Valorisation of polyolefins into magnetic carbon nanotubes: application as catalysts in wet peroxide oxidation of paracetamol

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Abstract. This work deals with the application of magnetic carbon nanotubes (MCNTs) in the catalytic wet peroxide oxidation (CWPO) of paracetamol (PCM), a pharmaceutical compound selected as model contaminant of emerging concern (CEC). MCNTs were synthetized by catalytic chemical vapor deposition (CCVD) at 850 ºC, considering low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) as carbon precursors representative of urban plastic solid waste. Magnetite supported in alumina (Fe_3O_4@Al_2O_3) nanoparticles previously synthesized by sol-gel were used as catalysts in the CCVD process. The synthesized MCNTs were tested in the CWPO of PCM at 80 ºC, monitoring during 24 h the concentration of H_2O_2, PCM, Total Organic Carbon (TOC) and aromatic compounds. All MCNT catalysts show activity allowing to decompose completely the pharmaceutical in aqueous solutions after 360 min. In particular, the MCNTs synthesized from HDPE lead to complete removal of the pollutant after 30 min of reaction. By TOC analysis, it was observed that the CNTs led to obtain mineralization degrees higher than 38% of the pollutant after 24 h. Aromaticity test indicated that the catalyst prepared from HDPE promotes more degradation of the intermediates than the catalyst prepared from LDPE and PP.

Keywords: Contaminants of emerging concern, carbon nanotubes, micropollutants, advanced oxidation processes, plastic waste.

1. Introduction

Contaminants of emerging concern (CECs), such as some personal care products, medicines and agricultural products, are defined as substances not listed in the regulatory standards of hazardous components. However, these substances can be harmful to aquatic and human life even at trace concentrations (U.S EPA, 2008). The problems of CECs arise because they can't be removed efficiently by conventional treatments used in wastewater treatment plants, thus accumulating in water bodies (U.S. Geological Survey, 2020).

Since the common treatment plants cannot efficiently remove these pollutants, alternative methods of water treatment, as advanced oxidation processes (AOPs), may be applied (Parsons, 2004). These methods consist in the use of highly oxidizing radicals ($HO^{\bullet}$) to degrade organic pollutants by oxidation (Pinho et al., 2015).

Another kind of pollution is caused by the inappropriate disposal of municipal solid wastes, which is more frequent in low-income countries (The World Bank, 2019). Plastics are one of the most generated solid wastes, predominantly composed by polymers, as LDPE, HDPE and PP (Singh et al., 2017). One of the problems associated with these materials is their degradation time, since plastics can last many years in natural environments. Thus, methods of reuse and valorisation of this kind of residues act as impactful alternatives to avoid drastic effects of its wrong disposal (Yaashikaa et al., 2020).

In this work, the synthesis of MCNTs by CCVD, considering HDPE, LDPE and PP as carbon precursors is assessed. Furthermore, the fresh prepared materials are used as catalysts for the degradation of paracetamol, chosen as model CEC, by CWPO. The parameters involved in the synthesis of the catalysts and in CWPO are also studied.

2. Methods

2.1. Synthesis of magnetite supported on alumina

The catalyst used in the CCVD process consists in magnetite supported on alumina (Fe_3O_4@Al_2O_3). To obtain the material, Fe_3O_4 was synthesized in presence of alumina adapting a sol-gel procedure described elsewhere (Giannakopoulou et al., 2002). The metal precursor undergoes rapid hydrolysis to produce a metal hydroxide solution, with a consecutive condensation leading to formation of a gel structure. Then, the gel is dried and the solid is calcined.

2.2. *Synthesis of carbon nanotubes by CCVD*

For the CCVD process, a vertical tubular furnace was equipped with 2 crucibles. The first crucible was loaded with 5 g of polymer (LDPE, HDPE, and PP) and in the second crucible was placed 1 g of CCVD-catalyst (Fe_3O_4@Al_2O_3). The working temperature was set at 850°C during 1 h under a N_2 flow of 50 mL min^{-1}. The synthesized carbon nanotubes were named MCNT_LDPE, MCNT_HDPE and MCNT_PP, the suffix representing the polymer used.

