compares the catalytic efficiency of these CNTs with literature benchmarks, highlighting their potential as sustainable and metal-free catalysts for ODS applications.

This chapter was adapted from the article:

- Fernanda F. Roman, Maria C. Batista, Ana J. Briganti, Adriano S. Silva, Jose L. Diaz de Tuesta, Raquel V Mambrini, Adrián M. T. Silva, Joaquim L. Faria, and Helder T. Gomes. Polyolefin and polystyrene-derived carbon nanotubes: Catalysts for oxidative desulfurization under a biphasic system. *ChemCatChem*, 2025, e202500233. <https://doi.org/10.1002/cctc.202500233> [Accepted – In Press].

7.1 Effect of acid washing

The removal of DBT from the simulated fuel phase according to the acid treatment used is shown in Figure 7.1. The CVD catalyst ($\text{NiFe}/\text{Al}_2\text{O}_3$) was also tested for comparison purposes. All tested materials displayed catalytic activity towards the removal of DBT (>30%) and H_2O_2 conversion (>20%) when compared to the non-catalytic run (removal of DBT and H_2O_2 conversion of 8% and 4%, respectively) in 8 h of reaction. POL-OX@NiFe displayed a significantly higher catalytic activity towards the removal of DBT (77%) compared to POL@NiFe (58%), POL-P@NiFe (*ca.* 30%) and the CVD catalyst (30%) in 8 h of reaction. For comparison purposes, the pure extraction effect under the conditions studied falls below 2% (Figure 7.2).

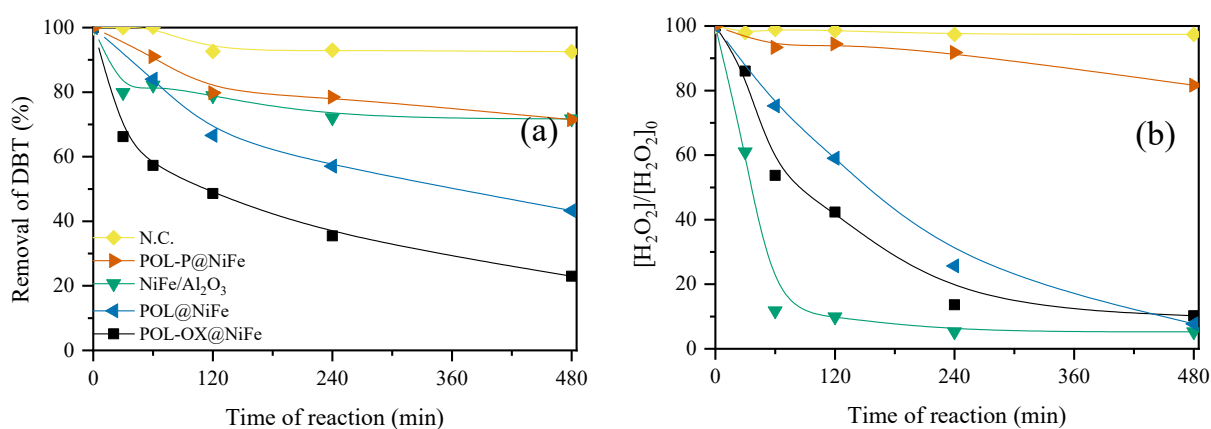


Figure 7.1. (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, water as extractant phase, O/W volume ratio of 80:20, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$ ($\text{H}_2\text{O}_2/S$ molar ratio of 15), $T = 70^\circ\text{C}$, 0.1 vol.% of 1M H_2SO_4 (equivalent to a pH_0 of 3.0).

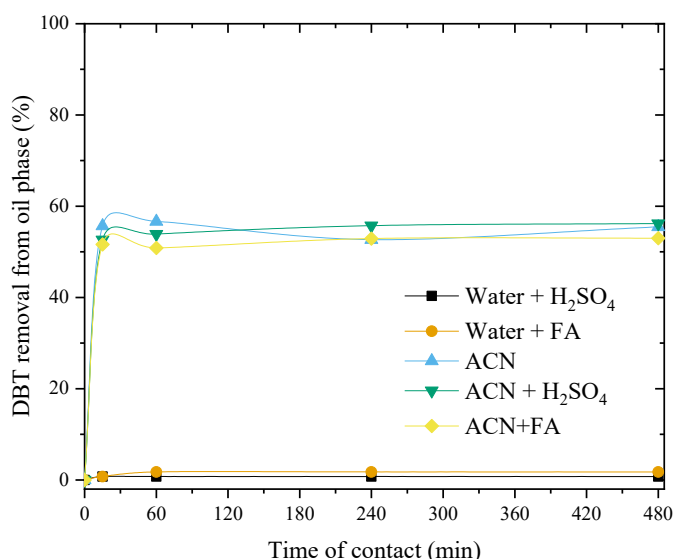


Figure 7.2. Extraction of DBT in the presence of the distinct extractant and co-catalysts. Conditions: $[\text{DBT}] = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $T = 70^\circ\text{C}$, O/E volume ratio 80:20, addition of 0.1 vol.% of sulfuric or formic acid (1 M).

On the other hand, the materials displayed distinct behavior toward the decomposition of hydrogen peroxide, with the $\text{NiFe}/\text{Al}_2\text{O}_3$ decomposing over 90% of the oxidant source in just 60 min of reaction, followed by POL-OX@NiFe (46%), POL@NiFe (25%) and POL-P@NiFe (*ca.* 6%). The

decomposition of hydrogen peroxide was found to be correlated to the amount of acidic groups on the surface of CNTs (Figure 7.3a, $R^2 > 0.98$). The DBT removal, on the other hand, was positively influenced by the amount of basic groups (Figure 7.3b, $R^2 > 0.91$) and the oxygen content (Figure 7.3c, $R^2 > 0.91$), meaning that the high activity of POL-OX@NiFe is likely ascribed to its oxygenated and basic content. The positive influence of oxygenated groups on the surface of carbon-based materials for ODS purposes has been previously reported [1-2]. The reason ascribed for that increased activity is related to the electron-withdrawing capacity of the oxygenated groups; it correlates well with the electron donor ability of the S center from DBT, likely increasing the adsorptive interactions between DBT and the catalyst [3]. In fact, among the polyolefin-derived CNTs (POL@NiFe, POL-P@NiFe, and POL-OX@NiFe), a positive correlation was found between oxygen content and DBT adsorption (Figure 7.4b, $R^2 = 0.98$). PS-OX@NiFe resulted in lower DBT adsorption than expected, given its oxygen content, although this result may be attributed to its lower contact angle, hindering proper contact with DBT.

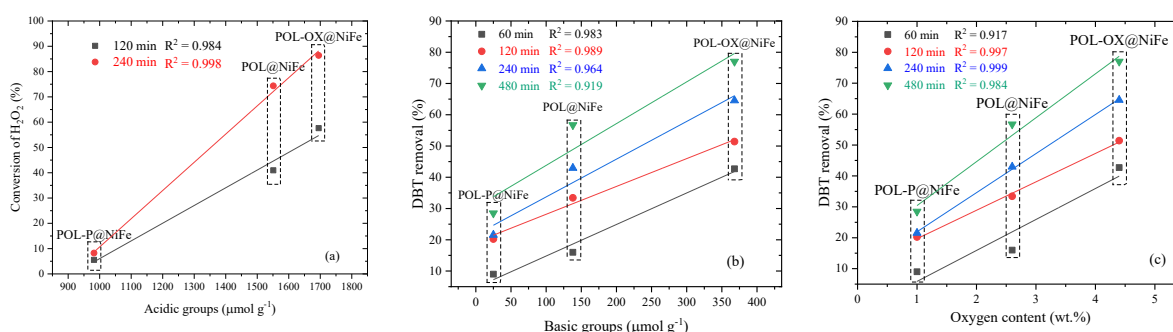


Figure 7.3. Correlation between (a) conversion of hydrogen peroxide at 120 and 240 min *versus* amount of acidic groups, removal of DBT *versus* (b) amount of basic groups and (c) oxygen content for POL-derived CNTs at 60, 120, 240 and 480 min.

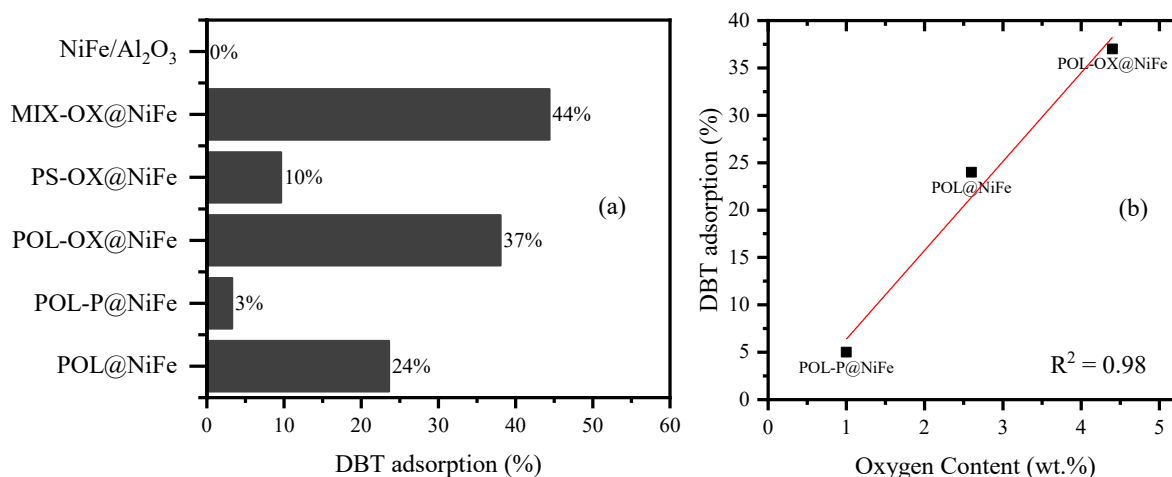


Figure 7.4. (a) Adsorption of DBT (Conditions: [DBT] = 500 mg L⁻¹ in 2,2,4-trimethylpentane, $T = 70\text{ }^{\circ}\text{C}$, $C_{\text{adsorbent}} = 2.5\text{ g L}^{-1}$, 2 h of contact time) and (b) correlation between oxygen content and DBT adsorption for polyolefin-derived CNTs.

