

Selective denitrification of lipophilic pollutants from oily wastewater by peroxidation using Janus-structured amphiphilic carbon nanotubes as catalysts

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Abstract: Carbon nanotubes (CNTs) were tested as catalysts in the selective denitrification of 4-nitrophenol (4-NP) from oily wastewater by catalytic wet peroxide oxidation (CWPO). The CNTs were prepared by chemical vapor deposition, feeding sequentially ethylene (E) and/or acetonitrile (A) during different times until 20 min, resulting in samples E20, A20 and E10A10, the number denoting the time feeding of each precursor and the order of appearance of the letter indicating the order of each precursor. The synthesized CNTs were tested in the CWPO of 4-NP in aqueous solutions and in simulated oily wastewater (2,2,4-trimethylpentane and water) at 80 °C, initial pH 3.5, $C_{4-NP} = 1 \text{ g L}^{-1}$, $C_{H_2O_2} = 3.56 \text{ g/L}$ and $C_{catalyst} = 2.5 \text{ g L}^{-1}$. The catalyst A20 promoted a faster decomposition of H_2O_2 and a lower degradation of 4-NP in the aqueous system, whereas the catalyst E20 displayed the opposite trend, since E20 was able to remove 99% of the pollutant and A20 only 69% after 8 h of reaction. E10A10 in biphasic L-L media presented the highest conversion of 4-NP after 24 h in the oily phase (51%), followed by A20 (38%) and then E20 (25%). This tendency may be ascribed to the formation of Pickering emulsions by E10A10. The amphiphilic characteristic of this material ensures a closer contact between the liquid phases, allowing higher mass transfer.

Keywords: Catalytic wet peroxide oxidation, 4-nitrophenol, Carbon nanotubes, Janus-structure, Pickering emulsion.

1. Introduction

Industrial development has led to an increase in oily wastewater pollution. The need to treat these waters is becoming very important since the industries generate

high volumes of wastewaters with a significant number of hazardous pollutants. An example is 4-NP, a compound with dangerous properties that the United States Environmental Protection Agency has included in the list of priority pollutants (Keith & Telliard, 1979). The conventional biological treatments are found inefficient to deal with wastewaters polluted with 4-NP, leading to study the use of advanced oxidation processes (AOPs) as alternative treatment. AOPs are based on the generation of oxidizing agents (HO^\bullet), which in turn degrade organic matter. Among AOPs, catalytic wet peroxide oxidation (CWPO) has been explored due to its low-cost (Ribeiro et al., 2016). In CWPO process, carbon-based materials have revealed promising results as catalysts (Diaz de Tuesta et al., 2019; Martin-Martinez et al., 2016, 2020; Ribeiro et al., 2016). In this regard, carbon nanotubes (CNTs) have displayed high catalytic activity in CWPO processes (Diaz de Tuesta et al., 2019; Martin-Martinez et al., 2016).

In addition to the water treatment challenges of, oily wastewaters, those containing lipophilic pollutants that may be dissolved in both aqueous and oily phases pose another difficulty. The reaction rates are hindered due to the limited interface between the phases. The use of amphiphilic catalysts (materials displaying both hydrophilic and hydrophobic characteristics), specially with a Janus-like structure, appears with clear advantages in this case. These materials can behave as emulsifiers, known as Pickering emulsions, allowing the formation and stabilization of oil-aqueous emulsions, increasing the contact between phases and the interfacial area. In biphasic L-L mixtures, the materials can act simultaneously as catalysts and emulsifiers, in an approach known as Pickering Interfacial Catalysts (PIC) (Diaz de Tuesta et al., 2019;

Nardello-rataj et al., 2021; Perro et al., 2005; Zhang et al., 2019).

This work aims at the removal of 4-NP, as a nitrogen-containing lipophilic model pollutant, from a biphasic oil-water medium (simulating contaminated oily wastewaters) by its oxidation with hydrogen peroxide employing amphiphilic Janus-structured CNTs as catalysts and emulsifiers. The CNTs were prepared by chemical vapor deposition (CVD) feeding sequentially ethylene (E) and/or acetonitrile (A) during different times resulting in amphiphilic CNTs with a double structure, also named as Janus-like materials.

2. Materials and methods

2.1 Reagents

The reactants used in the oxidation runs were 4-NP (98 wt.%) from Acros Organics and H₂O₂ (30%, w/v), provided by Fisher Chemical. 2,2,4-Trimethylpentane (isooctane), used as oil phase in the biphasic oxidation runs, was obtained from VWR Chemicals. Titanium (IV) oxysulfate (TiOSO₄, 15 wt.% in dilute sulfuric acid, H₂SO₄ 99.99%) sodium sulfite (Na₂SO₃, 98 wt.%) were supplied by from Sigma Aldrich and by Panreac. Distilled water was used throughout the work.

