BOOK OF ABSTRACTS

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P40. SELECTIVE OXIDATION OF 4-NITROPHENOL WITH H_2O_2 IN A BIPHASIC SYSTEM BY JANUS-LIKE CARBON NANOTUBES

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The use of petroleum-based products has increased drastically with the increase in population, resulting in the deposition of oily products in aquatic systems. It is estimated that for each ton of petroleum that undergoes refinement processes, between 0.5 and 1 ton of oily wastewaters are generated, bearing an oil concentration that may reach 40 g L^{-1} [1,2]. Hazardous pollutants dissolved both in oily and aqueous phases may also be found in those oily wastewaters [3], hindering their treatment through conventional processes. Furthermore, the oil phase is, in some cases, an added-value product, and its degradation results in economic losses. Thus, the development of processes that allow the removal of hazardous contaminants from oily and aqueous phases, providing an opportunity for recovering both phases, should be advantageous [3]. This work deals with the selective removal of a hazardous compound (4-nitrophenol, 4-NP) from a simulated oily wastewater (2,2,4-trimethylpentane:water = 10:90 v/v) by an oxidative process considering H_2O_2 as oxidant and amphiphilic Janus-like carbon nanotubes as catalysts. Amphiphilic catalysts were selected since they should present advantages in this process due to their ability to interact with both aqueous and oily compounds and phases [4].

The simulated oily wastewater was prepared by dissolving 4-NP ($C_{aqueous\ phase,0}$ = 1 g L^{-1}) in the water phase, adding 2,2,4-trimethylpentane and leaving the mixture undisturbed for more than 1 week to reach the concentration of 4-NP in both phases at the equilibrium state. The oxidation reactions were carried out at 80 °C, considering the stoichiometric concentration of H_2O_2 for full 4-NP mineralization, initial pH (pH_0) of the aqueous phase of 3.5, and a catalyst concentration of 2.5 g L^{-1} (considering the total volume of the system). In the first 10 min of reaction, the medium was exposed to an ultrasound (Ultrasons-H, JP-Selecta) and the reaction was carried out for 8 h. 4-NP and its oxidized intermediates concentration were monitored by HPLC (Jasco system), and H_2O_2 concentration was estimated via a colorimetric method with $TiOSO_4$ at a wavelength of 405 nm. TOC was monitored in a Shimadzu TOC-L analyser. The CNTs were prepared via chemical vapor deposition, considering a Fe/γ-Al_2O_3 as catalyst, and ethylene (E) and acetonitrile (A) as carbon and carbon/nitrogen sources, respectively. Ethylene or acetonitrile were fed to the system for 20 min, leading to E20 and A20, respectively. E1A19 was synthesized by feeding 1 min of ethylene, immediately followed by 19 min of acetonitrile. CNTs were subjected to acid washing to remove the metal particles (50% vol. H_2SO_4, 140 °C, 3 h), followed by abundant distilled water until neutrality of the rinsing waters.

The conversions of H_2O_2, 4-NP and TOC are observed in Fig. 1. E1A19 resulted in a higher consumption of H_2O_2 (95%) followed by A20 (65%), whereas E20 resulted in a very limited consumption of the oxidant (*ca*. 9%). 4-NP and TOC removals also followed the same trend as observed for the consumption of H_2O_2. E1A19 resulted in a higher degradation of 4-NP and TOC (99 and 43%, respectively), followed by A20 (92 and 32%, respectively) and E20 (75 and 14%, respectively). E1A19 was the only catalyst able to completely degrade the formed intermediate 4-nitrocatechol (4-NC) after 8 h of reaction. On the other hand, A20 and E20 were not able to completely degrade the formed 4-NC (43 and 131 mg L^{-1} after 8 h of reaction, respectively). As expected, the Janus-like CNT (E1A19) revealed the highest ability to degrade H_2O_2, 4-NP, oxidized intermediates of 4-NP and, hence, TOC. This activity is ascribed to its ability to interact with both H_2O_2 and lipophilic pollutant.

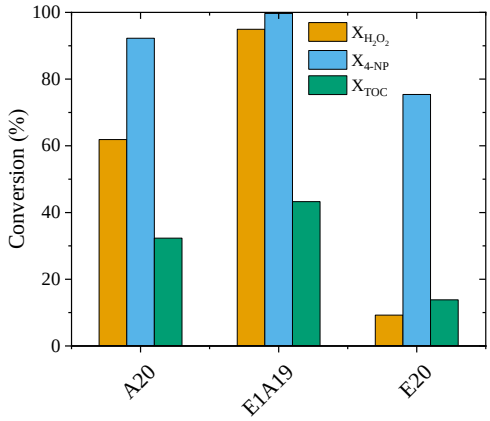

Figure 1. Conversions of H_2O_2, 4-NP and TOC after 8 h of reaction (Conditions: $C_{aqueous\ phase,0}$ = 1 g L^{-1}, $C_{H_2O_2,0}$ = 3.6 g L^{-1}, C_{cat} = 2.5 g L^{-1}, pH_0 = 3.5, T = 80 °C, 10 min ultrasound, 8 h of reaction)

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