17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

Carbon nanotubes synthesized from LDPE for application in wet peroxide oxidation of paracetamol

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Abstract Carbon nanotubes (CNTs) were produced by chemical vapor deposition (CVD) considering low-density polyethylene (LDPE) as a carbon source and as an alternative to upcycle plastic solid waste. The CNTs were synthesized over bimetallic catalysts (Ni and Fe) supported on Al_2O_3 and purified with H_2SO_4 to dissolve the metal particles from the material. Both original (CNT-O) and purified materials (CNT-P) were tested as catalysts in catalytic wet peroxide oxidation (CWPO) of paracetamol (PCM). Both catalysts promoted the complete conversion of PCM within 8 h of reaction and were able to mineralize 60% of the organic content of the effluent (measured as TOC) in 24 h. Catalyst CNT-O was able to completely decompose hydrogen peroxide (H_2O_2) within 24 h, whereas CNT-P was only able to decompose ~80%. Therefore, the efficiency of H_2O_2 consumption, measured as $X_{TOC}/X_{H_2O_2}$, was higher for catalyst CNT-P (0.75) than for CNT-O (0.61). Metal leaching, especially Ni, was observed during the CWPO run with CNT-O, while it is avoided when using CNT-P. Thus, purified CNTs have proved to be active in CWPO of PCM, allowing a more controlled decomposition of H_2O_2 and avoiding leaching of metal species.

Keywords: catalytic wet peroxide oxidation, paracetamol, plastic solid waste, carbon nanotubes.

1. Introduction

The occurrence of micropollutants in water bodies is of increasing concern. For instance, pharmaceutical substances are continuously introduced into the sewage system, and some of them are not removed from urban wastewater by traditional treatment processes (Rizzo *et al.*, 2019). This issue has become so severe that a watch list of pollutants found in water bodies was defined in the European Union that require monitorization and search for alternatives to traditional treatments (The European Commission, 2020).

One possible alternative is the treatment of these wastewaters using advanced oxidation processes (AOPs), which are based on the generation of hydroxyl radicals ($HO^•$). CWPO is an AOP that relies on H_2O_2 as a source of $HO^•$, promoting the oxidation of the organic matter into CO_2 and H_2O (Ribeiro *et al.*, 2016). CWPO can operate under mild conditions (25-130 ºC, 1-4 bar), allowing the destruction of the organic compounds (Ribeiro *et al.*, 2016), in opposition to other technologies that only transfer the pollutant from one phase to another (such as adsorption). The most common catalysts used in CWPO are based on metallic phases supported on a series of materials, including carbonaceous structures. With particular attention to iron, metallic species are well-known catalysts in the selective conversion of H_2O_2 into hydroxyl radicals (Ribeiro *et al.*, 2017). However, metal-based heterogeneous catalysts can suffer deactivation due to leaching of the metal species during CWPO, leading to additional downstream pollution. An alternative are metal-free carbon-based materials as catalysts (Rocha *et al.*, 2020).

Several carbon-based materials have shown suitable catalytic activity in CWPO, such as carbon xerogels (Ribeiro *et al.*, 2017), carbon blacks (Diaz de Tuesta *et al.*, 2020), graphene derivatives (Ribeiro *et al.*, 2015) and CNTs (Diaz de Tuesta *et al.*, 2020). CNTs are graphene sheets rolled in the form of cylinders. The primary route to obtain CNTs is by CVD (Wang *et al.*, 2019). In CVD, a carbon-rich gas is fed into the system at high temperatures, and the filamentous carbonaceous structures grow on the active sites of a catalyst - usually transition metals, such as Ni and Fe (Purohit *et al.*, 2014). A wide range of precursors can be used as carbon source in CVD (Wang *et al.*, 2019), as long as they are rich in carbon in their structure. Here, attention is paid to polymeric materials, mainly to plastic solid waste (PSW), such as LDPE, which present a carbon content of 85.6%

(Zhuo and Levendis, 2014). In this context, CVD can be used to upcycle PSW, adding value to this waste and introducing the concept of circular economy in the synthesis of CNTs (Zhuo and Levendis, 2014). CNTs obtained by CVD contain the metal particles in their structure, that can be removed by their dissolution with strong acids (Hou *et al.*, 2008).

