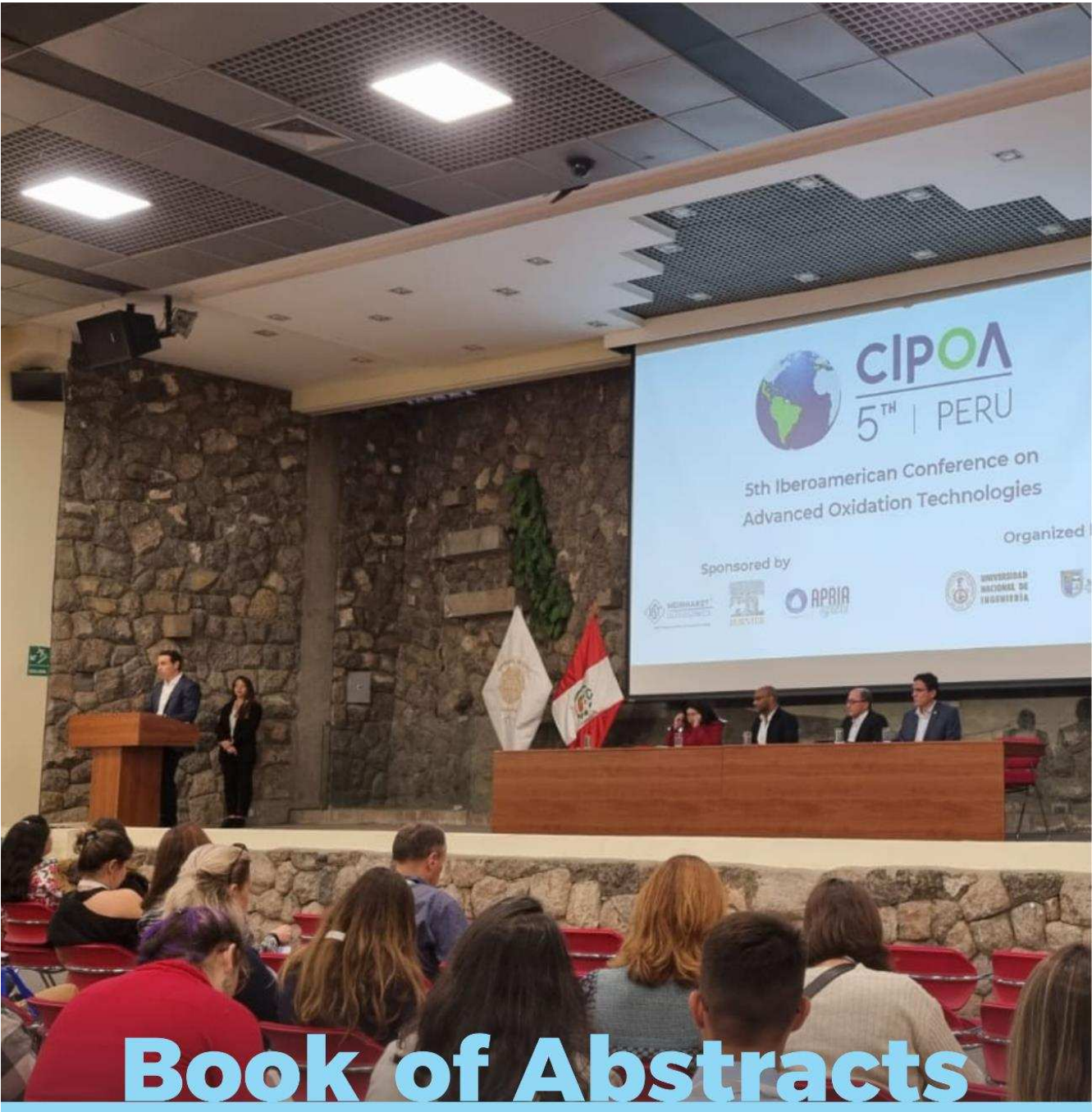

Book of Abstracts

CIPOA 5TH | PERU

5th Iberoamerican Conference on Advanced Oxidation Technologies

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Selective denitrification of a simulated oily wastewater using Janus-structured carbon nanotubes