By the end of the reaction, the adsorbed products on the catalyst surface were extracted using acetone, and the results regarding the amount of DBT, DBT 5-oxide and DBT 5,5-dioxide recovered from the CNT surface are reported in Figure 7.5. As seen, POL-OX@NiFe, which resulted in a much more

efficient ODS reaction, resulted in almost no DBT adsorbed by the end of the reaction; other intermediates (DBT 5-oxide and DBT-5,5-dioxide) were found in negligible amounts (below 0.1%). Other catalysts resulted in an accumulation of DBT at their surface by the end of the reaction. This accumulation indicates that their primary role, especially POL-P@NiFe, was that of an adsorbent rather than a catalyst. Other reaction products (DBT 5-oxide and DBT 5,5-dioxide) were also identified at the catalyst's surface by the end of the reaction, although they represent less than 0.55% of the sulfur initially loaded.

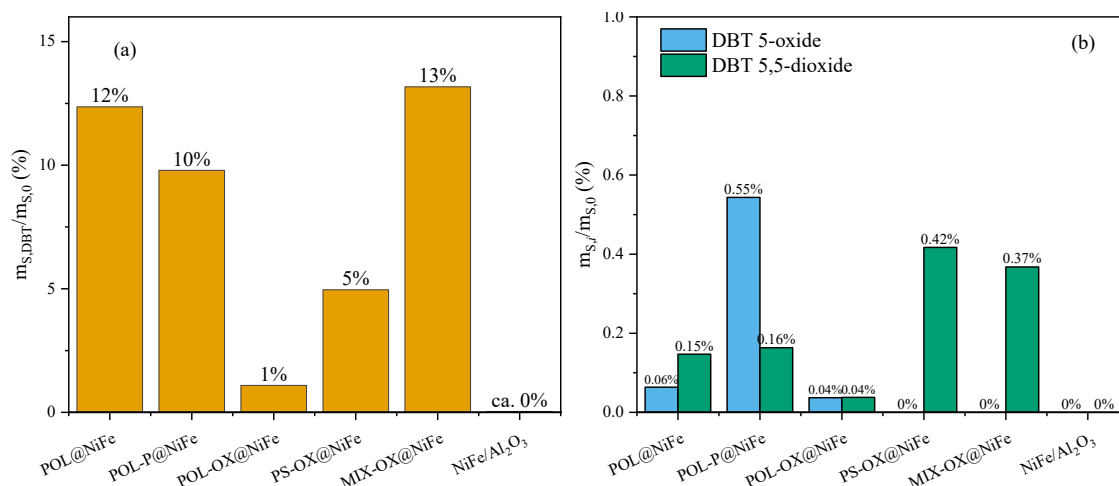


Figure 7.5. (a) DBT and (b) DBT 5-oxide and DBT 5,5-dioxide extracted from the catalyst phase at the end of the reaction.

The efficiency of DBT removal ($\eta_{H_2O_2}^{ODS}$), calculated according to Equation (3.19) – Chapter 3, is shown in Figure 7.6. As can be seen, the highest efficiency was achieved in the presence of POL-P@NiFe. However, this efficiency was only high because a significant amount of DBT remained adsorbed within the catalyst surface (as shown in Figure 7.5a), allied to a low H₂O₂ decomposition (Figure 7.1b). Given the results reported so far, oxidation of the CNT surface with strong acid (as for POL-OX@NiFe) was found to be more interesting for ODS purposes.

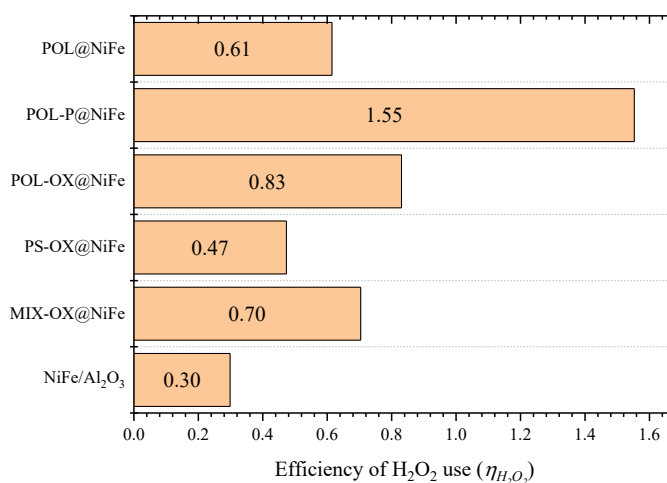


Figure 7.6. Efficiency of H₂O₂ use.

7.2 Effect of polymer source

The removal of DBT from the simulated fuel phase for HNO₃-treated CNTs derived from different polymer feedstock is shown in Figure 7.7. POL-OX@NiFe still maintained a higher removal rate for DBT than the other materials (MIX-OX@NiFe and PS-OX@NiFe), although the differences are not so evident compared to the previous section (Figure 7.1). MIX-OX@NiFe followed a similar trend to POL-OX@NiFe in the first 2 h of reaction (both with *ca.* 48-50% of DBT removal and 55-58% of H₂O₂ conversion), but the removal of DBT stabilized in *ca.* 50% up to the end of the reaction. Both CNTs allowed an H₂O₂ decomposition of 85-90% in 8 h of reaction. PS-OX@NiFe resulted in *ca.* 42% of DBT removal and 97% of H₂O₂ conversion in 8 h of reaction. The conversion of hydrogen peroxide was positively correlated to the total volume of pores of the samples (Figure 7.8a, $R^2 > 0.94$).

As seen in the previous section, the oxygen content was correlated with increased activity towards DBT removal, which all three materials (POL-OX@NiFe, PS-OX@NiFe and MIX-OX@NiFe) possess. Nevertheless, other parameters may also play significant roles in biphasic selective oxidation, such as the contact angle. The DBT removal was positively correlated with the contact angle of the catalyst particles (Figure 7.8b, $R^2 > 0.89$), especially at the first beginning of the reaction (up to 120 min), with a lower contact angle resulting in poorer removal of DBT. Other works have also reported that a suitable hydrophobic character is required for desulfurization activity [4-5]. A suitable wettability allows the catalyst particle to contact both hydrophobic DBT and hydrophilic H₂O₂ properly. The materials POL-OX@NiFe and MIX-OX@NiFe both resulted in materials with a better balance between hydrophilic and hydrophobic characteristics (translating into a contact angle in the range of 100-117°), which explains their similar behavior toward the removal of DBT at the beginning of the reaction. The amount of defects in the material surface, translated into the D/G ratio, was found to inversely correlate to the removal of DBT (Figure 7.8c, $R^2 > 0.91$), meaning that a higher degree of graphitization favors DBT removal (which also correlates inversely with the contact angle, as previously shown in Figure 4.10, Chapter 4). Thus, POL-OX@NiFe higher activity toward DBT removal is ascribed to its oxygen and basic content, associated with its suitable wettability (translated into a contact angle of *ca.* 117°) and degree of graphitization (D/G ratio).

MIX-OX@NiFe and PS-OX@NiFe resulted in a higher content of DBT remaining adsorbed into its surface by the end of the reaction (Figure 7.5a). Other sulfonated compounds (DBT 5-oxide and DBT 5,5-dioxide) were also found in the catalyst phase, representing less than 0.5% of the initially loaded S content for both PS-OX@NiFe and MIX-OX@NiFe.

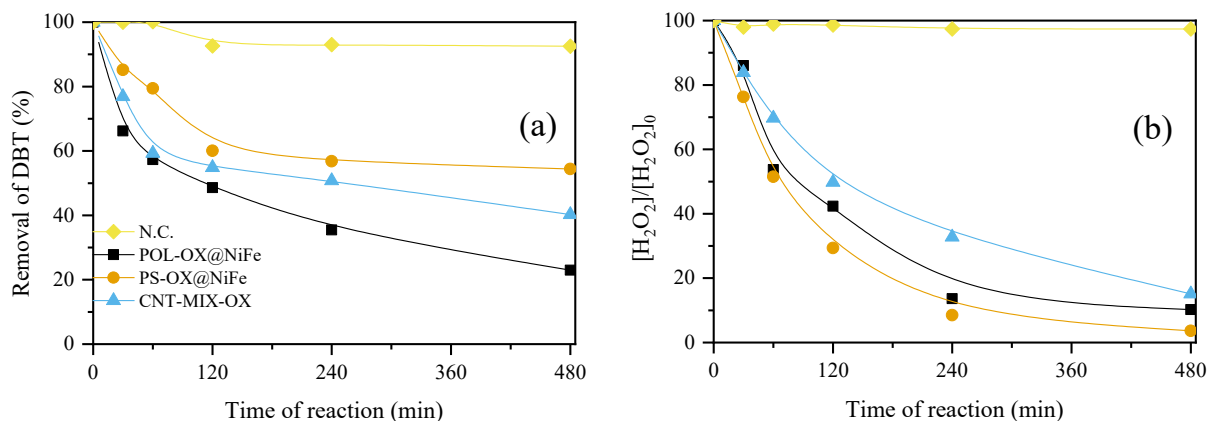


Figure 7.7. (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, water as extractant phase, O/W volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), $T = 70^\circ \text{C}$, 0.1 vol_{water}.% of 1M H_2SO_4 (equivalent to a pH_0 of 3.0).