2.2 Synthesis of CNTs

The CNTs were synthesized by CVD process in a fluidized-bed reactor using ethylene (carbon source) and acetonitrile (nitrogen/carbon sources), as described elsewhere (Diaz de Tuesta et al., 2019; Martin-Martinez et al., 2016; Purceno et al., 2015). The CVD synthesis was conducted by employing AlCoFeO₄, as catalyst. Three samples were produced by feeding sequentially the fluidized bed reactor with ethylene (E) and/or acetonitrile (A) during the following periods: (1) C₂H₄ for 20 min; (2) C₂H₄ for 10 min followed by C₂H₃N for 10 min; (3) C₂H₃N for 20 min; resulting in E20, E10A10, A20 samples, respectively. Eventually, the synthesized CNTs were purified under reflux at 140 °C in an aqueous solution of H₂SO₄ (50 vol. %) for 3 h, to facilitate the total dissolution of the alumina and exposed Fe particles.

2.3 CWPO runs

The oxidation reactions were carried out in a 250 mL round flask well-stirred reactor (600 rpm), attached to a condenser, and with a temperature measurement thermocouple. The reactor was loaded with 50 mL of a 4-NP solution with a concentration of 1 g L⁻¹ and heated by immersion in an oil bath until 80 °C. The solution was previously acidified to pH₀ 3.5 by using H₂SO₄ solution (0.5 M). A calculated volume of hydrogen peroxide (30% w/v) was injected into the system, to reach a H₂O₂ concentration of 3.56 g L⁻¹, which is the stoichiometry concentration needed for full mineralization (complete oxidation) of 4-NP. After its complete mixing, the catalyst is added to the solution, in a concentration of 2.5 g L⁻¹. Samples of 1 mL were

periodically withdrawn at different times to monitor the oxidation runs.

The conditions used in the biphasic oxidation runs are similar to the conditions described for the CWPO runs in aqueous solution (80 °C, pH₀ 3.5, 2.5 g L⁻¹ of catalyst and stoichiometric amount of H₂O₂ needed for total 4-NP mineralization), with a proportion of O/W = 1/9 (5 mL and 45 mL for the oily (isooctane) and aqueous phases, respectively). In the beginning of each run, the reactions were sonicated for 10 min to stabilize the emulsion (minimum time reported for the stabilization of emulsions (Diaz de Tuesta et al., 2019)). The samples were periodically withdrawn during 1440 min to monitor the reaction progress.

2.4 Analytical methods

The samples withdrawn from the reactor were analyzed by HPLC and by colorimetric methods, as described elsewhere (Diaz de Tuesta et al., 2019). 4-NP (in the aqueous phase) was identified using a Jasco HPLC system at a wavelength of 277 nm (UV-2075 Plus detector). A Nucleosil 100-5-C18 column was used as stationary phase feeding as eluent 0.3 mL/min (PU-2089 Plus) of an A:B (90:10) mixture containing (A) phosphoric acid in ultrapure water and acetonitrile (B). To determine the concentration of H₂O₂, the sample was added to a 20 mL volumetric flask containing 1 mL of H₂SO₄ solution (0.5 mol L⁻¹) and 0.1 mL of TiOSO₄. The mixture was diluted with distilled water and then analyzed by UV-Vis spectrophotometry (T70 spectrometer, PG Instruments Ltd.) at a wavelength of 405 nm. The oily phase was also analyzed by UV-Vis to determine the concentration of 4-NP present in 2,2,4-trimethylpentane at a wavelength of 284 nm.

2.5 Emulsion formation

The ability of the catalyst to form emulsion was tested in flasks of 9 mL loaded with 4.5 mL, 0.5 mL of distilled water and isooctane respectively (W/O = 9:1 (v/v)) and 12.5 mg (C_{cat} = 2.5 g L⁻¹) of which catalyst. During 10 min the medium was sonicated and then immediately taken to the optical microscope for observation.