In summary, this work deals with the production of CNTs by CVD, considering LDPE as a model polymer of PSW. The as-synthesized CNT (CNT-O) is purified to remove the metal particles used as catalyst in the growth of the CNT, leading to CNT-P. Then, the CNT materials and the catalyst used during CVD are tested in the CWPO of paracetamol (PCM). Their catalytic activities towards PCM and TOC removals, as well as H_2O_2 decomposition, are compared.

2. Methodology

2.2. *Materials*

Alumina (Al_2O_3) was purchased from BASF. Before use, alumina was ground and sieved to select particles in the range 53-106 µm. The remaining chemicals were used as received. VWR Chemicals supplied iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) (98%) and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) (99%). Merck provided ammonia solution (28-30%). Low-density polyethylene (average Mw ~35000 by GPC, average Mn ~7700 by GPC) and $TiOSO_4$ (99.99 wt.% metal basis, c.a. 15 wt.% solution in dilute sulfuric acid) were supplied by Sigma Aldrich. Fisher Chemicals supplied H_2SO_4 (95%). Fluka supplied H_2O_2 (30 wt.%). Paracetamol (98%) was obtained from Alfa Aesar.

2.3. *Synthesis of materials*

A bimetallic catalyst containing 20% $NiFe_2O_4$ supported on Al_2O_3 was synthesized by coprecipitation of Ni (0.027 M) and Fe (0.054 M) nitrates in the presence of Al_2O_3 (6.28 g). The coprecipitation was promoted by dropwise addition of ammonia solution (1 M) until reaching a pH of 8. The solid was then centrifuged and washed with distilled water until neutral pH and dried in oven at 60 °C for 24 h. Then, the solid was calcined in air atmosphere at 800 °C for 3 h, leading to catalyst $NiFe_2O_4/Al_2O_3$.

$NiFe_2O_4/Al_2O_3$ was used as catalyst in the growth of filamentous carbon nanostructures by CVD. Briefly, 5 g of LDPE was loaded into a crucible located in the upper region of a vertical tubular furnace. Likewise, 1 g of catalyst $NiFe_2O_4/Al_2O_3$ was loaded in a second crucible situated in the lower region of the furnace. The CNT synthesis was conducted at 850 °C for 1 h under N_2 atmosphere (acting as both carrier gas and promotor of the inert atmosphere), leading to the material CNT-O, which contains the metal particle CVD catalysts in its structure.

Part of CNT-O was subject to acid washing to remove the metal particles from the structure. For that purpose, 1 g of CNT-O was mixed with 50 mL of H_2SO_4 (50% vol./vol.) and heated up to 140 °C for 3 h under vigorous stirring. The solid was recovered by filtration, abundantly washed with distilled water until reaching the neutrality of the rinsing waters and then dried in oven at 60 °C overnight, leading to CNT-P.

2.4. *Catalytic wet peroxide oxidation runs*

A PCM solution (100 mg L^{-1}) at pH 3.5 was heated to 80 °C in an oil bath equipped with temperature control and a condenser. Upon reaching the desired temperature, H_2O_2 (474 mg L^{-1}) and the catalyst (2.5 g L^{-1}) were added, defining this instant as $t = 0$ min. PCM and its intermediaries were monitored by HPLC (Jasco) at 277 nm, using a Kromasil C-18 (15 x 5 mm x 2.1 id) column. H_2O_2 concentration was monitored using the $TiOSO_4$ method described elsewhere (Santos Silva *et al.*, 2019), and TOC was measured using a Shimadzu equipment (TOC-L CSH/CSN). The reaction was conducted for 24 h. At the end of the reaction, metal leaching was evaluated by atomic absorption (Pinaacle 900 T, Perkin Elmer), whereas the aromatic compounds (ARM) were determined by UV-Vis spectrophotometry at 254 nm. Total phenolic (TP) compounds were determined by UV-Vis spectrophotometry at 765 nm by using the Folin-Ciocalteu methodology, as described elsewhere (Singleton *et al.*, 1999). The efficiency of H_2O_2 consumption was estimated according to Equation (1).

