

Article

Heteroatom (N, S) Co-Doped CNTs in the Phenol Oxidation by Catalytic Wet Air Oxidation

Raquel P. Rocha ^{*}, Olívia Salomé G. P. Soares , José J. M. Órfão , Manuel Fernando R. Pereira 
and José L. Figueiredo 

Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; salome.soares@fe.up.pt (O.S.G.P.S.); jjmo@fe.up.pt (J.J.M.Ó.); fpereira@fe.up.pt (M.F.R.P.); jlfig@fe.up.pt (J.L.F.)

* Correspondence: rprocha@fe.up.pt; Tel.: +351-22-041-4874

Abstract: The N, S-co-doping of commercial carbon nanotubes (CNTs) was performed by a solvent-free mechanochemical approach using thiourea. CNTs were mixed with the N, S-dual precursor in a ball-milling apparatus, and further thermally treated under inert atmosphere between 600 and 1000 °C. The influence of the temperature applied during the thermal procedure was investigated. Textural properties of the materials were not significantly affected either by the mechanical step or by the heating phase. Concerning surface chemistry, the developed methodology allowed the incorporation of N (up to 1.43%) and S (up to 1.3%), distributed by pyridinic (N6), pyrrolic (N5), and quaternary N (NQ) groups, and C–S–, C–S–O, and sulphate functionalities. Catalytic activities of the N, S-doped CNTs were evaluated for the catalytic wet air oxidation (CWAQ) of phenol in a batch mode. Although the samples revealed a similar catalytic activity for phenol degradation, a higher total organic carbon removal (60%) was observed using the sample thermally treated at 900 °C. The improved catalytic activity of this sample was attributed to the presence of N6, NQ, and thiophenic groups. This sample was further tested in the oxidation of phenol under a continuous mode, at around 30% of conversion being achieved in the steady-state.

Keywords: metal-free carbon catalysts; N, S-co-doping; carbon nanotubes; catalytic wet air oxidation



Citation: Rocha, R.P.; Soares, O.S.G.P.; Órfão, J.J.M.; Pereira, M.F.R.; Figueiredo, J.L. Heteroatom (N, S) Co-Doped CNTs in the Phenol Oxidation by Catalytic Wet Air Oxidation. *Catalysts* **2021**, *11*, 578. <https://doi.org/10.3390/catal11050578>

Academic Editor: Francisco Javier Rivas Toledo

Received: 9 April 2021
Accepted: 26 April 2021
Published: 30 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Wet air oxidation (WAO) is an alternative to conventional technologies for the treatment of organic pollutants in wastewaters, especially from highly pollutant industries such as pulp and paper industries, petrochemicals, and wine distilleries [1,2]. The process is suitable to treat organic compounds that show some resistance to conventional treatment technologies or to treat effluents presenting concentrations too high to be treated by biological processes or too low for incineration. It is classified as an advanced oxidation process (AOP), since it is based on the production and use of strongly reactive radicals to mineralise the organic compounds into CO₂ and H₂O or into easily biodegradable by-products. In this case, the strongly oxidizing radicals are formed by the use of pure oxygen or air. To ensure the solubility of oxygen and to promote fast mineralisation and degradation rates, high temperatures (200–320 °C) and pressures (20–200 bar) are required [3–5]. In the last decades, efforts have been made to decrease such severe operating conditions by the addition of homogeneous or heterogeneous catalysts, mostly based on the use of noble metals and metal oxides [6–13]. However, the scarcity of these materials, and the frequent leaching and deactivation phenomena, have prevented the design of a clean catalytic wet air oxidation (CWAQ) process [7,14]. During some of these studies, carbon materials were tested as supports for these metals and oxides, and it was found that the carbon material could act as a catalyst on its own, and not only as a support. This opened the opportunity for carbon materials as an alternative metal-free catalyst for CWAQ [15–25]. Along the years,

mesoporous carbon xerogels, carbon fibers and foams, carbon blacks, carbon nanotubes (CNTs) and nanofibers (CNFs), and also graphene-based materials were investigated in CWAQ [26–33]. The outstanding ability to tune the textural and chemical properties of carbon materials make them potential catalyst candidates for a sustainable technology. To improve the performance of carbon materials in CWAQ, several authors have taken advantage of the unsaturated carbon atoms at the edges of the graphene layers and at basal plane defects to form various types of surface functional groups containing O, N, S, B or P [34–40]. However, almost all of these studies were dedicated to studying each isolated heteroatom (N, S, B, P), while synergic benefits of using two or more heteroatoms have been reported in the literature [41–43], at least in the field of renewable energy, where metal-free carbon materials have also been widely studied [44–48]. As far as we know, the combination of two heteroatoms, particularly N and S, was never investigated in previous works as metal-free catalysts for CWAQ. Exploiting our expertise in developing novel catalysts using fine surface functionalisation of carbon materials by easy-to-handle solvent-free methodologies [34,37,38,49], a systematic study was performed to assess the influence of surface N and S heteroatoms in CWAQ. Nitrogen and sulphur have been selected since both can act as electron donors, and show different changes in the electronic density of states [50] that affect π electrons in the carbon lattice. Thiourea was selected as a precursor for the N, S-doping of CNTs.