3. Results and discussion

3.1 CWPO of 4-NP in aqueous phase

Figure 1 shows the conversion of H₂O₂ and 4-NP in the CWPO reaction runs carried out in the aqueous phase experiments. As can be observed, the three materials have shown high catalytic activity in the CWPO of 4-NP, the conversions of hydrogen peroxide and 4-NP being much higher in the presence of the catalysts than in the non-catalytic run (X_{H₂O₂} = 5% and X_{4-NP} = 3% for the non-catalytic run). The removal of 4-NP by CWPO reaches the highest value when the sample E20 was used (99%), followed by the sample E10A10 (98%) and then A20 (69%). On the other hand, the conversion of

H₂O₂ follows the inverse order, decreasing with the decrease of the N-content in the samples: A20 (90%) > E10A10 (61%) > E20 (52%). This result means that a higher N-content, corresponding to materials with higher hydrophilic character, leads to higher conversions of hydrogen peroxide and lower removal of 4-NP. Similar results were observed in the literature. Martin-Martinez *et al.* (2016) also reported an inverse trend between 4-NP removal and hydrogen peroxide consumption for CNTs with different N-contents (Martin-Martinez *et al.*, 2016). Diaz de Tuesta *et al.* (2019) have also shown that a higher hydrophilic character leads to higher hydrogen peroxide conversion and lower removal of pollutants for the CWPO of 2-NP (Diaz de Tuesta *et al.*, 2019).

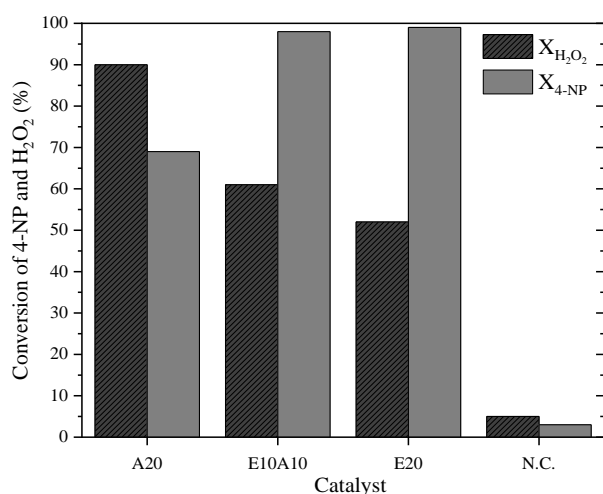


Figure 1. Conversion of hydrogen peroxide (X_{H₂O₂}) and 4-NP (X_{4-NP}) carried out with the synthesized CNTs in aqueous phase after 8 h. Operating conditions: 80 °C, pH₀ = 3.5, C_{cat} = 2.5 g L⁻¹, C_{4-NP,0} = 1 g L⁻¹ and stoichiometric quantity of H₂O₂ needed for the complete mineralization of 4-NP (3.56 g L⁻¹). N.C. = non-catalytic run.

3.2 Pickering emulsion of CNTs

The ability of the CNTs to act as Pickering emulsifiers was tested in the stabilization of a water-isooctane biphasic mixture (W/O = 4.5:0.5 mL/mL, m_{cat} = 12.5 mg). The emulsion stabilization was achieved under sonication during 15 min. CNT synthesized with both acetonitrile and ethylene precursors (E10A10) formed perfectly stable Pickering emulsions. The E20 material also emulsifies the isooctane/water mixture, as schematized in Figure 2 with both catalysts. As know that the presence of two different sections (hydrophilic-hydrophobic) is important for the stabilization of the Pickering emulsions, we can assume that E20 emulsion is much unstable compared to E10A10. No emulsion was formed in the presence of A20 catalyst for isooctane/water mixture even after 120 min of sonication.

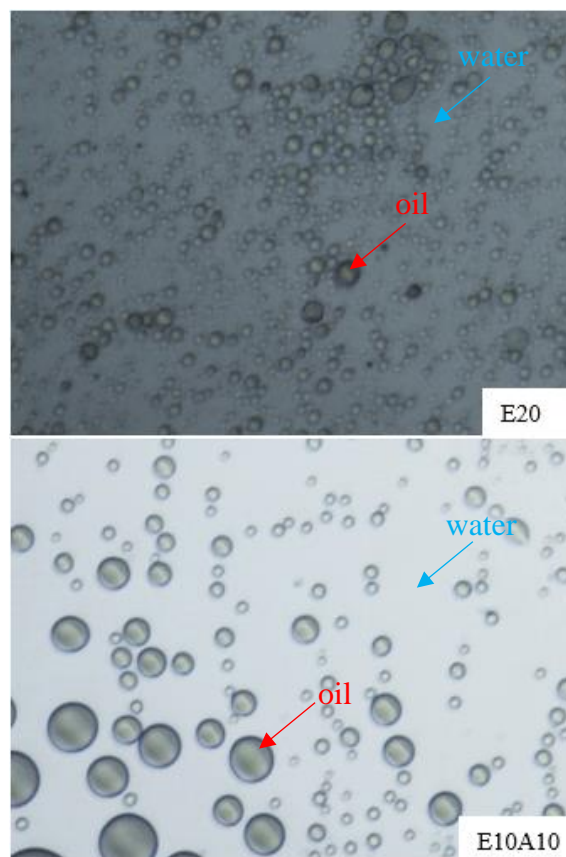


Figure 2. Optical Microscope Images of the isooctane in water pickering emulsions stabilized by the CNTs W/O = 9:1 (v/v) C_{cat} = 2.5 g L⁻¹.