$$\eta_{H_2O_2}(\%) = \frac{X_{TOC\ t=24\ h}}{X_{H_2O_2\ t=24\ h}} \times 100 \qquad (1)$$

3. Results and discussion

Figure 1 shows the concentration profiles of PCM, H_2O_2 and TOC obtained in the CWPO of PCM using CNT-O, CNT-P and $NiFe_2O_4/Al_2O_3$ as catalysts. CNT-P and $NiFe_2O_4/Al_2O_3$ led to the same conversion of H_2O_2 (~ 80%) after 24 h of reaction (Figure 1,b), although the latter resulted in faster rates than CNT-P. On the other hand, CNT-O led to obtaining a complete conversion of H_2O_2 in 24 h. As observed in previous works, this behavior can be ascribed to a synergic interaction between the metal particles and the carbon nanostructure (Ribeiro *et al.*, 2017). However, $NiFe_2O_4/Al_2O_3$ resulted in a more deficient PCM removal than CNT-O and CNT-P (Figure 1, a). CNT-O and CNT-P led to a conversion higher than 95% of the micropollutant within the first 6 h of reaction. In comparison, $NiFe_2O_4/Al_2O_3$ was only able to remove around 50% of PCM after 24 h of reaction. Similar observations can be found in the literature. It has been reported that hybrid catalysts consisting of CNT and ferrihydrite in heterogeneous Fenton reactions led to a 7.1× increase in the degradation of bisphenol A compared to a catalyst only based on ferrihydrite (Zhu *et al.*, 2020). The faster removal of pollutants in the presence of the hybrid material was ascribed to the ability of CNTs to accelerate the Fe^{2+}/Fe^{3+} cycles characteristics of the Fenton reaction (Zhu *et al.*, 2020). Both CNT-O and CNT-P allow reaching similar TOC abatement (removal of ~65% within 8 h of reaction).

The main cost of running a CWPO operation unit is the consumption of H_2O_2 (Diaz de Tuesta *et al.*, 2020). Therefore, efficient H_2O_2 consumption should be assessed to avoid side reactions, which could lead to the formation of molecular oxygen (Ribeiro *et al.*, 2013). Comparing the efficiency of H_2O_2 consumption obtained with the catalysts used in CWPO, it can be observed that CNT-P allows for more efficient use of H_2O_2: 75% vs. 61% for CNT-O. The higher efficiency is due to a more controlled decomposition of H_2O_2 obtained when using CNT-P compared with the other two catalysts (Figure 1, b). More efficient consumption of hydrogen peroxide means that each mol of H_2O_2 consumed by CNT-P results in higher TOC removal than with CNT-O. Figure 2 shows the metal leaching occurring during CWPO with each catalyst after 24 h of reaction. Ni leaching using CNT-P was 90 and 69% lower than with CNT-O or $NiFe_2O_4/Al_2O_3$, respectively. Similarly, Fe leaching decreased by 40 and 48% compared to CNT-O and $NiFe_2O_4/Al_2O_3$, respectively.

Furthermore, both CNTs allowed higher removals of TP and aromatic compounds than with $NiFe_2O_4/Al_2O_3$, reaching values > 99%, while $NiFe_2O_4/Al_2O_3$ only led to removals of 42% of aromatic compounds and 44% of TP. Thus, CNT-P appears as a promising alternative to replace metal-bearing catalysts commonly used in CWPO due to similar behavior in the abatement of contaminants with more efficient H_2O_2 use.