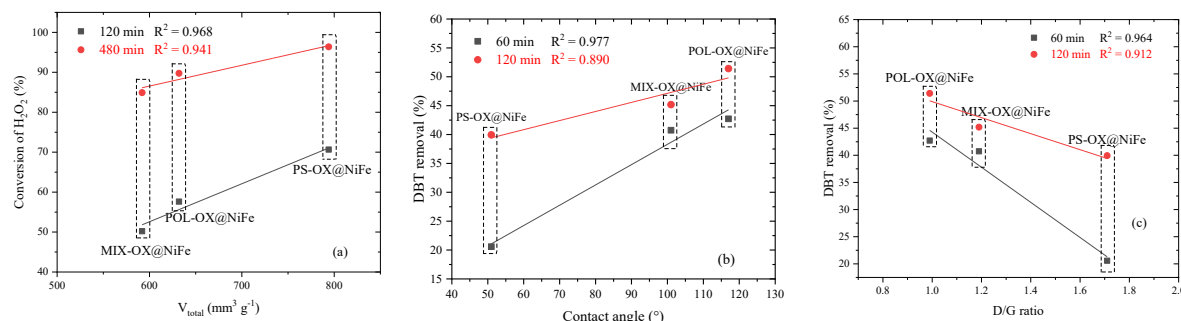


Figure 7.8. Correlations between the (a) conversion of hydrogen peroxide at 120 and 480 min and the total volume of pores and DBT removal at 60 and 120 min (b) versus contact angle and (c) D/G ratio.

7.3 Effect of extractant and co-catalyst

The effect of ACN as extractant, which is frequently used for ODS and ODN purposes, was also investigated using POL-OX@NiFe as catalyst. The results are displayed in Figure 7.9.

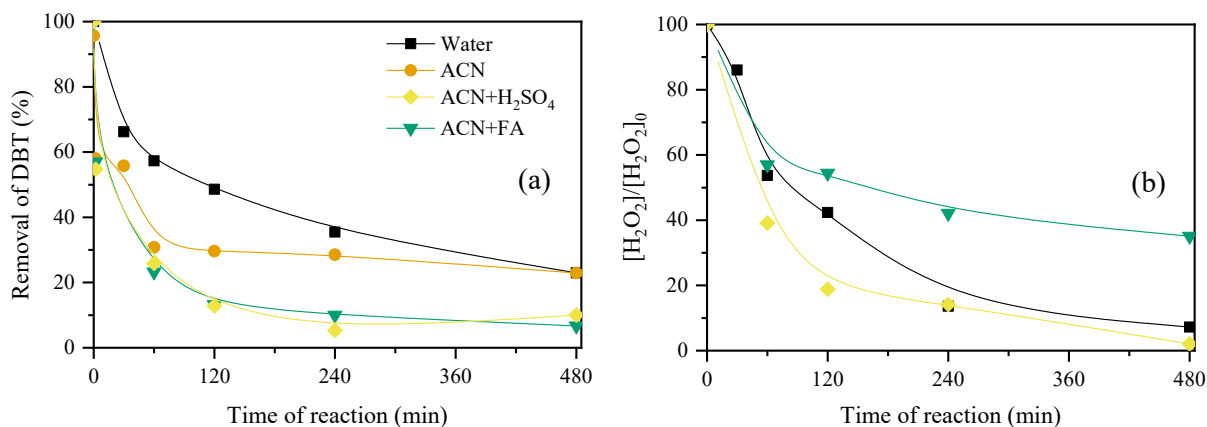


Figure 7.9. (a) Removal of DBT from the oil phase and (b) decomposition of hydrogen peroxide upon time of reaction using POL-OX@NiFe as a catalyst while varying the extractant and co-catalysts. Conditions: $[DBT]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, O/E volume ratio of 80:20, $C_{cat} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $[H_2O_2]_0 = 5.5 \text{ g L}^{-1}$ (H_2O_2/S molar ratio of 15), $T = 70^\circ \text{C}$, 0.1 vol_{extractant}.% of 1M H_2SO_4 or FA.

The replacement of the water phase by pure ACN resulted in a similar removal of DBT from the fuel phase, achieving *ca.* 77% in 8 h of reaction. Nevertheless, the kinetic profile was much more accelerated in the case of ACN as the extractant due to the pure extraction effect (*ca.* 50-60%) of DBT in the presence of ACN (Figure 7.2).

Two co-catalysts were also added to the ACN system (H_2SO_4 and FA). Adding either FA or H_2SO_4 to ACN increased activity towards removing DBT from the fuel phase, resulting in *ca.* 85% of DBT removal in 2 h of reaction. Increasing the reaction time to 8 h resulted in a removal of *ca.* 91% and 94% with H_2SO_4 and FA, respectively. Adding FA resulted in a less pronounced H_2O_2 conversion, whereas adding H_2SO_4 resulted in accelerated H_2O_2 decomposition when ACN is used as extractant. The increased removal of DBT in the presence of both acids may be linked to the lowering of the pH of the medium (initial apparent pH of *ca.* 3.0-3.3), which is associated with a higher yield of oxidizing species, such as hydroxyl radicals [6], given that the redox potential of both H_2O_2 and $\text{HO}^\bullet$ is influenced by the pH, with lower pHs significantly increasing their redox potential [7].

7.4 Reaction products

DBT and its main oxidized products (DBT 5-oxide and DBT 5,5-dioxide) were followed in the extractant phase, and the results are depicted in Figure 7.10. As seen, when ACN is used as an extractant, DBT is initially extracted. For pure ACN or ACN with H_2SO_4 , DBT concentration in the extractant phase reaches its peak within the first 30-60 min of the reaction (Figure 7.1a) and accumulates in the extractant phase. On the other hand, when using formic acid as a co-catalyst, the maximum concentration of DBT in the extractant phase is only reached at 1 h of reaction, likely because FA resulted in a much faster formation of oxidized intermediates (Figure 7.10b and 7.10c). Using FA as co-catalyst resulted in the highest conversion of DBT into DBT 5-oxide (Figure 7.10b), peaking at around 2 h of reaction, with *ca.* 28% of the initially loaded S in the system (equivalent to a concentration of *ca.* 620 mg L^{-1}). As the reaction moves further, the concentration of DBT 5-oxide decreases to *ca.* 500 mg L^{-1} (20% of the initially loaded S). The concentration of DBT 5,5-dioxide (Figure 7.10c), in turn, only achieves its peak by the end of the reaction (*ca.* 35% of the initially loaded S, *ca.* 980 mg L^{-1}).

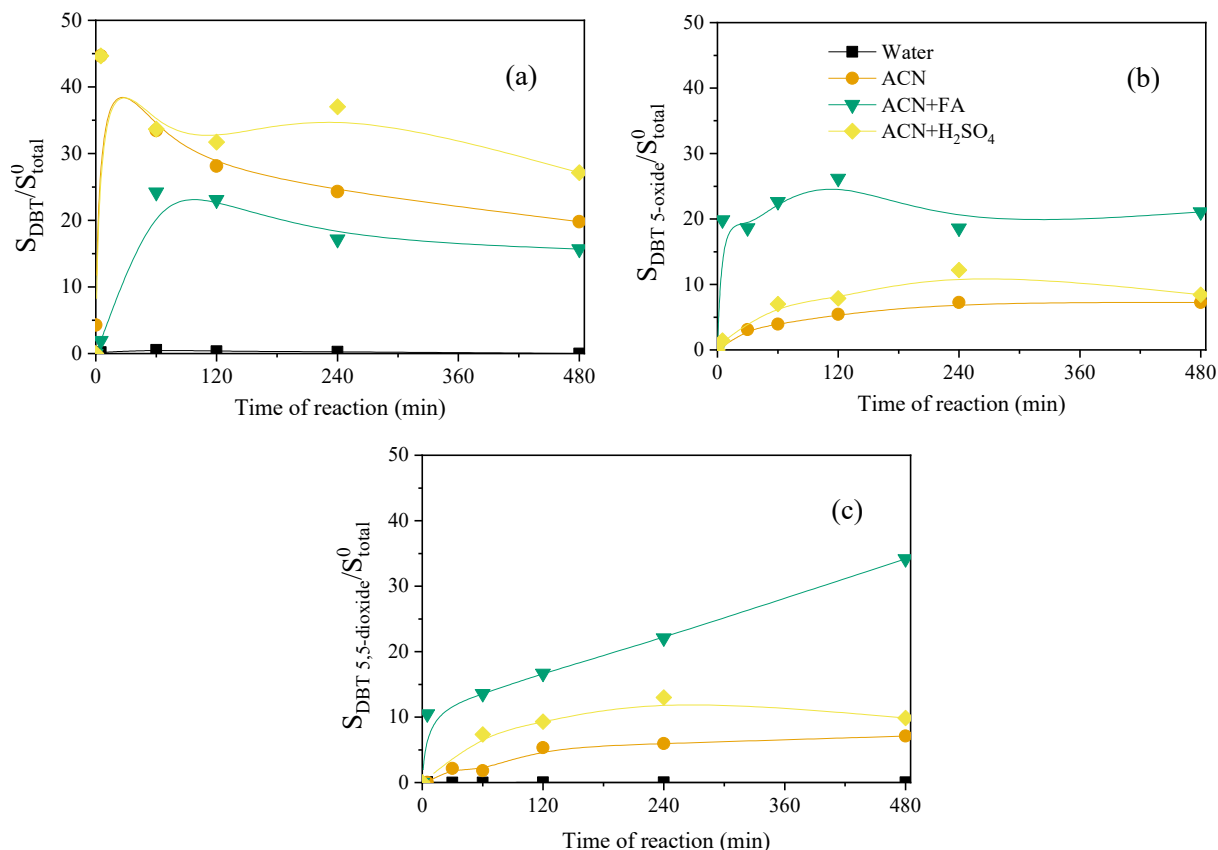


Figure 7.10. (a) DBT in the extractant phase and formation of (b) DBT 5-oxide and (c) DBT 5,5-dioxide using POL-OX@NiFe as a catalyst while varying the extractant and co-catalysts. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$ ($\text{H}_2\text{O}_2/\text{S}$ molar ratio of 15), O/E volume ratio of 80:20, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70^\circ\text{C}$, 0.1 vol_{extractant}.% of 1 M H₂SO₄ or FA.

In the presence of H₂SO₄, DBT 5,5-dioxide peaks at around 2 h of reaction (ca. 13% of initially loaded S) and then its concentration slightly decreases (ca. 9%). The distribution of S per phase is shown in Figure 7.11. The addition of acids in the extractant phase is crucial to ensure deeper desulfurization, and the non-identified S products remain in the range of 3-7%, which is within an acceptable range considering the possible errors in estimating the concentration of DBT and its oxidized intermediates.