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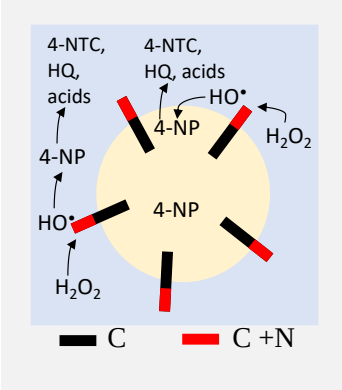

Carbon nanotubes (CNTs) bearing a Janus-like structure were synthesized by chemical vapor deposition considering ethylene and acetonitrile as carbon and nitrogen sources. The developed materials were applied as catalyst in the oxidation of 4-nitrophenol (4-NP) dissolved in a biphasic medium (water/2,2,4-trimeylpentane) simulating a contaminated oily wastewater. The CNT prepared using both ethylene and acetonitrile precursors shows a Janus-structure, leading to the highest abatement of 4-NP as well as to the highest removal of TOC, proving to be an alternative towards the removal of lipophilic pollutants from oily effluents, allowing to reclaim the oily phase.

Introduction

The discharge of oily compounds in water bodies as a consequence of the intense industrial development has created a challenge-to-treat effluents known as oily wastewaters [1]. The oily fraction can be comprised of petroleum-based products, fats, vegetable oils, residues from biodiesel production, among others [2], and bio-refractory compounds dispersed in both oily and aqueous phases are commonly present [3]. Those oily wastewaters have been ascribed to a series of health and environmental issues [4] and their proper management is mandatory. In some cases, there is an associated high-value to the oily compounds, and reclaiming this valuable oily fraction is of interest [3]. Thus, the development of treatment protocols for the removal of bio-refractory compounds from oily wastewaters, allowing the recovery of both oily and aqueous phase is an interesting approach. One alternative is the use of oxidation-based processes to selectively degrade hazardous compounds simultaneously treating oily and aqueous phases. Such type of processes are highly studied for the removal of nitrogenated and sulfonated compounds from liquid fuels [5], and could be extended for the treatment of oily wastewaters. However, oxidation-based processes under biphasic systems suffer with limited reaction rates due to the low interfacial area between phases. The use of a phase interfacial catalyst (PIC), especially particles comprising a Janus structure, could allow overcoming the issues of low interfacial area [6]. This work deals with the selective removal of 4-nitrophenol (4-NP) from a simulated oily wastewater composed by water and 2,2,4-trimeylpentane by oxidation with hydrogen peroxide using carbon nanotubes (CNTs) bearing a Janus structure in a PIC-like approach.

Material and Methods

CNTs were obtained by chemical vapour deposition using ethylene and acetonitrile as carbon and nitrogen sources, respectively, as described elsewhere [3] and grown over a $AlCoFeO_4$ catalyst obtained using a citrate–nitrate gel combustion method [7]. E20 was synthesized by feeding ethylene for 20 min. Similarly, acetonitrile feeding for 20 min led to A20. E1A19 was obtained by feeding 1 min of ethylene immediately followed by 19 min of acetonitrile. All CNTs were then washed with H_2SO_4 50% vol./vol. for 3 h at 140 °C under reflux to remove the metal particles. TEM images were taken to confirm the Janus structure of E1A19.

Oxidation reactions were conducted at 80 °C, C_{CNT} = 2.5 g L^{-1}, initial pH of 3.5, O/W ratio of 1:9 vol./vol., with an initial concentration of 4-NP in the aqueous phase of 1 g L^{-1} and in the oily phase of 10 mg L^{-1}, and a concentration of H_2O_2 of 3.6 g L^{-1}. The reaction medium was sonicated for 10 min, and the reaction was conducted for 24 h.