2.3. *Characterization by Fourier Transform Infra-Red (FTIR) spectroscopy analysis*

FTIR spectra of the three materials were recorded on a Perkin Elmer FTIR spectrophotometer UATR Two infrared spectrophotometer, with a resolution of 4 cm^{-1}. The range of wavenumbers used in the analysis was from 450 to 4000 cm^{-1}. All the measurements were done with the solid samples at room temperature.

2.4. Catalytic Wet Peroxide Oxidation (CWPO)

For the CWPO runs, 100 mL of a paracetamol solution with 100 ppm and its pH adjusted to 3.5 by means of H_2SO_4 (0.5 M) was added in a 250 mL two-necked round bottom flask equipped with a condenser. The stoichiometric quantity of H_2O_2 needed to fully mineralize paracetamol was then poured into the system. The mixture remained under stirring at 80 ºC for 5 min and samples were taken for reference values of the initial concentrations. To start the reaction, 0.25 g of catalyst was added to the system.

During the reaction, samples were collected to analyze TOC, aromaticity and concentrations of H_2O_2 and paracetamol at 0, 15, 30, 60, 120, 240, 360, 480 and 1440 min. After the reaction, the catalyst was washed with distilled water, filtered and dried in an air oven for 24 h.

2.5. Analytical techniques

H_2O_2 concentration was measured following the procedure reported in the literature (Masso et al., 2018) The method is based on by a colourimetric analysis, where 1 mL of a solution of H_2SO_4 (0.5 M), 0.1 mL of $TiOSO_4$ and 1 mL of the sample are added in a volumetric flask of 5 mL and then diluted with distilled water. Subsequently, each sample is analysed by UV-VIS spectrophotometry Jasco V-530 at the wavelength of 405 nm.

To evaluate the degradation of paracetamol in the CWPO runs, it was used a Jasco high-performance liquid chromatography (HPLC) equipped with a UV-VIS detector (UV-2075 Plus), a RES ELUT 5 µm C18-90 Å column (150 mm x 4.6 mm) of VARIAN and a quaternary gradient pump (PU-2089 Plus) for solvent delivery (0.3 mL min^{-1}). The wavelength used for the peaked absorbance detection of paracetamol was 277 nm.

A Shimadzu TOC-LCSH/CPH was used to determine total organic carbon (TOC).

Aromatic compounds formed during the reaction were evaluated following the method described in the literature (Alonso et al., 2004). Firstly, a phosphate buffer solution (PBS) with pH 7 was prepared to be used as a solvent. For the analysis, 0.5 mL of sample was diluted with the previous PBS in a 5 mL volumetric flask. Thereafter, the sample was analysed in a Jasco V-530 UV-VIS spectrophotometer at the wavelength of 254 nm.

3. Results and discussion

3.1. Synthesis of carbon nanotubes

The yields of polymer conversion into carbon in the produced MCTNs is shown in Table 1. The use of PP had a slightly higher yield, followed by LDPE and HDPE, respectively, same as reported in the literature (Veksha et al., 2017).

Table 1. Yields of MCNTs production

Material	Yield (polymer/carbon) (%)
MCNT_LDPE	22,0
MCNT_HDPE	17,8
MCNT_PP	23,6

The difference in the yield can be attributed to the different compositions of gases generated in the pyrolysis of each polymer. Each carbon source can be degraded into a variety of hydrocarbons such as methane, ethane, ethylene, propane, propylene and butane (Bajad et al., 2017). Accordingly, the CCVD process occurs via different routes depending on the gaseous composition.

The materials produced can be observed in Figure 1. All materials show magnetic properties, attributed to the presence of magnetite.