3.3 CWPO of 4-NP in biphasic L-L mixture

Figure 3 presents the results obtained for the oxidation runs carried out under biphasic conditions after 24 h. The H₂O₂ consumption followed the same trend as observed in the aqueous systems. A20 shows the highest conversion of hydrogen peroxide (100%), followed by E10A10 (86%) and E20 (38.8%). However, when it comes to the conversion of the pollutant, all materials display a similar conversion of 4-NP in the aqueous phase (A20 = 99%, E10A10 = 100%, and E20 = 97.7%). On the other hand, in the oily phase, E10A10 reveals the highest removal of 4-NP (51%), followed by A20 (38%). E20 shows the lowest conversion of the pollutant (25%) in the oily phase. Due to its more hydrophilic nature, A20 is mostly located in the aqueous phase, and it does not allow a close contact between the pollutant in the oily phase and the generated hydroxyl radicals. On the other hand, E20 is mostly located in the oily phase due to its more hydrophobic characteristic, thus not being able to completely decompose hydrogen peroxide into hydroxyl radicals and compromising the conversion of 4-NP. Finally, E10A10, due to its amphiphilic characteristic, is located on the interface of the aqueous-oily phase, forming a Pickering emulsion. The Pickering emulsion allows for more intimate contact between the phases, thus overcoming mass transfer issues seen with other catalysts and helping to promote the oxidation of the pollutant located in the oily phase.

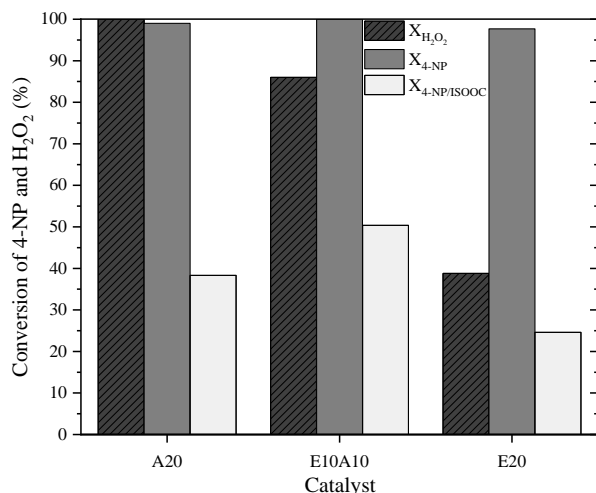


Figure 3. Conversion of hydrogen peroxide ($X_{H_2O_2}$), 4-NP (X_{4-NP}) in aqueous phase, and 4-NP in the organic phase ($X_{4-NP/ISOOC}$) in the CWPO of 4-NP after 24 h performed in biphasic water-isooctane mixtures with CNTs. Operating conditions: 80 °C, W/O = 9:1 (v/v), $pH_0 = 3.5$, $C_{cat} = 2.5 \text{ g L}^{-1}$ of total volume, $C_{4-NP,0}$, oil = 10 mg L^{-1} and stoichiometric quantity of H_2O_2 needed for the total mineralization of 4-NP (3.56 g L^{-1}).

4. Conclusions

The CNTs prepared in this study show high catalytic activity in the CWPO of 4-NP, allowing a good removal of the pollutant with all the materials prepared. In the aqueous oxidation experiments, the samples E20 and E10A10 allowed for the highest removal of the pollutant (99% and 98%, respectively). The chosen precursor (ethylene (E) and/or acetonitrile (A)) influences the carbon nanotubes and their character. A higher N-content on the materials indicates a higher hydrophilic character, which leads to a higher conversion of hydrogen peroxide and to a lower removal of 4-NP. The CNTs synthesized from a sequential feed of both precursors (E10A10), known for its Janus-structure, showed the best conversion of 4-NP in the L-L biphasic reaction system (isooctane-water). The results observed with E10A10 in biphasic media can be explained by its ability to form and stabilize Pickering emulsions, allowing the contact between both phases, and providing a higher mass transfer.

Acknowledgments

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