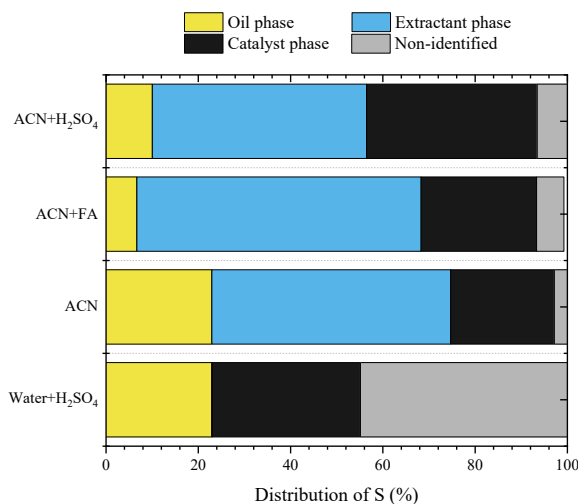


Figure 7.11. Distribution of quantified S-compounds.

The presence of FA in the ACN yield performic acid (HCOOOH) [8] upon reaction with H_2O_2 . Performic acid has a higher potential for direct oxygen transfer compared to H_2O_2 due to a more polarized O-O bond [9]. Additionally, H_2O_2 can also yield hydroxyl radicals (redox potential of 2.80 V_{SHE} at acidic pH [10]) in the presence of suitable catalysts (such as POL-OX@NiFe), contributing to oxidation through a radical pathway. In the ACN/FA system, both pathways are expected to contribute to oxidation, whereas, in the ACN/ H_2SO_4 system, oxidation is expected to be primarily radical-driven due to the absence of performic acid formation. To assess the role of hydroxyl radicals in each system, radical scavenger experiments were performed using ethanol, and the results are depicted in Figure 7.12. In the ACN/ H_2SO_4 system, ethanol addition reduced the formation of DBT 5-oxide (from 9% to 5%) and DBT 5,5-dioxide (from 10% to 4%) after 8 hours, confirming that oxidation predominantly occurs via radical pathways. In contrast, in the ACN/FA system, although a decrease in oxidation was also observed, the effect was less pronounced, with DBT 5-oxide formation reducing from 21% to 18% and DBT 5,5-dioxide from 34% to 20% after 8 hours. This suggests that while hydroxyl radicals contribute to oxidation in the FA-containing system, direct oxygen transfer from performic acid also plays a significant role.

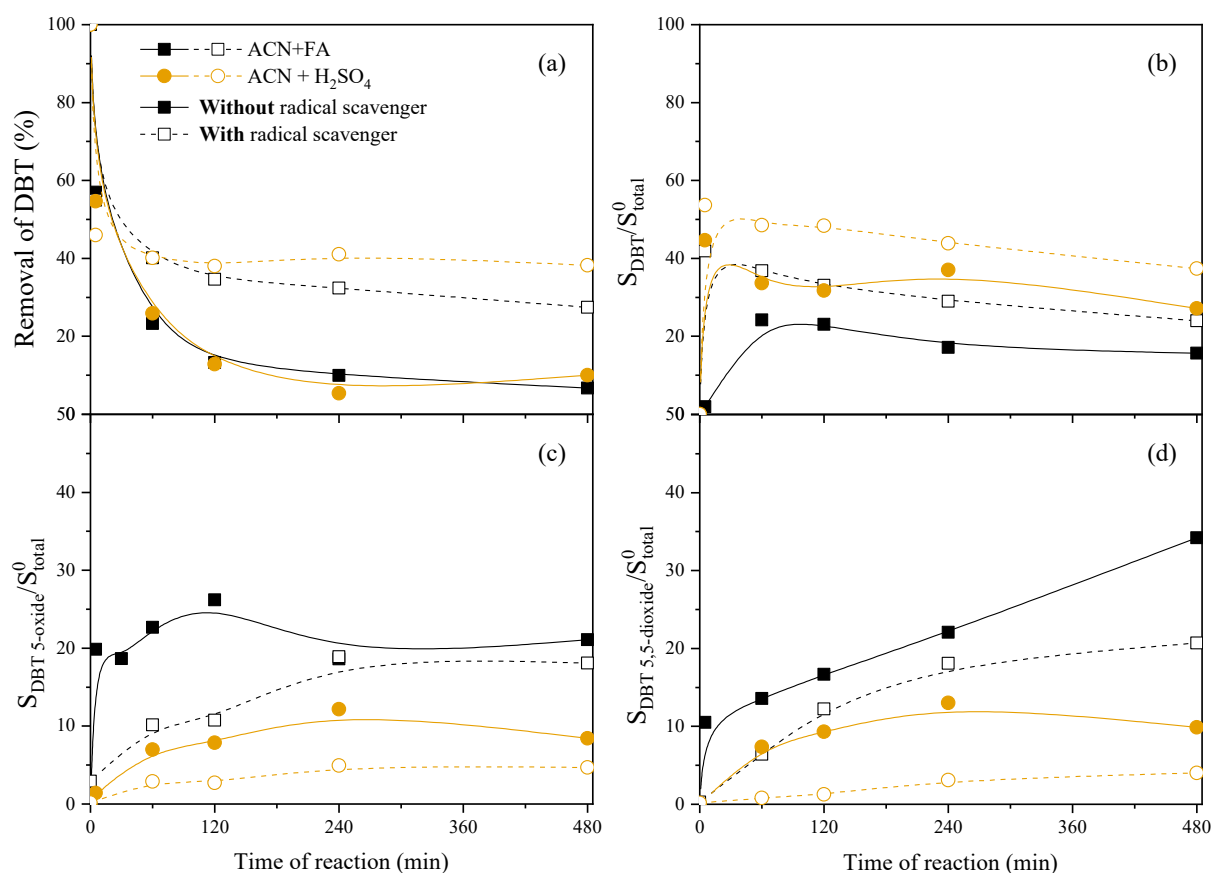


Figure 7.12. (a) DBT in the oil, (b) DBT, (c) DBT 5-oxide and (d) DBT 5,5-dioxide in the extractant phase (ACN) using POL-OX@NiFe as a catalyst in the presence of a radical scavenger. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$ ($\text{H}_2\text{O}_2/\text{S}$ molar ratio of 15), O/E volume ratio of 80:20, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70^\circ\text{C}$, 0.1 vol_{extractant}-% of 1M FA or H_2SO_4 , $\text{H}_2\text{O}_2/\text{EtOH}$ volume ratio of 2.

To further elucidate the effect of FA, additional experiments were conducted (Figure 7.13): (i) in the absence of H_2O_2 and (ii) with FA introduced at 60 min. No significant DBT conversion was observed without H_2O_2 , confirming that FA alone does not induce oxidation. However, when FA was added after 60 min, DBT 5-oxide formation increased sharply from $\sim 5\%$ to $\sim 20\%$ within 5 minutes (data was collected at 65 min to allow for FA homogenization). Simultaneously, DBT concentration in the ACN phase decreased from 35% to 17%, with DBT removal in the oil phase increasing from 61% to 74% within the same timeframe. The effect on DBT 5,5-dioxide formation was minimal. These findings indicate that FA significantly accelerates DBT oxidation upon introduction, reinforcing its role in enhancing oxidation efficiency via performic acid formation.

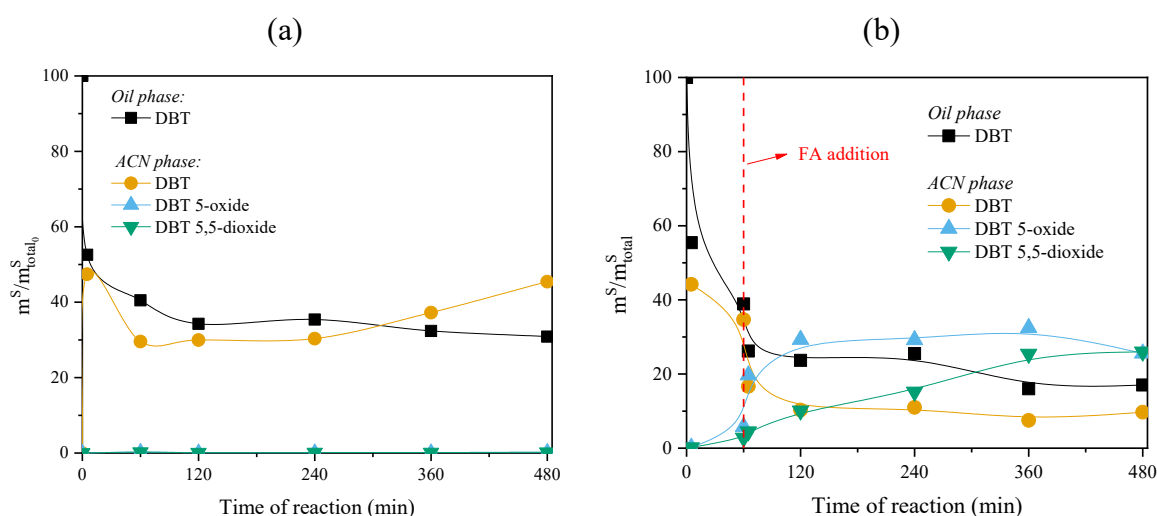


Figure 7.13. DBT in the oil phase and DBT and its oxidized intermediates in the extractant phase using POL-OX@NiFe as a catalyst (a) in the absence of H_2O_2 and (b) with delayed addition of FA. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$ (where applicable), O/E volume ratio of 80:20, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70^\circ \text{C}$, 0.1 vol_{extractant}.% of 1M FA.

When water is used as an extractant, it is barely possible to identify DBT or its oxidized intermediates in the water phase (Figure 7.10), and a significant fraction of the initially loaded S (44%) cannot be identified (Figure 7.11). In the water-oil system, the radical-induced pathway is expected to be the sole oxidation mechanism. Given the high redox potential of hydroxyl radicals and supporting evidence from the literature related to the over-oxidation of DBT 5,5-dioxide [11-12], we anticipate that DBT 5,5-dioxide undergoes further oxidation into other molecules. Such a conclusion was also drawn upon analyzing the TOC of the aqueous phase (Figure 7.14) which could not be explained by the theoretical TOC arising from DBT, DBT 5-oxide or DBT 5,5-dioxide (theoretical TOC was calculated based on concentrations of DBT, DBT 5-oxide and DBT 5,5-dioxide in the water phase as determined by HPLC).