2. Results and Discussion

2.1. Materials Characterisation

Table 1 summarises the textural properties of the prepared samples. The textural properties were determined from the N_2 adsorption isotherms, with the available surface area of the samples being determined according to the standard Brunauer, Emmett, and Teller method (S_{BET}). The mechanical and thermal treatment promoted an increase of S_{BET} from 291 to 350 $m^2 g^{-1}$, when the pristine CNT and CNT@TU600 are compared, respectively. The slight increase may be due to the opening of the CNT closed tips during ball milling, commonly observed when CNTs and powder precursors are mixed under ball milling [37]. The thermal treatments applied at higher temperatures did not promote additional changes in S_{BET} (differences smaller than 24 $m^2 g^{-1}$, which is close to the estimated experimental error of 20 $m^2 g^{-1}$). The total pore volume (V_p , experimental error $\pm 0.005 cm^3 g^{-1}$) of the CNT@TU600 sample decreases by almost half of the pristine CNT sample (determined from the N_2 uptake at $p/p_0 = 0.95$), but after that slightly increases for the samples heat treated at 700 °C. For the samples treated at the other temperatures, V_p marginally increases. While in the CNT@TU600 sample a higher agglomeration of the material may cause the abrupt V_p decrease, the increase of the temperature to higher temperatures contributes to the recovery of free space in the CNT bundles.

Table 1. Textural characterisation of N, S-co-doped CNT samples.

Sample	Textural Properties N_2 Adsorption	
	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)
Pristine CNT	291	1.103
CNT@TU600	350	0.578
CNT@TU700	371	0.690
CNT@TU800	374	0.696
CNT@TU900	362	0.692
CNT@TU1000	363	0.712

The samples' bulk and surface compositions were determined by elemental (C, N, H, S, and O contents) and XPS analyses, respectively (Table 2). N- and S-containing groups were incorporated onto the carbon surface by the mechanical mixture of the CNTs with

thiourea during ball milling. With a carbon content of around 95% by elemental analysis, the samples revealed that the continuous temperature increase in the thermal treatment promotes a decrease in the N content of the samples between 1.43 and 0.02%. A constant decrease is also observed concerning the O-content. However, a non-regular trend was found regarding S, with the S-content varying from 0.6 up to 1.3%. Regarding the XPS results (Table 2), a similar bulk/surface composition was noticed.

Table 2. Evolution of bulk and surface composition of N, S-co-doped CNT samples, determined by elemental and XPS analyses, respectively, during the thermal treatment.

Sample	Elemental Analysis				XPS			
	C	N	S	O	C	N	S	O
Pristine CNT	98.9	0.15	0.0	0.8	99.2	n.d.	n.d.	0.8
CNT@TU600	93.7	1.43	0.6	2.4	94.2	1.2	0.3	3.6
CNT@TU700	94.9	1.09	1.3	1.7	95.6	0.8	0.4	2.4
CNT@TU800	95.6	0.81	0.8	1.5	97.1	0.9	0.8	1.2
CNT@TU900	96.3	0.70	0.7	1.3	98.2	0.6	0.3	0.9
CNT@TU1000	95.7	0.02	1.3	1.1	97.9	0.2	0.8	1.1

N.d.: Not detected.

The nature of the N, S-functionalities incorporated on the CNTs was investigated using the N1s and S2p XPS spectra of the samples (Figure 1). The N1s and S2p spectra revealed asymmetric peak shapes, suggesting overlapping of individual peaks. Curve-fittings were performed taking into account the nature N and S-bonds present in the N, S-precursor (thiourea), the possible formed bonds as a function of the temperature of the thermal treatment, in agreement with the literature reported characteristics of binding energies [37,48,51].

For the samples treated at the lowest temperatures (600, 700, and 800 °C), the N1s spectra were deconvoluted into three peaks assuming the presence of quaternary nitrogen (NQ), pyrrolic (N5), and pyridinic (N6) structures. The corresponding binding energies and percentages of the N-functionalities are presented in Table 3. These species are typical of carbonaceous surfaces with N-containing precursors treated at temperatures above 550 °C. Despite the reduction of the N-content with the temperature of the thermal treatment, the N6 structure was always the most abundant, the disappearance of the N5 group being observed as the temperature increased.

Table 3. Relative peak contents and positions obtained by the N1s and S2p spectra fitting of the N, S-co-doped CNT samples.

Sample	Peak #1 (N6)		Peak #2 (N5)		Peak #6 (NQ)		Peak #1 (C–S)		Peak #2 (S–O)		Peak #3 (Sulphate)	
	B.E. (eV)	% Rel.	B.E. (eV)	% Rel.	B.E. (eV)	% Rel.	B.E. (eV)	% Rel.	B.E. (eV)	% Rel.	B.E. (eV)	% Rel.
CNT@TU600	398.2	50.0	399.7	39.4	401.2	10.6	163.7	53.2	164.5	18.8	168.7	28.0
CNT@TU700	398.2	65.0	399.8	24.8	400.6	10.2	163.4	59.9	164.0	24.8	167.7	15.3
CNT@TU800	398.3	55.4	399.8	18.7	400.6	25.9	163.6	51.7	164.2	23.4	168.7	24.9
CNT@TU900	398.2	67.0	—	—	400.1	33.0	163.8	100.0	—	—	—	—
CNT@TU1000	398.3	57.8	—	—	400.3	42.2	163.7	100.0	—	—	—	—

In the S2p spectra of the CNT@TU600/700/800 samples, three components were identified: C–S bonds around 163.6 ± 0.2 eV, C–S–O species at 164.3 ± 0.2 eV, and sulphate species at 168.2 ± 0.5 eV. It was assumed that the C–S and C–S–O species have S2p_{3/2} and 2p_{1/2} doublets separated by 1.18 eV and with an intensity ratio of 2:1 [48,51,52]. The fitted peak positions and relative areas are shown in Table 3. Since the precursor used does not contain oxygen in its composition, these sulphate species may have been formed by the oxidation of sulphur during air exposure [52,53]. However, at temperatures higher than 900 °C, this sulphate completely disappears. After the thermal treatments at 900 °C, the shape and the peaks identified in the S2p spectra drastically changed, and only C–S

bonds have been identified. This suggests that C–S–O species and sulphates are thermally degraded beyond 900 °C.