Results and Discussion

Figure 1 shows the TEM images of the three CNTs. Ethylene feeding results in a CNT with fewer walls and smaller diameters (E20, Fig.1,a), whereas acetonitrile results in materials with higher diameters and a 'cup-stacked' structure (A20, Fig.1,b). In the case of E1A19, both structures can be observed, and they are highlighted in Fig. 1,c., thus allowing to conclude that the methodology is

effective to synthesize CNTs bearing a Janus structure. Similar characteristics were observed in previous studies [3].

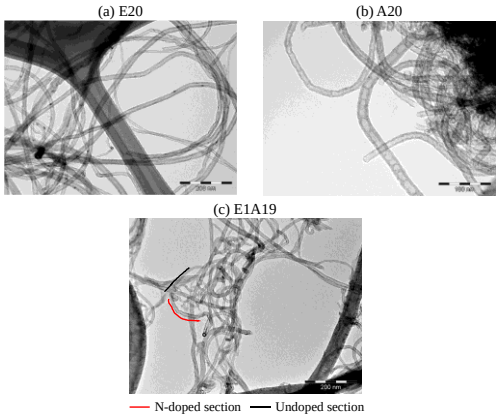

Figure 1. TEM images of (a) E20, (b) A20 and (c) E1A19 with highlighted N-doped (red) and (black) undoped sections.

Figure 2 summarizes the results obtained in the oxidation of 4-NP in the biphasic system using the CNTs as PIC. A clear distinction in the removal of 4-NP from the oily phase can be observed in the presence of A20, E20 and E1A19. In 24 h, the highest removal of the pollutant from the oily phase was observed for the reactions conducted in the presence of E1A19 (~76%), followed by A20 (~48%) and E20 (30%). This can be ascribed to the defined Janus structure of E1A19, which allows a closer contact between the pollutant and the oxidant, favoring its removal from the oily phase.

The overall removal of 4-NP (accounting for 4-NP removal from both oily and aqueous phase) was maintained above 98% regardless the CNT used, although the trend was the same as observed for the removal of 4-NP from the oily phase (E1A19 > A20 > E20). Likewise, the abatement of TOC was more pronounced in the presence of E1A19 (~50%), whereas in the presence of A20 and E20 lower abatements were obtained (31 and 36%, respectively). Similar tendencies using Janus particles in biphasic reactions were observed for the removal of 2-nitrophenol from an oily wastewater [3].

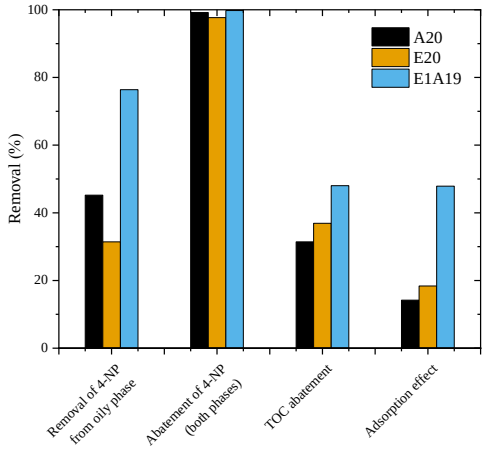

Figure 2. Removal of 4-NP, TOC and aromatic compounds and adsorption contribution after 24 h of reaction in the presence of A20, E20 and E1A19.

Conclusions

The proposed methodology allows to obtain CNTs with a Janus-like structure. The CNT bearing a Janus structure, as observed for E1A19, results in higher removal of 4-NP from the oily phase as well as in higher TOC abatement, thus indicating that the presence of both N-doped and undoped sections in the CNT structure favors reactions conducted in biphasic systems, allowing a closer contact between the lipophilic pollutant and the hydrophilic oxidant.

Acknowledgments

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