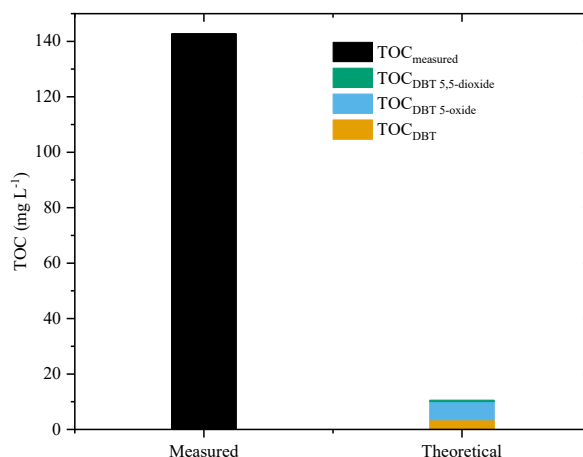


Figure 7.14. TOC of the aqueous phase of the reaction carried out with POL-OX@NiFe. Conditions: $[\text{DBT}]_0 = 500 \text{ mg L}^{-1}$ in 2,2,4-trimethylpentane, $[\text{H}_2\text{O}_2]_0 = 5.5 \text{ g L}^{-1}$, O/W volume ratio of 80:20, $C_{\text{cat}} = 2.5 \text{ g L}^{-1}$ (considering the whole volume of the system), $T = 70^\circ \text{C}$, 0.1 vol_{extractant}.% of 1M H_2SO_4 .

To investigate which compounds were being formed, oil and extractant phases of selected systems were analyzed by GC-MS. The chromatogram for oil and extractant phases is shown in Figures 7.15 and 7.16, respectively. As seen, ACN as extractant results in less DBT in the organic phase compared to water, especially in combination with FA, further confirming the deep desulfurization achieved under this system. Furthermore, it is also possible to identify DBT 5,5-dioxide in the organic phase for reactions carried out with ACN, indicating that oxidation can take place in the oily phase or at the interface between oil-ACN phase. The concentration of DBT 5,5-oxide found in the oil phase corresponds to *ca.* 5 and 15 mg L^{-1} for ACN/ H_2SO_4 and ACN/FA, respectively (equivalent to *ca.* 0.85% and 2.5% of the initially loaded S).

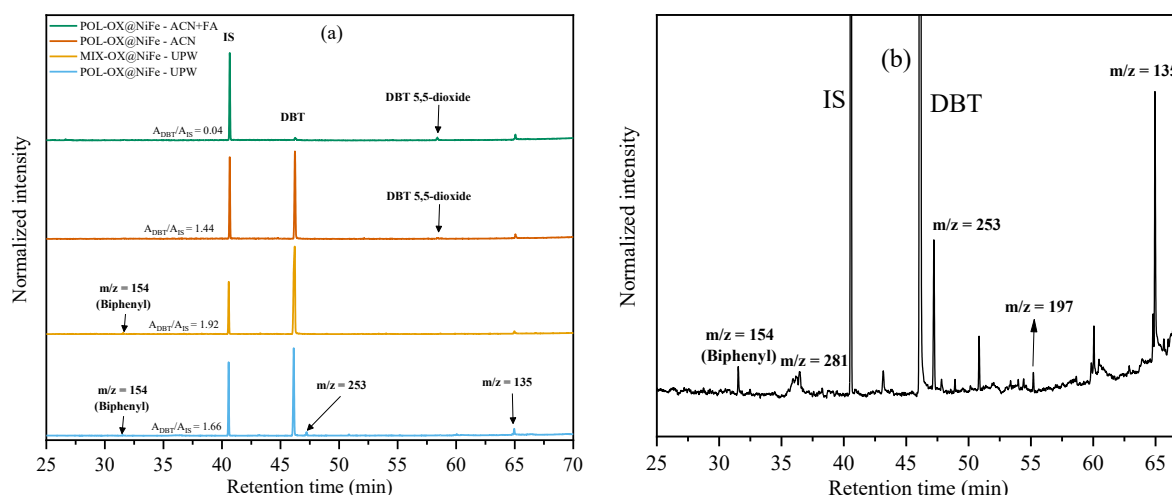


Figure 7.15. (a) Gas chromatogram of oil phase by the end of reaction with different CNTs and extractants and (b) close-up for POL-OX@NiFe using water as extractant.

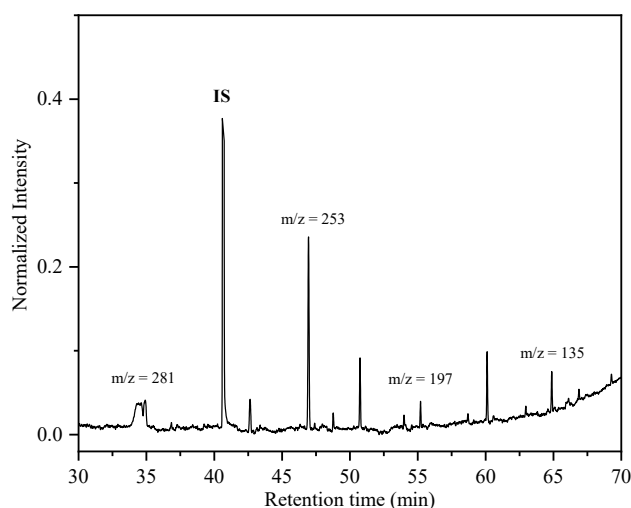


Figure 7.16. Gas chromatogram for the water phase using POL-OX@NiFe as catalyst.

Other reaction products were observed in the reactions carried out in the presence of water as extractant, such as a reaction product with an m/z of 154 (mass spectra Figure 7.17), which has been ascribed to biphenyl (95% of correspondence), indicating that the DBT molecule loses the sulfur atom. Previous reports have indicated that C-S cleavage may take place in the presence of H_2O_2 [13] and in reactions using water phases [14], although such reports are more common for UV- [15-17] or ultrasound-assisted [18-19] desulfurization. Desulfurization processes where C-S cleavage is achieved are highly advantageous, as the removal of bulky sulfonated molecules such as DBT 5,5-dioxide may result in a significant loss of carbon (which means, in fact, a loss of fuel), especially for oily phases with high initial sulfur content [20]. POL-OX@NiFe also resulted in other products with m/z of 253, 281, 197, and 135 in the oil phase (Figure 7.15b) and water phase (Figure 7.16).

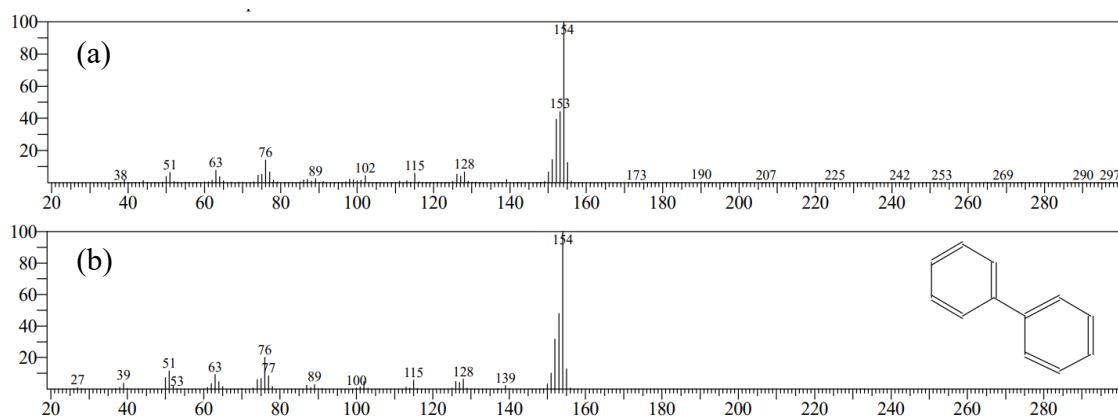


Figure 7.17. (a) Mass spectra of the compound retained at 31 min and (b) mass spectra of biphenyl obtained from the NIST database (correspondence: 95%)

Based on the results gathered, a mechanism for the degradation of DBT in biphasic systems has been proposed (Figure 7.18). Initially, DBT is adsorbed at the catalyst surface, which should display an adequate water contact angle, graphitization degree, oxygen content, and basic groups (as previously identified as the key reasons for POL-OX@NiFe high activity). For reactions carried out in the oil-ACN

system, oxidation follows two possible pathways: (i) radical-driven oxidation, where H_2O_2 is decomposed into hydroxyl radicals ($\text{HO}^\bullet$) by a suitable catalyst or (ii) direct oxygen transfer (if FA is present), where formic acid reacts with H_2O_2 to generate performic acid (HCOOOH). In the oil-ACN system only two oxidized products are observed, DBT 5-oxide and DBT 5,5-dioxide (Figure 7.18a). This is likely due to the lower redox potential of HCOOOH (reported as 1.537 V_{SHE} [21]) and reduced reactivity of hydroxyl radicals in the presence of aprotic solvents, such as ACN [22], resulting in a more controlled and selective oxidation.