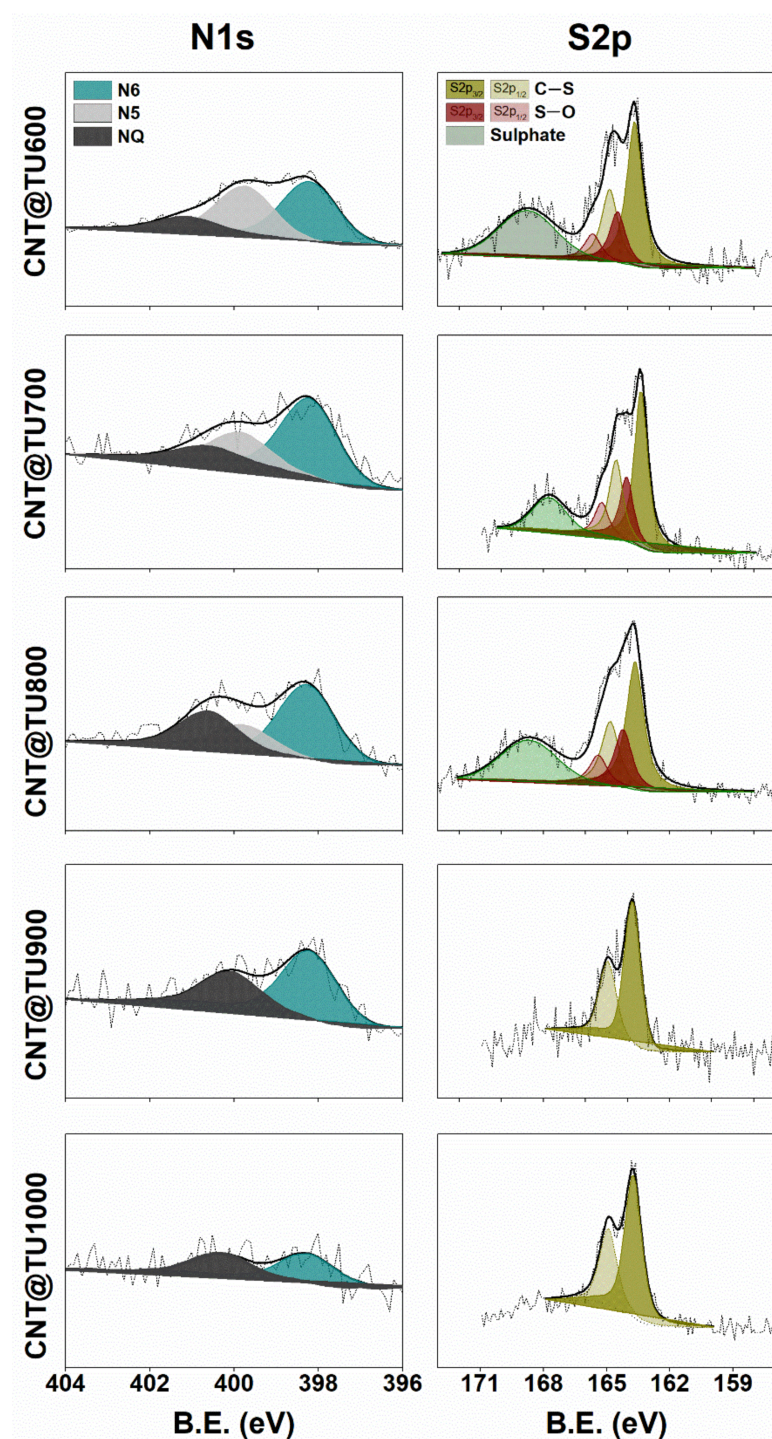


Figure 1. The N1s and S2p XPS spectra for the N, S-co-doped CNT samples.

2.2. Catalytic Activity in CWAO

The catalytic activity of the N, S-co-doped CNTs was preliminary assessed using oxalic acid as a representative of low molecular weight carboxylic acids. This compound has been extensively used in our previous works leading to the development of metal-free carbon materials for CWAO. Under the experimental conditions described elsewhere [34], an extremely fast removal of oxalic acid was observed (total conversion in less than 5 min of reaction using the CNT@TU600 sample, results are not shown). Despite the outstand-

ing catalytic performance over oxalic acid oxidation, such rapid removal will not allow a clear distinction between the catalytic activity of the prepared samples and, for this reason, phenol has been chosen as an alternative model compound. Phenol is a more complex molecule also commonly found in industrial wastes, and extensively studied in the literature as probe species to evaluate the process efficiency. Figure 2a shows the evolution of phenol degradation during the CWAO reaction using the pristine CNT and N, S-CNT samples in a batch mode. In the absence of a catalyst (WAO curve), phenol is not oxidised under the operating conditions employed. Using the pristine CNT sample it is possible to achieve around 50% of phenol degradation after 120 min of reaction. The introduction of the N, S-co-doped CNT catalysts improved the degradation of the aromatic compound to removals between 60 and 70%, after 120 min of reaction, wherein around 50% conversion is obtained in the first 30 min in the presence of the most active samples. However, the TOC removal measured at the end of the catalytic experiments (Figure 2b), revealed a lower removal percentage. While in WAO the difference between the TOC decay and phenol concentration abatement is near 4 percentage points, experiments using the N, S-CNT samples, revealed that those difference may be 4 up to 30 percentage points. The highest TOC conversion (around 60%, corresponding to a phenol removal of 71%) was obtained using the CNT@TU900 sample. Due to the non-microporous nature of the CNTs, as expected, there is no contribution of adsorption to the presented results (results are not shown).