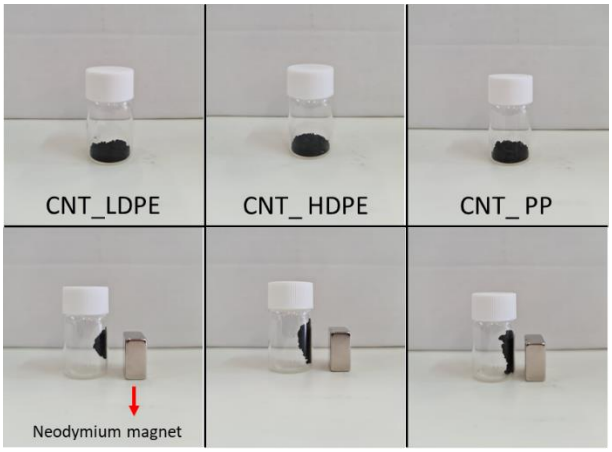

Figure 1. Magnetism interaction of the MCNTs

3.2. *Fourier Transform Infra-Red (FTIR) spectroscopy analysis*

The FTIR spectra of the materials can be seen in Figure 2. All materials show similar bands, the most relevant appearing at 584, 847, 1387, 1433, 1629 and 3430 cm^{-1},

which corresponds to Fe–O stretching vibrations due to the presence of magnetite, C–O functional groups, carboxylate groups, CH_2 and CH_3 stretching vibrations, C=C stretching vibrations, and –OH groups with the moisture of the material, respectively (Țucureanu et al., 2016).

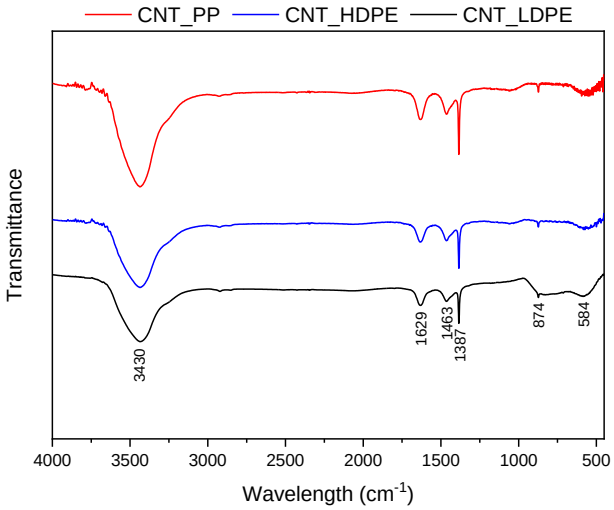

Figure 2. FTIR spectra of the three evaluated MCNTs

3.3. *CWPO of paracetamol*

3.3.1. H_2O_2 concentration

The H_2O_2 concentration against time obtained during the CWPO can be observed in Figure 3. All the three materials present similar results, leading to obtain the complete decomposition of H_2O_2 before 480 min of reaction. However, MCNT_HDPE shows a slightly higher decomposition rate, followed by MCNT_PP and MCNT_LDPE. The materials presents a notorious catalytic activity for H_2O_2 decomposition if compared with the non-catalytic run. It is possible to observe that the amount of H_2O_2 is capable of degrading all the paracetamol in all runs (Figure 4). This indicates that the amount of H_2O_2 used was efficiently consume to fully decompose the targeted pollutant (Rodrigues et al., 2017).

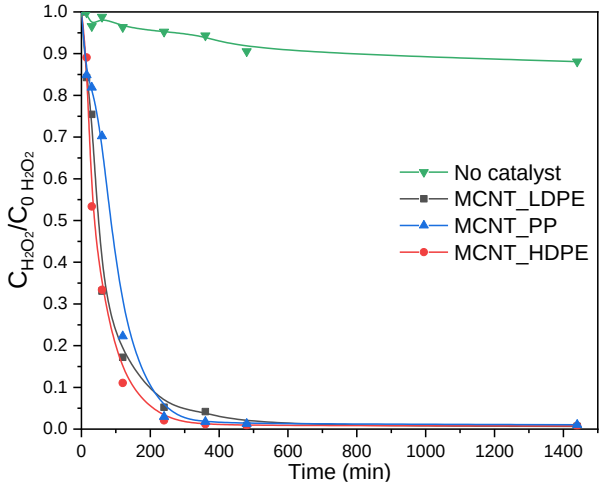

Figure 3. H_2O_2 concentration decay curves obtained with the MCNT materials.