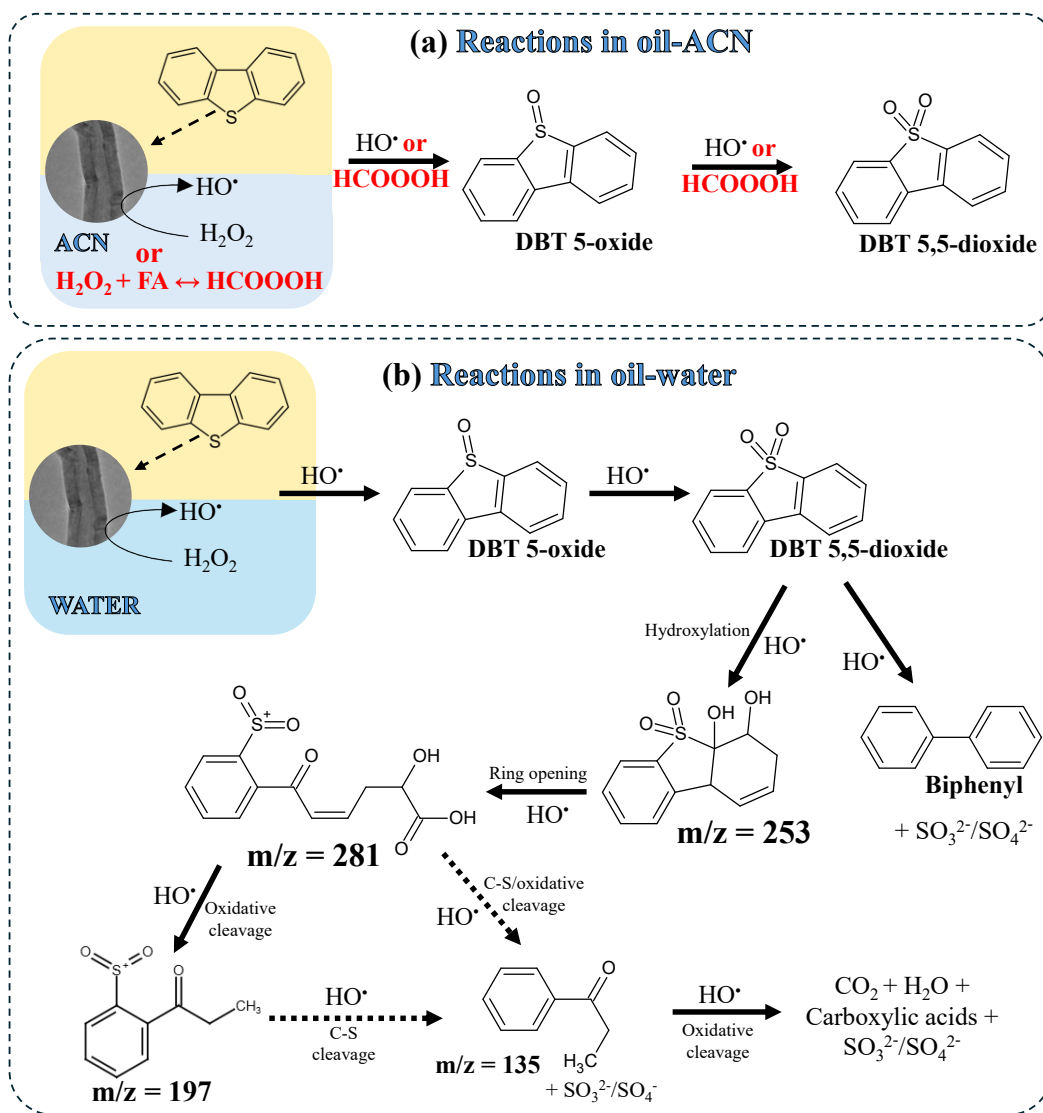


Figure 7.18. Possible reaction pathway in biphasic systems: (a) oil-ACN and (b) oil-water.

For the water-oil biphasic system, only the radical-driven pathway is expected, as no direct oxygen transfer agent is present. A suitable catalyst facilitates H_2O_2 decomposition into $\text{HO}^\bullet$ radicals, which oxidize DBT stepwise to DBT 5-oxide and DBT 5,5-dioxide. Given the high redox potential of $\text{HO}^\bullet$ [10], C–S bond cleavage occurs, yielding biphenyl, similarly as reported elsewhere [12], and sulfate species ($\text{SO}_3^{2-}/\text{SO}_4^{2-}$), which dissolve into the oily and aqueous phase, respectively. Mass spectrometry

(GC-MS) analysis revealed additional oxidation products. A product with m/z 253 is likely a hydroxylated derivative of DBT 5,5-dioxide, formed through additional hydroxyl radical attack, similar to reported in [18]. Further oxidation results in ring opening, forming a compound with m/z of 281, which subsequently can cleavage into smaller species of m/z 197 and 135 (which can also result from C-S cleavage from the molecule with m/z 197), similar to what has been reported elsewhere [18]. These byproducts, predominantly found in the aqueous phase, may undergo further oxidation to carboxylic acids, water, and carbon dioxide. The MS spectra of the possibly oxidized products are shown in Figure 7.19. Other products were also observed at the chromatograms (retention times of 42.7, 48.8, 50.7 and 60.1 min, Figure 7.15b and Figure 7.16) but it was not possible to identify them.

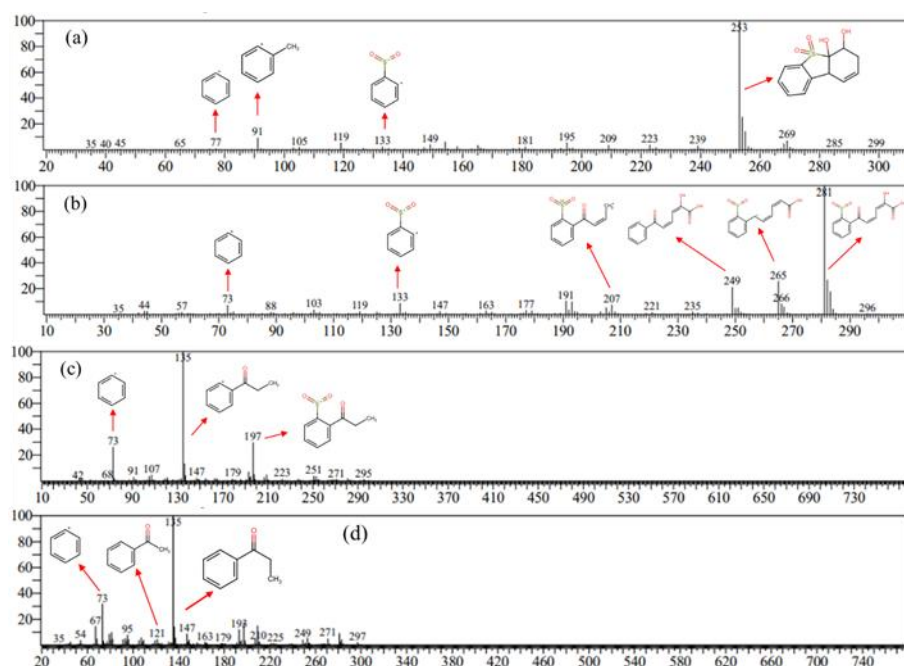


Figure 7.19. MS spectra and fragmentation pattern of compound retained at (a) 47.2 min (m/z of the molecular ion of 253), (b) 36.5 min (m/z molecular ion of 281), (c) compound retained at 55.2 min (m/z molecular ion of 197), (d) compound retained at 64.9 min (m/z molecular ion of 135).

7.5 Comparison with literature

Table 7.1 reports a series of ODS using carbon-based materials using H_2O_2 as an oxidant and either water [8, 23-27] or ACN [28-31] as an extractant phase. Reactions carried out in an oil-acetonitrile biphasic system have been reported using a catalyst concentration in the range $0.8\text{--}10\text{ g L}^{-1}$, an H_2O_2/S molar ratio of 3-330, a temperature of $25\text{--}60\text{ }^\circ\text{C}$, for reaction times of 60-120 min, for an initial sulfur concentration of $0.8\text{--}2189\text{ ppm}$, yielding desulfurization extents from 60-100%. For water-oil biphasic systems, reports indicate desulfurization extents in the range of 20-100% for initial sulfur concentration in the range of $17\text{--}1400\text{ ppm}$, using catalyst concentration in the range $0.5\text{--}3.33\text{ g L}^{-1}$, temperature $25\text{--}90\text{ }^\circ\text{C}$, H_2O_2/S molar ratio of $40\text{--}>3000$, and reaction times of 12-120 min. The present work achieved comparable results (77-91%) using significantly less H_2O_2 (H_2O_2/S of 15) and similar catalyst concentration (2.5 g L^{-1}) and temperature ($70\text{ }^\circ\text{C}$), although it did require significantly higher reaction

times (up to 4 h for ACN/FA system to achieve >91% of DBT removal and 8 h for water as extractant to result in 77% DBT removal).

Table 7.1. ODS using carbon materials as catalysts, H_2O_2 as oxidant and water or ACN as extractant.