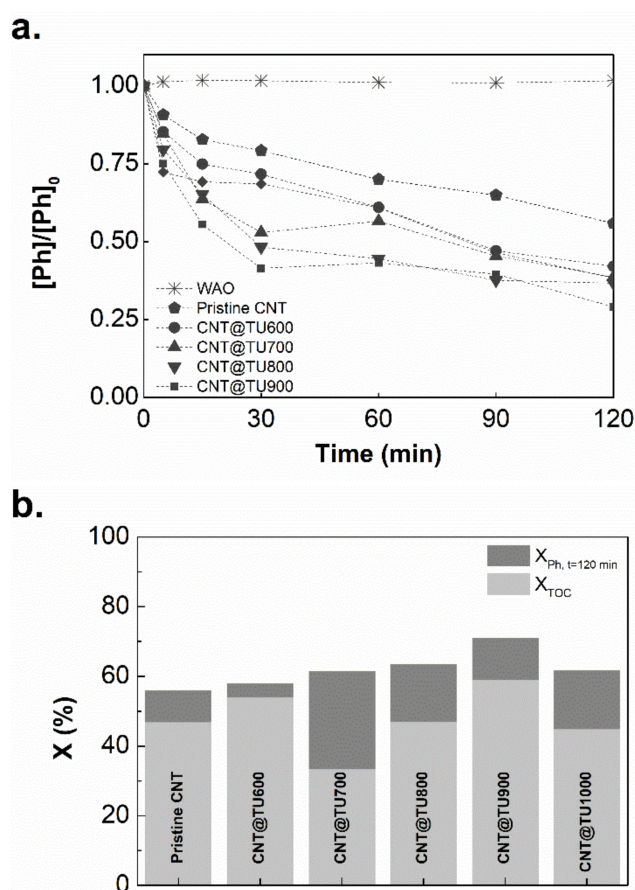


Figure 2. (a) Evolution of normalised phenol concentration in a batch mode at 160 °C and 60 bar of total pressure under non-catalytic conditions (WAO) and using the N, S-co-doped CNT samples in CWAO. (b) Phenol degradation and TOC removal after 120 min of reaction.

According to the previous works, the increase of the available surface area and the incorporation of N-groups on the CNTs improve the catalytic activity in comparison to the pristine CNTs [34,35,37,38]. In this set of samples, the effect of the surface area is

not measurable, since the difference in S_{BET} is smaller than $24 \text{ m}^2 \text{ g}^{-1}$. Regarding the N, S or O contents, the CNT@TU900 sample does not correspond to the richest sample in any of those elements and, therefore, no correlation between the amounts of N, S or O and the degradation extension is observed. However, among the prepared samples, CNT@TU900 presents a distinct nature of N, S-functionalities. As reported in the materials characterisation section, the thermal treatment at 900°C revealed distinct N1s and S2p spectra, showing the disappearance of some species. The S2p spectrum of this sample revealed only the presence of C–S species, unlike the samples treated at lower temperatures, where other S-functionalities were also present. While sulfur in the thiophenic (C–S–C) configuration is presumed to induce strain and defects in the carbon matrix, which facilitate a charge localisation for favorable O_2 chemisorption [50], the C–S–O groups present in the samples treated at lower temperatures may decompose forming strongly oxidant sulphate radicals. Although these radicals can be responsible for initiating the degradation of phenol in the liquid phase, they do not allow high levels of mineralisation, suggesting that they can be selective for phenol oxidation but are not able to degrade the various by-products formed. In a previous paper [36], we have observed a similar behavior with $-\text{SO}_3\text{H}$ groups, promoting low TOC removals in phenol oxidation by CWAQ. By other way, the CNT@TU900 sample is also rich in N6 and NQ functionalities, groups that increase the electron density of the surface, enhancing chemisorption and oxygen activation. This explains the better catalytic performance of the CNT@TU900 sample in comparison with the CNT@TU1000 sample, that in addition to not having the S–O and sulphate groups, is also poor in electron donor N-containing groups, resulting in a catalyst with lower catalytic activity.

In order to check the activity and stability of the CNT@TU900 catalyst, a continuous CWAQ experiment was carried out until the steady-state was reached (Figure 3). A severe deactivation of the catalyst is observed in the first 10 h, becoming less pronounced after 20 h, with a phenol removal near 27% after 75 h. This represents a slight improvement in the face of the reported result obtained using N-doped CNTs by Santos et al. [54] under similar conditions (a phenol removal near 15% for a similar time). In the previous work, the deactivation phenomenon was also observed and explained by the deposition of phenolic polymers on the surface of the catalyst [55], in which the catalyst is not able to decompose. Although it has not been studied in this work, sometimes it is possible to regenerate the catalyst by carrying out thermal treatments to remove those deposited compounds that block the access to the active sites.

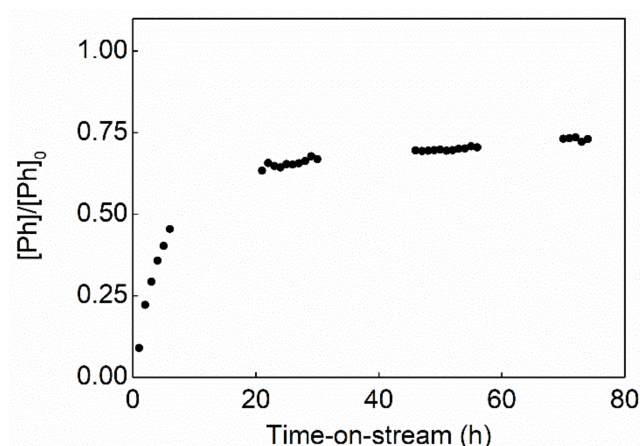


Figure 3. Evolution of normalized phenol concentration in a continuous mode using the CNT@TU900 sample ($[\text{Ph}]_0 = 75 \text{ mg L}^{-1}$; $T = 160^\circ\text{C}$; $P_{\text{O}_2} = 8 \text{ bar}$; liquid flow rate = 0.25 mL min^{-1}).