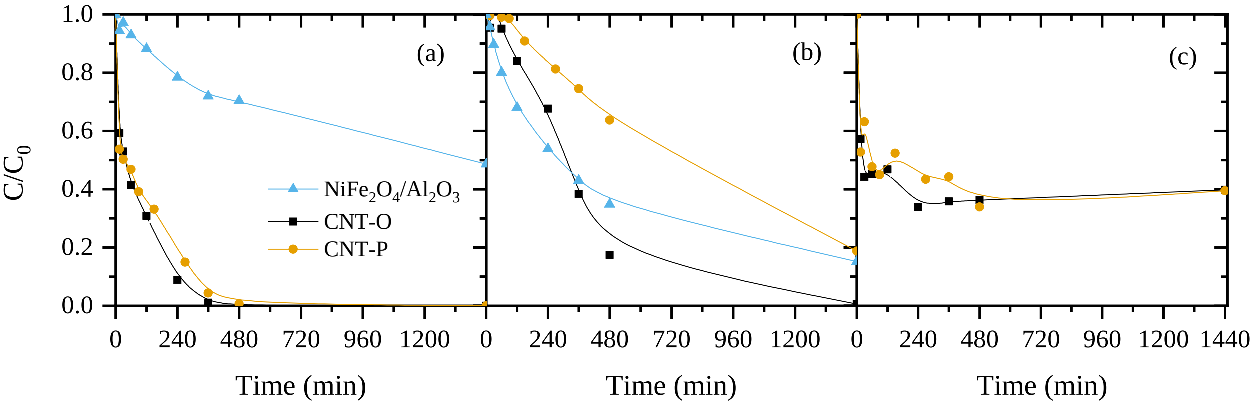

Figure 1. Normalized concentration of (a) PCM, (b) H_2O_2 and (c) TOC upon time for the CWPO of PCM using CNT-O (■), CNT-P (●) and $NiFe_2O_4/Al_2O_3$ (▲). Reaction conditions: $[PCM]_0 = 100$ mg L^{-1}, $[H_2O_2]_0 = 474$ mg L^{-1}, $pH_0 = 3.5$, T = 80 °C and [catalyst] = 2.5 g L^{-1}.

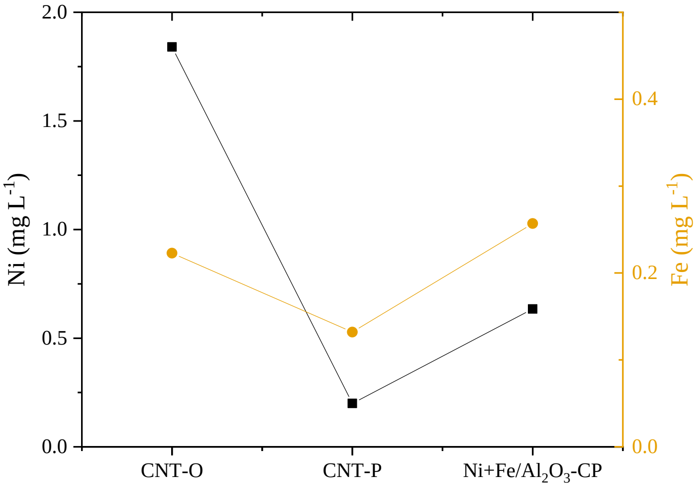

Figure 2. Metal leaching after CWPO using CNT-O, CNT-P and $Ni+Fe/Al_2O_3$-CP catalysts. Left Y-axis, black ■: nickel leaching, and right Y-axis, yellow ●: iron leaching.

4. Conclusions

The CNTs synthesized from LDPE in this work proved to have an adequate activity towards the decomposition of H_2O_2 and consequent removal of PCM and TOC by CWPO. It is particularly placed in evidence the suitability of the purified CNT (CNT-P) as an alternative to obtain similar removal rates of organic compounds when compared to a CNT bearing a metal phase. CNT-P proved to be more suitable since it allows a more controlled consumption of H_2O_2, leading to more efficient use of the oxidant. In addition, CNT-P has the advantage of reducing the leaching of metal species during the oxidation reaction, avoiding extra pollution and catalyst deactivation by leaching.

Acknowledgments
This work was financially supported by project "PLASTIC_TO_FUEL&MAT – Upcycling Waste Plastics into Fuel and Carbon Nanomaterials" (PTDC/EQU-EQU/31439/2017), Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC), and CIMO (UIDB/00690/2020) through FEDER under Program PT2020. Fernanda F. Roman acknowledges the national funding by FCT, Foundation for Science and Technology, through the individual research grant SFRH/BD/143224/2019.

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