Fuel	Catalyst	Extractant	Operational Conditions	Main Results	Ref.
DBT in n-Octane ([S] ₀ = 0.8 ppm)	WO ₃ /CNT	ACN	$V_{fuel}/V_{ACN} = 5:1$, $C_{cat} = 5 \text{ g L}^{-1}$, $H_2O_2/S = 5$, $T = 50 \text{ }^\circ\text{C}$, $t = 60 \text{ min}$.	90% for 4 cycles	[30]
DBT in n-Octane ($C_0 = 2000 \text{ ppm}$)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{fuel}/V_{water} = 10:1$, $C_{cat} = 0.5 \text{ g L}^{-1}$, $H_2O_2/S = 80$, $T = 60 \text{ }^\circ\text{C}$, $t = 12 \text{ min}$, 70 W.	100%	[26]
DBT in Hexane ($C_0 = 1000 \text{ ppm}$)	PET- modified red mud	ACN	$V_{fuel}/V_{ACN} = 10:2$, $C_{cat} = 0.8 \text{ g L}^{-1}$, $H_2O_2/S = 330$, $T = 25 \text{ }^\circ\text{C}$.	80%	[29]
JP-8 fuel ([S] ₀ = 720- 1400 ppm)	AC	H ₂ O ₂ /FA+ Adsorption (Al ₂ O ₃)	$V_{fuel}/V_{water} = 180:45$, $H_2O_2/S = 40-80$, $C_{cat} = 0.5 \text{ g L}^{-1}$, $T = 60 \text{ }^\circ\text{C}$, $t = 90 \text{ min}$.	3–20%. + Adsorption: 75–95%	[8]
DBT in Cyclohexane ([S] ₀ = 50 ppm)	FeMo/CNT	Aqueous H ₂ O ₂ Phase	$V_{fuel}/V_{water} = 5:1$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $H_2O_2/S = 1100$, $T = 25 \text{ }^\circ\text{C}$, $t = 120 \text{ min}$. Emulsion	>60% for 3 cycles	[24]
DBT in Cyclohexane ($C_0 = 500 \text{ ppm}$)	FeMo/CNT	Aqueous H ₂ O ₂ Phase	$V_{fuel}/V_{water} = 5:1$, $C_{cat} = 3.333 \text{ g L}^{-1}$, $H_2O_2/S = 660$, Emulsion	20–100%	[25]
DBT in Cyclohexane ([S] ₀ = 500 ppm)	nZVI@CNT	ACN (2-step)	$V_{fuel} = 10 \text{ mL}$, $C_{cat} = 3.5 \text{ g L}^{-1}$, $H_2O_2/S = 6$, $T = 60 \text{ }^\circ\text{C}$, $t = 120 \text{ min}$.	96% (80% for 6 cycles)	[28]
DBT in Cyclohexane ($C_0 = 100 \text{ ppm}$)	CNT/red mud	Aqueous H ₂ O ₂ Phase	$V_{fuel}/V_{water} = 5:1$, $C_{cat} = 3.333 \text{ g L}^{-1}$, $H_2O_2/S = 3300$, $t = 1 \text{ h}$, Emulsion	82%	[27]
Commercial Diesel ([S] ₀ = 2189 ppm)	AC	ACN /acetic acid	$V_{fuel} = 50 \text{ mL}$, $C_{cat} = 10 \text{ g L}^{-1}$, $H_2O_2/S = 3$, $T = 50 \text{ }^\circ\text{C}$, $t = 1 \text{ h}$.	60%	[31]
Th in n-Hexane) ([S] ₀ = 489 ppm)	HPW/AC	H ₂ O ₂ Aqueous Solution	$V_{fuel}/V_{water} = 20:4$, $C_{cat} = 2 \text{ g L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, $H_2O_2/S = 115$, $t = 120 \text{ min}$, Emulsion.	90%	[23]
DBT in 2,2,4- Trimethylpentane ($C_0 = 500 \text{ ppm}$)	CNT@NiFe +FA	ACN	$V_{fuel}/V_{water} = 80:20$, $C_{cat} = 2.5 \text{ g L}^{-1}$, $H_2O_2/S = 15$, $T = 70 \text{ }^\circ\text{C}$, $t = 240 \text{ min}$.	91%	This study
DBT in 2,2,4- Trimethylpentane ($C_0 = 500 \text{ ppm}$)	CNT@NiFe	Aqueous H ₂ O ₂ Phase	$V_{fuel}/V_{water} = 80:20$, [cat] = 2.5 g L^{-1} , $H_2O_2/S = 15$, $T = 70 \text{ }^\circ\text{C}$, $t = 480 \text{ min}$.	77%	This study

7.6 Conclusions

This study demonstrates the effectiveness of acid-treated carbon nanotube catalysts, especially those derived from polyolefins, for the oxidative desulfurization of dibenzothiophene in a biphasic system. Among the catalysts tested, POL-OX@NiFe exhibited the highest catalytic performance, achieving up to 77% DBT removal in a water-oil system in 8 h of reaction, which further increased to 91% in an ACN-oil system with formic acid as co-catalyst in just 4 h of reaction. Several aspects of the materials

correlate with the displayed activity, and the content of oxygen, D/G ratio, textural properties and contact angle should be highlighted as key characteristics that need to be tuned to ensure suitable results.

Using water as an extractant resulted in over-oxidation of typically found DBT oxidized products (DBT 5-oxide and DBT 5,5-dioxide), resulting in C-S bond cleavage. Such a result allows for true desulfurization by forming smaller sulfur-free products. However, it does come with lower overall DBT removal efficiency compared to the ACN-oil biphasic system.

These results demonstrate that CNTs derived from polymers, in particular polyolefins, are promising for deep desulfurization, aligning with both waste valorization and cleaner fuel production goals. By replacing traditional non-renewable carbon sources with plastic waste, this approach helps reducing plastic accumulation in landfills and decreases reliance on fossil resources. Furthermore, it offers a more sustainable and circular pathway for upcycling plastic waste while enhancing fuel purification efficiency, contributing to a greener and more eco-friendly fuel production process.

7.7 References

- [1] Z.C. Kampouraki, D.A. Giannakoudakis, K.S. Triantafyllidis, E.A. Deliyanni, Catalytic oxidative desulfurization of a 4,6-DMDBT containing model fuel by metal-free activated carbons: the key role of surface chemistry, *Green Chemistry*, 21 (2019) 6685-6698. <https://doi.org/10.1039/C9GC03234G>
- [2] Q. Gu, Y. Ding, Z. Liu, Y. Lin, R. Schlögl, S. Heumann, D. Su, Probing the intrinsic catalytic activity of carbon nanotubes for the metal-free oxidation of aromatic thiophene compounds in ionic liquids, *Journal of Energy Chemistry*, 32 (2019) 131-137. <https://doi.org/10.1016/j.jechem.2018.07.004>
- [3] F.F. Roman, J.L. Diaz de Tuesta, A.M.T. Silva, J.L. Faria, H.T. Gomes, Carbon-Based Materials for Oxidative Desulfurization and Denitrogenation of Fuels: A Review, *Catalysts*, 11 (2021) 1239. <https://doi.org/10.3390/catal11101239>
- [4] S. Dou, Y. Feng, K. Liu, X. Wang, B. Zhang, C. Yang, M. Sun, Y. Liu, F. Cheng, W. Zhou, E. Duan, A deep-insight into the relation between structure of graphene oxide-based interfacial catalyst and fuel oil desulfurization performance in Pickering emulsion, *Separation and Purification Technology*, 334 (2024) 125992. <https://doi.org/10.1016/j.seppur.2023.125992>
- [5] H. Liu, C. Liu, N. Zhen, J. Dong, Y. Chi, C. Hu, Amphiphilic polyoxoniobate-based recoverable Pickering emulsion for effective oxidative desulfurization, *Applied Catalysis A: General*, 656 (2023) 119133. <https://doi.org/10.1016/j.apcata.2023.119133>
- [6] A. Fischbacher, C. von Sonntag, T.C. Schmidt, Hydroxyl radical yields in the Fenton process under various pH, ligand concentrations and hydrogen peroxide/Fe(II) ratios, *Chemosphere*, 182 (2017) 738-744. <https://doi.org/10.1016/j.chemosphere.2017.05.039>
- [7] G. Yu, S. Lu, H. Chen, Z. Zhu, Oxidative Desulfurization of Diesel Fuels with Hydrogen Peroxide in the Presence of Activated Carbon and Formic Acid, *Energy & Fuels*, 19 (2004) 447-452. <https://doi.org/10.1021/ef049760b>
- [8] M.T. Timko, E. Schmois, P. Patwardhan, Y. Kida, C.A. Class, W.H. Green, R.K. Nelson, C.M. Reddy, Response of Different Types of Sulfur Compounds to Oxidative Desulfurization of Jet Fuel, *Energy & Fuels*, 28 (2014) 2977-2983. <https://doi.org/10.1021/ef500216p>
- [9] C. Shi, C. Li, Y. Wang, J. Guo, S. Barry, Y. Zhang, N. Marmier, Review of Advanced Oxidation Processes Based on Peracetic Acid for Organic Pollutants, *Water*, 14 (2022) 2309. <https://doi.org/10.3390/w14152309>
- [10] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes, Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review, *Applied Catalysis B: Environmental*, 187 (2016) 428-460. <https://doi.org/10.1016/j.apcatb.2016.01.033>
- [11] S.A. Hosseini, V. Majidi, A.R. Abbasian, Photocatalytic desulfurization of dibenzothiophene by NiCo₂O₄ nanospinel obtained by an oxidative precipitation process modeling and optimization, *Journal of Sulfur Chemistry*, 39 (2018) 119-129. <https://doi.org/10.1080/17415993.2017.1369981>
- [12] M. Zarrabi, M.H. Entezari, E.K. Goharshadi, Photocatalytic oxidative desulfurization of dibenzothiophene by C/TiO₂@MCM-41 nanoparticles under visible light and mild conditions, *RSC Advances*, 5 (2015) 34652-34662. <https://doi.org/10.1039/C5RA02513C>
- [13] N. d'Alessandro, L. Tonucci, M. Bonetti, M. Di Deo, M. Bressan, A. Morvillo, Oxidation of dibenzothiophene by hydrogen peroxide or monopersulfate and metal-sulfophthalocyanine catalysts: an easy access to biphenylsultone or 2-(2'-hydroxybiphenyl)sulfonate under mild conditions, *New Journal of Chemistry*, 27 (2003) 989-993. <https://doi.org/10.1039/B212152B>
- [14] B. Bertleff, J. Claußnitzer, W. Korth, P. Wasserscheid, A. Jess, J. Albert, Extraction Coupled Oxidative Desulfurization of Fuels to Sulfate and Water-Soluble Sulfur Compounds Using Polyoxometalate Catalysts and Molecular Oxygen, *ACS Sustainable Chemistry & Engineering*, 5 (2017) 4110-4118. <https://doi.org/10.1021/acssuschemeng.7b00087>
- [15] W. Shi, X. Zhou, Y. Kong, J. Li, I.E. Marko, Unique Thia-Baeyer-Villiger-Type Oxidation of Dibenzothiophene Sulfoxides Derivatives, *Chemistry: An Asian Journal*, 15 (2020) 511-517. <https://doi.org/10.1002/asia.201901671>
- [16] S. Moradi, M. Vossoughi, M. Feilizadeh, S.M.E. Zakeri, M.M. Mohammadi, D. Rashtchian, A. Yoosefi Booshehri, Photocatalytic degradation of dibenzothiophene using La/PEG-modified TiO₂ under visible light