3. Experimental

3.1. Materials: Preparation and Characterisation

Commercial multiwalled carbon nanotubes (CNTs) purchased from NanocylTM (NC3100 series) were subjected to a mechanochemical treatment to incorporate N, S-heteroatoms onto the graphitic lattice. Thiourea was selected as a precursor for the N, S-co-doping. Briefly, 0.6 g of CNTs were ball milled with thiourea (equivalent to 0.26 g of N). The grinding step was carried out in a Retsch MM200 equipment (Retsch GmbH) using zirconium oxide balls inside the grinding jars without any gas flow. The CNTs and thiourea were mixed and homogenised during 4 h by the radial oscillations of the grinding jars in a horizontal position (15 vibrations s^{−1}), using milling conditions determined in a previous work [37]. After the mechanical mixing, the samples were subjected to a thermal treatment under N₂ (100 cm³ min^{−1}, at 10 °C min^{−1}) until 600, 700, 800, 900, and 1000 °C, and kept at the final temperature during 1 h. The corresponding samples were designated as CNT@TU, followed by the temperature of the thermal treatment (e.g., CNT@TU600 for the sample thermally treated at 600 °C).

The developed materials were further characterised using the appropriate techniques. Textural properties were based on the N₂ equilibrium adsorption isotherms determined at −196 °C in a Quantachrome NOVA 4200e multi-station apparatus. The surface chemistry was assessed using X-ray photoelectron spectroscopy (XPS). Analyses were performed using a Kratos AXIS Ultra HAS with VISION software for data acquisition and CASAXPS software for data analysis. The chemical composition was evaluated by elemental (CHNS/O) analysis carried out on a vario MICRO cube and a rapid OXY cube analyser from Elemental GmbH. Thermogravimetric analyses (TGA) were carried out using a STA 409 PC/4/H Luxx Netzsch thermal analyser.

3.2. Experimental Procedure

3.2.1. Batch Mode

CWAO experiments in a batch mode were carried in a 160 mL 316-stainless-steel high-pressure batch reactor (Parr Instruments, Moline, IL, Mod. 4564, USA) using phenol as a model pollutant (detailed description elsewhere [39]). In addition, 75 mL of a 75 mg L^{−1} phenol solution and 0.1 g of catalyst were placed inside the reactor. The reactor was purged with nitrogen until the complete removal of oxygen and then pressurised with 5 bar of nitrogen and pre-heated up to 160 °C under continuous stirring (500 rpm). After reaching the desired temperature, pure air was injected until a total pressure of 60 bar inside the reactor was reached. This was considered time zero for the reaction.

3.2.2. Continuous Mode

CWAO experiments in a continuous mode were carried out in a completely automated tubular reactor from Microactivity PID Eng&Tech equipped with a HPLC pump and a high-pressure liquid–gas separator working in down-flow [39]. In addition, 0.2 g of the catalyst were mixed with 1.8 g of carborundum and introduced into the tubular reactor. The system was pre-heated under nitrogen flow (4 bar of pressure) until the desired temperature (160 °C). Then, nitrogen was replaced by pure oxygen, the pressure inside the reactor increased to the desired value (8 bar), and the model pollutant solution (75 mg L^{−1} of phenol) was fed at 0.25 mL min^{−1}.

The operating conditions have been selected taking into account the previous study of Santos et al. [54], where the influence of distinct operating conditions in the same experimental system and using phenol as a model compound, for batch and continuous mode operations, was investigated.

3.3. Analytical Techniques

Liquid aliquots were withdrawn during the reactions and centrifuged (if necessary) for further analysis by high performance liquid chromatography (HPLC) with a Hitachi Elite LACHrom system equipped with a Diode Array Detector (L-2450). The samples were

analysed in a Purospher Star RP-18 endcapped column ($250 \times 4.6 \text{ m}^2$, $5 \text{ }\mu\text{m}$ particles) working at room temperature. The mobile phase was a mixture of water and methanol 40/60 (*v/v*) with a flow rate of 0.8 mL min^{-1} . Analyses were made using an injection volume of $50 \text{ }\mu\text{L}$. The quantification of phenol was performed at $\lambda = 270 \text{ nm}$. The total organic carbon (TOC) was also determined for the selected experiments in a TOC-L Analyser from Shimadzu by the non-purgable organic carbon (NPOC) method.

4. Conclusions

The introduction of N, S-functional groups onto the carbon surface of commercial CNTs has been successfully carried out using a mechanochemical approach with thiourea as a precursor for the N, S heteroatoms. Without significant damage of the textural properties of the CNTs, quaternary nitrogen (NQ), pyrrolic (N5) and pyridinic (N6) structures, as well as C–S, C–S–O, and sulphate species, were incorporated at different temperatures in the thermal step. Some of these specific groups were found to improve the catalytic activity of the N, S-doped CNT towards phenol oxidation by CWAQ, with around 60% of TOC removal being achieved with the CNT@TU900 sample. The enhanced phenol degradation and TOC removal were explained by the synergic contribution of the N6 and NQ groups that increase the electron density of the surface, enhancing chemisorption and oxygen activation, and the presence of thiophenic-like groups (C–S–C), responsible for promoting charge localisation for favorable O_2 chemisorption.