3.3.2. Paracetamol concentration

The results obtained regarding paracetamol concentration against time in the CWPO runs can be seen in Figure 4. Compared with the non-catalytic run, the materials reveal high catalytic activity, with the complete degradation of PCM being obtained before 240 min of reaction. The material that shows higher catalytic activity is MCNT_HDPE, followed by MCNT_LDPE and MCNT_PP. This fact can be attributed to a possible difference in the composition of Fe in each material, leading to different oxidation capacities.

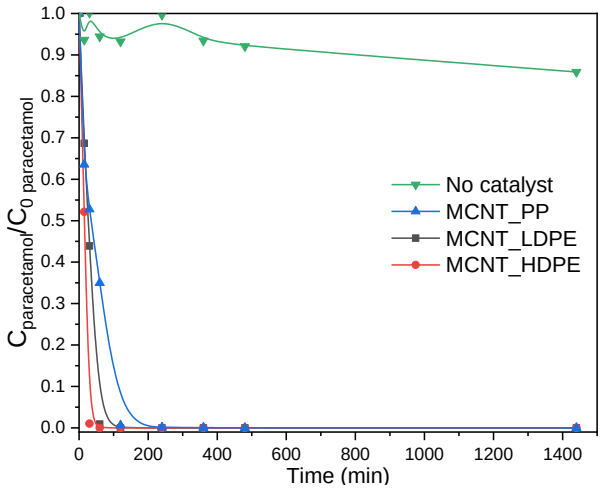

Figure 4. Paracetamol concentration decay curves obtained with the MCNT materials.

3.3.3. TOC analysis

By TOC analysis it was found that the catalysts are able to degrade the TOC content until 75%, presenting a capability to degrade the great part of the intermediates. The highest TOC conversion was achieved with MCNT_LDPE (75%). Furthermore, the lower level of TOC conversion from the other materials can be an indicative of formation of refractory components that couldn't be removed by the catalysts.

3.3.4. Aromatic compounds

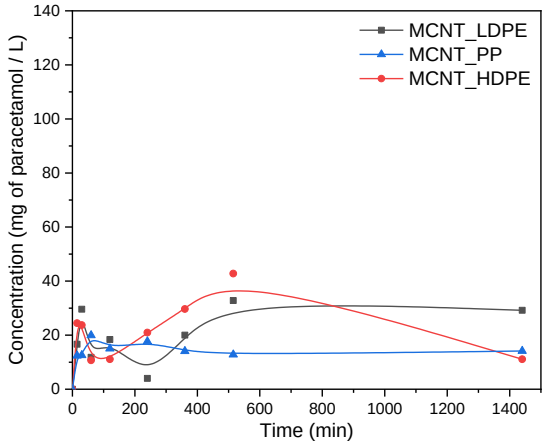

Figure 5. Aromatic compounds formed during the CWPO runs.

The evolution of the formation of aromatic compounds were depecited in Figure 5. With these results, it is possible to see that MCNT_PP enabled the formation of lower quantities of aromatic compounds than the other materials. However, at the end of the reaction, MCNT_HDPE also could degrade most of the aromatic compounds generated. It is also possible to see that MCNT_LDPE could not degrade the aromatic compounds, also suggesting a formation of refractory substances to CWPO.

4. Conclusions

The CCVD process successfully produced carbon nanotubes materials with Fe in its structure, confirmed by Fe vibrations on FTIR, giving the desired characteristics to the MCNTs, such as magnetism and catalytic activity in CWPO. The reaction runs carried out showed a fast decrease in the H_2O_2 and paracetamol concentrations during the reaction time, indicating high catalytic activity of the materials. The TOC removals were higher with MCNT_LDPE than with MCNT_HDPE. The aromaticity test indicated a higher formation of refractory aromatic intermediates in the case of MCNT_LDPE than with the other MCNTs. All the materials could degrade completely the pollutant in a time lower than 240 min, demonstrating high activity as catalysts in CWPO.

Acknowledgements

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