- irradiation, *Research on Chemical Intermediates*, 41 (2014) 4151-4167. <https://doi.org/10.1007/s11164-013-1519-z>
- [17] M. Bagheri, M.Y. Masoomi, A. Morsali, A MoO₃-Metal-Organic Framework Composite as a Simultaneous Photocatalyst and Catalyst in the PODS Process of Light Oil, *ACS Catalysis*, 7 (2017) 6949-6956. <https://doi.org/10.1021/acscatal.7b02581>
- [18] D. Margeta, I. Grcic, S. Papic, K. Sertic-Bionda, L. Foglar, Impact of ultrasound application on oxidative desulphurization of diesel fuel and on treatment of resulting wastewater, *Environmental Technology*, 37 (2016) 293-299. <https://doi.org/10.1080/09593330.2015.1068870>
- [19] I. Grčić, S. Papić, Sonochemical treatment of effluent originating from desulfurization process; validation of predictive models, *Applied Acoustics*, 103 (2016) 232-238. <https://doi.org/10.1016/j.apacoust.2015.09.005>
- [20] G.H.C. Prado, Y. Rao, A. de Klerk, Nitrogen Removal from Oil: A Review, *Energy Fuels*, 31 (2017) 14-36. <https://doi.org/10.1021/acs.energyfuels.6b02779>
- [21] C. Nabintu Kajoka, J. Gasperi, S. Brosillon, E. Caupos, E. Mebold, M. Oliveira, V. Rocher, G. Chebbo, J. Le Roux, Reactivity of Performic Acid with Organic and Inorganic Compounds: From Oxidation Kinetics to Reaction Pathways, *ACS ES&T Water*, 3 (2023) 3121-3131. <https://doi.org/10.1021/acsestwater.3c00279>
- [22] S. Mitroka, S. Zimmeck, D. Troya, J.M. Tanko, How solvent modulates hydroxyl radical reactivity in hydrogen atom abstractions, *Journal of the American Chemical Society*, 132 (2010) 2907-2913. <https://doi.org/10.1021/ja903856t>
- [23] J. Xiao, L. Wu, Y. Wu, B. Liu, L. Dai, Z. Li, Q. Xia, H. Xi, Effect of gasoline composition on oxidative desulfurization using a phosphotungstic acid/activated carbon catalyst with hydrogen peroxide, *Applied Energy*, 113 (2014) 78-85. <https://doi.org/10.1016/j.apenergy.2013.06.047>
- [24] R.V. Mambrini, C.Z. Maia, J.D. Ardisson, P.P. de Souza, F.C.C. Moura, Fe/C and FeMo/C hybrid materials for the biphasic oxidation of fuel contaminants, *New Journal of Chemistry*, 41 (2017) 142-150. <https://doi.org/10.1039/C6NJ02718K>
- [25] I.F. Teixeira, A.A.d.S. Oliveira, T. Christofani, F.C.C. Moura, Biphasic oxidation promoted by magnetic amphiphilic nanocomposites undergoing a reversible emulsion process, *Journal of Materials Chemistry A*, 1 (2013) 10203-10208. <https://doi.org/10.1039/C3TA11535F>
- [26] L. Liu, Y. Zhang, W. Tan, Synthesis and characterization of phosphotungstic acid/activated carbon as a novel ultrasound oxidative desulfurization catalyst, *Frontiers of Chemical Science and Engineering*, 7 (2013) 422-427. <https://doi.org/10.1007/s11705-013-1353-2>
- [27] A.A.S. Oliveira, I.F. Teixeira, T. Christofani, J.C. Tristão, I.R. Guimarães, F.C.C. Moura, Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue, *Applied Catalysis B: Environmental*, 144 (2014) 144-151. <https://doi.org/10.1016/j.apcatb.2013.07.015>
- [28] G. Zhang, F. Yang, W. Yang, Y. Li, N-doped carbon nanotube encapsulated nZVI as a high-performance bifunctional catalyst for oxidative desulfurization, *Particuology*, 81 (2023) 109-118. <https://doi.org/10.1016/j.partic.2023.01.002>
- [29] N.T. do Prado, A.P. Heitmann, H.S. Mansur, A.A. Mansur, L.C.A. Oliveira, C.S. de Castro, PET-modified red mud as catalysts for oxidative desulfurization reactions, *Journal of Environmental Sciences*, 57 (2017) 312-320. <https://doi.org/10.1016/j.jes.2017.01.011>
- [30] C. Wang, A. Li, J. Xu, J. Wen, H. Zhang, L. Zhang, Preparation of WO₃/CNT catalysts in presence of ionic liquid [C₁₆mim]Cl and catalytic efficiency in oxidative desulfurization, *Journal of Chemical Technology & Biotechnology*, 94 (2019) 3403-3412. <https://doi.org/10.1002/jctb.6154>
- [31] K.-G. Haw, W.A.W.A. Bakar, R. Ali, J.-F. Chong, A.A.A. Kadir, Catalytic oxidative desulfurization of diesel utilizing hydrogen peroxide and functionalized-activated carbon in a biphasic diesel-acetonitrile system, *Fuel Processing Technology*, 91 (2010) 1105-1112. <https://doi.org/10.1016/j.fuproc.2010.03.021>

CHAPTER 8 - GENERAL CONCLUSIONS

8.1 Conclusions

This Ph.D. thesis proposed a coupled strategy that converts PSW into functional catalysts for low-sulfur and low-nitrogen fuel production, addressing pressing environmental and industrial challenges. This innovative approach not only mitigates plastic waste accumulation but also contributes to cleaner fuel technologies, offering an economically viable solution for a more sustainable and resource-efficient future.

This study successfully demonstrated the synthesis of graphitic carbon nanomaterials, including carbon nanotubes (CNTs), from simulated and real plastic waste (PSW) using catalytic chemical vapor deposition (CVD) over Fe- and NiFe-based catalysts. The results highlight the significant influence of synthesis temperature and catalyst composition on the yield, morphology, and properties of the CNTs. Increasing the synthesis temperature from 600 °C to 800 °C using Fe/Al₂O₃ not only improved the yield (from 5% to 12%) but also facilitated the formation of hollow tubes, characteristic of CNTs. The use of a bimetallic catalyst NiFe/Al₂O₃ further enhanced the yield, reaching up to 25%, and resulting in diverse CNT morphologies, including cup-stacked and coiled structures, compared to the predominantly straight-walled CNTs synthesized using Fe-based catalysts. The higher D/G ratios (>0.92) observed for NiFe-derived CNTs compared to Fe-derived CNTs (0.67–0.91) reflect their increased structural defects, which could be tailored for specific catalytic applications.

Post-synthesis acid treatments introduced surface functional groups, especially oxygenated species, which enhanced the hydrophilicity and catalytic activity of the CNTs and partially removed impurities. However, harsher oxidative treatments increased structural defects and reduced CNT diameters. Thermogravimetric analysis (TGA) revealed that NiFe-derived CNTs exhibited higher thermal stability, with decomposition temperatures of 640–650 °C, compared to Fe-derived CNTs, which decomposed at 590–600 °C, likely due to catalytic effects from residual metal particles.

The synthesized CNTs were highly active catalysts for various oxidation reactions. The Fe-derived CNTs were highly active in the degradation of quinoline during catalytic wet peroxide oxidation. Building upon those results, they were tested for oxidative denitrogenation (ODN) of quinoline (QN) under an oil-water biphasic system. Fe-derived catalysts enabled complete QN removal within 60–240 min, depending on the specific CNT catalyst, under operating conditions of 80 °C, aqueous-phase pH 3.0, catalyst loading of 2.5 g L⁻¹, oil-to-water volume ratio of 80:20, and initial H₂O₂ concentration of 247 g L⁻¹. POL-P@Fe, synthesized from a blend of LDPE, HDPE, and PP, achieved over 98% QN removal in 1 h and retained its activity across six catalytic cycles. Furthermore, the CNTs acted as phase transfer catalysts, overcoming mass transfer limitations between the oil and aqueous phases, significantly enhancing the reaction efficiency. POL-P@Fe also demonstrated versatility by removing significant amounts of pyridine and effectively addressing mixtures of quinoline and pyridine in

simulated fuel systems. Optimization of reaction conditions using NiFe-based materials was also carried out, and POL-OX@NiFe demonstrated superior catalytic activity, mainly attributed to its enhanced phase transfer properties, which has been found as the rate-determining step in the ODN of QN. Under optimized conditions (70 °C, aqueous-phase pH of 3.0, catalyst loading of 2.5 g L⁻¹, oil-to-water volume ratio of 80:20, and initial H₂O₂ concentration of 12 g L⁻¹), 89% of QN was removed from the fuel phase using POL-OX@NiFe in 1 h of reaction, allowing to reach an efficiency of hydrogen peroxide consumption of 77%.

In addition to ODN, NiFe-derived CNTs were also tested for the oxidative desulfurization (ODS) of dibenzothiophene (DBT) in biphasic systems (oil-water and oil-ACN). Acid-treated CNTs such as POL-OX@NiFe demonstrated superior performance, achieving up to 91% DBT removal in 4 h using an ACN-oil system with formic acid as co-catalyst. Up to 77% DBT removal was achieved in water-oil systems in 8 h. Key material properties such as oxygen content, D/G ratio, textural characteristics, and wettability strongly influenced the activity. Notably, using water as an extractant resulted in the over-oxidation of DBT to smaller, sulfur-free compounds, demonstrating true desulfurization, though with a slightly lower overall efficiency than the ACN-oil system.

This study highlights the potential of upcycled CNTs derived from PSW as efficient, sustainable, and versatile catalysts for oxidation processes, such as ODS and ODN. The findings emphasize the role of CNT structural and surface properties in determining catalytic performance and highlight the importance of tailored synthesis and post-treatment methods. This approach not only promotes the valorization of plastic solid waste but also contributes to cleaner fuel production and aligns with the principles of circular economy, demonstrating a pathway toward integrating waste management and sustainable energy technologies.

8.2 Future Work

Some suggestions for future work are presented below:

- Investigate other support for the preparation of CVD catalysts (such as SiO₂ and MgO), including waste sources (such as red mud), to understand the effects of the support on the carbon nanotubes.
- Investigate the introduction (during or post-synthesis) of other heteroatoms (N and S) and their effect on CNTs properties and catalytic activity.
- Investigate the ODS/ODN system using more complex fuels, including simulated fuels containing different solvents, nitrogenated and sulfonated compounds, and real fuels.
- Model the reaction kinetics for the ODS system, comparing water and acetonitrile as extractants.

- Develop pilot-scale processes for CNT production from waste plastics and assess the techno-economic feasibility of integrating this into industrial applications.
- Conduct a life cycle assessment (LCA) to understand better the environmental benefits of upcycling plastics into CNTs and their application in fuel purification.
- Expand the use of these CNT materials to other catalytic applications, such as wastewater treatment, CO₂ capture, or biomass conversion.