Author Contributions: Writing—original draft preparation, investigation, methodology, conceptualization, R.P.R.; writing—reviewing and editing, conceptualization, O.S.G.P.S.; writing—reviewing and editing, conceptualization, J.J.M.Ó.; supervision, conceptualization, funding acquisition, writing—reviewing and editing, M.F.R.P.; supervision, conceptualization, writing—reviewing and editing, resources, J.L.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by Base Funding—UIDB/50020/2020 of the Associate Laboratory LSRE-LCM—funded by national funds through FCT/MCTES (PIDDAC) and by NORTE-01-0145-FEDER-000054 funded by CCDR-N (Norte2020). O.S.G.P.S. acknowledges FCT funding under the Scientific Employment Stimulus—Institutional Call CEECINST/00049/2018.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors are indebted to Carlos M. Sá (CEMUP) for assistance with XPS analyses.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mishra, V.S.; Mahajani, V.V.; Joshi, J.B. Wet Air Oxidation. *Ind. Eng. Chem. Res.* **1995**, *34*, 2–48. [\[CrossRef\]](#)
2. Mantzavinos, D.; Sahibzada, M.; Livingston, A.G.; Metcalfe, I.S.; Hellgardt, K. Wastewater treatment: Wet air oxidation as a precursor to biological treatment. *Catal. Today* **1999**, *53*, 93–106. [\[CrossRef\]](#)
3. Kolaczowski, S.T.; Plucinski, P.; Beltran, F.J.; Rivas, F.J.; McLurgh, D.B. Wet air oxidation: A review of process technologies and aspects in reactor design. *Chem. Eng. J.* **1999**, *73*, 143–160. [\[CrossRef\]](#)
4. Luck, F. Wet air oxidation: Past, present and future. *Catal. Today* **1999**, *53*, 81–91. [\[CrossRef\]](#)
5. Debellefontaine, H.; Foussard, J.N. Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Manag.* **2000**, *20*, 15–25. [\[CrossRef\]](#)
6. Bhargava, S.K.; Tardio, J.; Prasad, J.; Föger, K.; Akolekar, D.B.; Grocott, S.C. Wet oxidation and catalytic wet oxidation. *Ind. Eng. Chem. Res.* **2006**, *45*, 1221–1258. [\[CrossRef\]](#)
7. Levec, J.; Pintar, A. Catalytic wet-air oxidation processes: A review. *Catal. Today* **2007**, *124*, 172–184. [\[CrossRef\]](#)
8. Gallezot, P.; Laurain, N.; Isnard, P. Catalytic wet-air oxidation of carboxylic acids on carbon-supported platinum catalysts. *Appl. Catal. B Environ.* **1996**, *9*, L11–L17. [\[CrossRef\]](#)
9. Roy, S.; Saroha, A.K. Ceria promoted $[\gamma\text{-Al}_2\text{O}_3]$ supported platinum catalyst for catalytic wet air oxidation of oxalic acid: Kinetics and catalyst deactivation. *RSC Adv.* **2014**, *4*, 56838–56847. [\[CrossRef\]](#)
10. Pruden, B.B.; Le, H. Wet air oxidation of soluble components in waste water. *Can. J. Chem. Eng.* **1976**, *54*, 319–325. [\[CrossRef\]](#)
11. Martín-Hernández, M.; Carrera, J.; Suárez-Ojeda, M.E.; Besson, M.; Descorme, C. Catalytic wet air oxidation of a high strength p-nitrophenol wastewater over Ru and Pt catalysts: Influence of the reaction conditions on biodegradability enhancement. *Appl. Catal. B Environ.* **2012**, *123–124*, 141–150. [\[CrossRef\]](#)

12. Stüber, F.; Font, J.; Fortuny, A.; Bengoa, C.; Eftaxias, A.; Fabregat, A. Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater. *Top. Catal.* **2005**, *33*, 3–50. [\[CrossRef\]](#)
13. Aguilar, C.; García, R.; Soto-Garrido, G.; Arriagada, R. Catalytic wet air oxidation of aqueous ammonia with activated carbon. *Appl. Catal. B Environ.* **2003**, *46*, 229–237. [\[CrossRef\]](#)
14. Cybulski, A. Catalytic Wet Air Oxidation: Are Monolithic Catalysts and Reactors Feasible? *Ind. Eng. Chem. Res.* **2007**, *46*, 4007–4033. [\[CrossRef\]](#)
15. Shende, R.V.; Levec, J. Wet Oxidation Kinetics of Refractory Low Molecular Mass Carboxylic Acids. *Ind. Eng. Chem. Res.* **1999**, *38*, 3830–3837. [\[CrossRef\]](#)
16. Quintanilla, A.; Casas, J.A.; Mohedano, A.F.; Rodríguez, J.J. Reaction pathway of the catalytic wet air oxidation of phenol with a Fe/activated carbon catalyst. *Appl. Catal. B Environ.* **2006**, *67*, 206–216. [\[CrossRef\]](#)
17. Quintanilla, A.; Casas, J.A.; Zazo, J.A.; Mohedano, A.F.; Rodríguez, J.J. Wet air oxidation of phenol at mild conditions with a Fe/activated carbon catalyst. *Appl. Catal. B Environ.* **2006**, *62*, 115–120. [\[CrossRef\]](#)
18. Quintanilla, A.; Casas, J.A.; Rodríguez, J.J. Catalytic wet air oxidation of phenol with modified activated carbons and Fe/activated carbon catalysts. *Appl. Catal. B Environ.* **2007**, *76*, 135–145. [\[CrossRef\]](#)
19. Quintanilla, A.; Casas, J.A.; Rodríguez, J.J.; Kreutzer, M.T.; Kapteijn, F.; Moulijn, J.A. Kinetics of the wet oxidation of phenol over an Fe/activated carbon catalyst. *Int. J. Chem. React. Eng.* **2007**, *5*. [\[CrossRef\]](#)
20. Quintanilla, A.; Fraile, A.F.; Casas, J.A.; Rodríguez, J.J. Phenol oxidation by a sequential CWPO-CWAO treatment with a Fe/AC catalyst. *J. Hazard. Mater.* **2007**, *146*, 582–588. [\[CrossRef\]](#)
21. Quintanilla, A.; Menéndez, N.; Tornero, J.; Casas, J.A.; Rodríguez, J.J. Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: Influence on activity, selectivity and stability. *Appl. Catal. B Environ.* **2008**, *81*, 105–114. [\[CrossRef\]](#)
22. Quintanilla, A.; Dominguez, C.M.; Casas, J.A.; Rodriguez, J.J. Emerging catalysts for wet air oxidation process. In *Focus on Catalysis Research: New Developments*; Nova Science Publishers, Inc.: New York, NY, USA, 2012; pp. 237–259.
23. Suarez-Ojeda, M.E.; Stüber, F.; Fortuny, A.; Fabregat, A.; Carrera, J.; Font, J. Catalytic wet air oxidation of substituted phenols using activated carbon as catalyst. *Appl. Catal. B Environ.* **2005**, *58*, 105–114. [\[CrossRef\]](#)
24. Suárez-Ojeda, M.E.; Fabregat, A.; Stüber, F.; Fortuny, A.; Carrera, J.; Font, J. Catalytic wet air oxidation of substituted phenols: Temperature and pressure effect on the pollutant removal, the catalyst preservation and the biodegradability enhancement. *Chem. Eng. J.* **2007**, *132*, 105–115. [\[CrossRef\]](#)
25. Suárez-Ojeda, M.E.; Kim, J.; Carrera, J.; Metcalfe, I.S.; Font, J. Catalytic and non-catalytic wet air oxidation of sodium dodecylbenzene sulfonate: Kinetics and biodegradability enhancement. *J. Hazard. Mater.* **2007**, *144*, 655–662. [\[CrossRef\]](#)
26. Rocha, R.P.; Pereira, M.F.R.; Figueiredo, J.L. Metal-free carbon materials as catalysts for wet air oxidation. *Catal. Today* **2019**. [\[CrossRef\]](#)
27. Eftaxias, A.; Font, J.; Fortuny, A.; Fabregat, A.; Stüber, F. Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 677–687. [\[CrossRef\]](#)
28. Eftaxias, A.; Font, J.; Fortuny, A.; Fabregat, A.; Stüber, F. Catalytic wet air oxidation of phenol over active carbon catalyst: Global kinetic modelling using simulated annealing. *Appl. Catal. B Environ.* **2006**, *67*, 12–23. [\[CrossRef\]](#)
29. Santiago, M.; Stüber, F.; Fortuny, A.; Fabregat, A.; Font, J. Modified activated carbons for catalytic wet air oxidation of phenol. *Carbon* **2005**, *43*, 2134–2145. [\[CrossRef\]](#)
30. Cordero, T.; Rodríguez-Mirasol, J.; Bedia, J.; Gomis, S.; Yustos, P.; García-Ochoa, F.; Santos, A. Activated carbon as catalyst in wet oxidation of phenol: Effect of the oxidation reaction on the catalyst properties and stability. *Appl. Catal. B Environ.* **2008**, *81*, 122–131. [\[CrossRef\]](#)
31. Fortuny, A.; Font, J.; Fabregat, A. Wet air oxidation of phenol using active carbon as catalyst. *Appl. Catal. B Environ.* **1998**, *19*, 165–173. [\[CrossRef\]](#)
32. Sousa, J.P.S.; Silva, A.M.T.; Pereira, M.F.R.; Figueiredo, J.L. Wet Air Oxidation of Aniline Using Carbon Foams and Fibers Enriched with Nitrogen. *Sep. Sci. Technol.* **2010**, *45*, 1546–1554. [\[CrossRef\]](#)
33. Tukač, V.; Hanika, J. Catalytic effect of active carbon black Chezcarb in wet oxidation of phenol. *Collect. Czechoslov. Chem. Commun.* **1996**, *61*, 1010–1017. [\[CrossRef\]](#)
34. Soares, O.S.G.P.; Rocha, R.P.; Órfão, J.J.M.; Pereira, M.F.R.; Figueiredo, J.L. Mechanochemical Approach for N-, S-, P-, and B-Doping of Carbon Nanotubes: Methodology and Catalytic Performance in Wet Air Oxidation. *C—J. Carbon Res.* **2019**, *5*, 30. [\[CrossRef\]](#)
35. Rocha, R.P.; Sousa, J.P.S.; Silva, A.M.T.; Pereira, M.F.R.; Figueiredo, J.L. Catalytic activity and stability of multiwalled carbon nanotubes in catalytic wet air oxidation of oxalic acid: The role of the basic nature induced by the surface chemistry. *Appl. Catal. B Environ.* **2011**, *104*, 330–336. [\[CrossRef\]](#)
36. Rocha, R.P.; Silva, A.M.T.; Romero, S.M.M.; Pereira, M.F.R.; Figueiredo, J.L. The role of O- and S-containing surface groups on carbon nanotubes for the elimination of organic pollutants by catalytic wet air oxidation. *Appl. Catal. B Environ.* **2014**, *147*, 314–321. [\[CrossRef\]](#)
37. Soares, O.S.G.P.; Rocha, R.P.; Gonçalves, A.G.; Figueiredo, J.L.; Órfão, J.J.M.; Pereira, M.F.R. Easy method to prepare N-doped carbon nanotubes by ball milling. *Carbon* **2015**, *91*, 114–121. [\[CrossRef\]](#)

-
38. Soares, O.S.G.P.; Rocha, R.P.; Gonçalves, A.G.; Figueiredo, J.L.; Órfão, J.J.M.; Pereira, M.F.R. Highly active N-doped carbon nanotubes prepared by an easy ball milling method for advanced oxidation processes. *Appl. Catal. B Environ.* **2016**, *192*, 296–303. [\[CrossRef\]](#)
 39. Rocha, R.P.; Santos, D.F.M.; Soares, O.S.M.P.; Silva, A.M.T.; Pereira, M.F.R.; Figueiredo, J.L. Metal-Free Catalytic Wet Oxidation: From Powder to Structured Catalyst Using N-Doped Carbon Nanotubes. *Top. Catal.* **2018**, *61*, 1957–1966. [\[CrossRef\]](#)
 40. Santos, D.F.M.; Soares, O.S.G.P.; Silva, A.M.T.; Figueiredo, J.L.; Pereira, M.F.R. Degradation and mineralization of oxalic acid using catalytic wet oxidation over carbon coated ceramic monoliths. *J. Environ. Chem. Eng.* **2021**, *9*, 105369. [\[CrossRef\]](#)
 41. Li, X.; Yang, S.X.; Zhu, W.P.; Wang, J.B.; Wang, L. Catalytic wet air oxidation of phenol and aniline over multi-walled carbon nanotubes. *Huanjing Kexue/Environ. Sci.* **2008**, *29*, 2522–2528.
 42. Yang, S.; Wang, X.; Yang, H.; Sun, Y.; Liu, Y. Influence of the different oxidation treatment on the performance of multi-walled carbon nanotubes in the catalytic wet air oxidation of phenol. *J. Hazard. Mater.* **2012**, *233–234*, 18–24. [\[CrossRef\]](#)
 43. Yang, S.; Sun, Y.; Yang, H.; Wan, J. Catalytic wet air oxidation of phenol, nitrobenzene and aniline over the multi-walled carbon nanotubes (MWCNTs) as catalysts. *Front. Environ. Sci. Eng.* **2014**. [\[CrossRef\]](#)
 44. He, W.; Xue, P.; Du, H.; Xu, L.; Pang, M.; Gao, X.; Yu, J.; Zhang, Z.; Huang, T. A facile method prepared nitrogen and boron doped carbon nano-tube based catalysts for oxygen reduction. *Int. J. Hydrogen Energy* **2017**, *42*, 4123–4132. [\[CrossRef\]](#)
 45. Huang, X.; Wang, Q.; Jiang, D.; Huang, Y. Facile synthesis of B, N co-doped three-dimensional porous graphitic carbon toward oxygen reduction reaction and oxygen evolution reaction. *Catal. Commun.* **2017**, *100*, 89–92. [\[CrossRef\]](#)
 46. Liu, Y.; Zhang, Y.; Cheng, K.; Quan, X.; Fan, X.; Su, Y.; Chen, S.; Zhao, H.; Zhang, Y.; Yu, H.; et al. Selective Electrochemical Reduction of Carbon Dioxide to Ethanol on a Boron- and Nitrogen-Co-doped Nanodiamond. *Angew. Chem. Int. Ed.* **2017**, *56*, 15607–15611. [\[CrossRef\]](#)
 47. Zeng, L.; Shi, J.; Luo, J.; Chen, H. Silver sulfide anchored on reduced graphene oxide as a high -performance catalyst for CO₂ electroreduction. *J. Power Sources* **2018**, *398*, 83–90. [\[CrossRef\]](#)
 48. Yuan, Q.; Ma, Z.; Chen, J.; Huang, Z.; Fang, Z.; Zhang, P.; Lin, Z.; Cui, J. N, S-Codoped Activated Carbon Material with Ultra-High Surface Area for High-Performance Supercapacitors. *Polymers* **2020**, *12*, 1982. [\[CrossRef\]](#)
 49. Rocha, I.M.; Soares, O.S.G.P.; Fernandes, D.M.; Freire, C.; Figueiredo, J.L.; Pereira, M.F.R. N-doped Carbon Nanotubes for the Oxygen Reduction Reaction in Alkaline Medium: Synergistic Relationship between Pyridinic and Quaternary Nitrogen. *Chem. Sel.* **2016**, *1*, 2522–2530. [\[CrossRef\]](#)
 50. Kiciński, W.; Szala, M.; Bystrzejewski, M. Sulfur-doped porous carbons: Synthesis and applications. *Carbon* **2014**, *68*, 1–32. [\[CrossRef\]](#)
 51. Zhou, G.; Yin, L.-C.; Wang, D.-W.; Li, L.; Pei, S.; Gentle, I.R.; Li, F.; Cheng, H.-M. Fibrous Hybrid of Graphene and Sulfur Nanocrystals for High-Performance Lithium–Sulfur Batteries. *ACS Nano* **2013**, *7*, 5367–5375. [\[CrossRef\]](#)
 52. Zheng, X.; Wu, J.; Cao, X.; Abbott, J.; Jin, C.; Wang, H.; Strasser, P.; Yang, R.; Chen, X.; Wu, G. N-, P-, and S-doped graphene-like carbon catalysts derived from onium salts with enhanced oxygen chemisorption for Zn-air battery cathodes. *Appl. Catal. B Environ.* **2019**, *241*, 442–451. [\[CrossRef\]](#)
 53. Schaufuß, A.G.; Nesbitt, H.W.; Kartio, I.; Laajalehto, K.; Bancroft, G.M.; Szargan, R. Incipient oxidation of fractured pyrite surfaces in air. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *96*, 69–82. [\[CrossRef\]](#)
 54. Santos, D.F.M.; Soares, O.S.G.P.; Silva, A.M.T.; Figueiredo, J.L.; Pereira, M.F.R. Catalytic wet oxidation of organic compounds over N-doped carbon nanotubes in batch and continuous operation. *Appl. Catal. B Environ.* **2016**, *199*, 361–371. [\[CrossRef\]](#)
 55. Delgado, J.J.; Chen, X.; Pérez-Omil, J.A.; Rodríguez-Izquierdo, J.M.; Cauqui, M.A. The effect of reaction conditions on the apparent deactivation of Ce–Zr mixed oxides for the catalytic wet oxidation of phenol. *Catal. Today* **2012**, *180*, 25–33. [\[CrossRef\]](#)