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CARBON NANOTUBE CATALYSTS FOR THE CWPO OF 2-NITROPHENOL IN BIPHASIC SYSTEMS: KINETIC INSIGHTS

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Carbon nanotubes (CNTs) were used as catalysts in the removal of 2-nitrophenol (2-NP) by catalytic wet peroxide oxidation (CWPO). Different CNTs were synthesized by catalytic chemical vapour deposition (CVD) using Fe/γ-Al_2O_3, as described elsewhere (Purceno *et al.*, 2015 and Martin-Martinez *et al.*, 2016). A fluidized-bed reactor was employed by feeding a gas mixture of hydrogen and: i) ethylene alone for 30 min (sample E30); ii) acetonitrile for 20 min, followed by ethylene for 20 min (sample A20E20); iii) acetonitrile for 20 min, followed by ethylene for 10 min (sample A20E10); iv) ethylene for 10 min, followed by acetonitrile for 20 min (sample E10A20); and v) acetonitrile alone for 30 min (sample A30). The CNTs were tested for the oxidation of 2-nitrophenol (2-NP) in aqueous-phase (Martin-Martinez *et al.*, 2016) and in biphasic conditions (cyclohexane-water) simulating oily wastewater effluents as described in previous works (Diaz de Tuesta *et al.*, 2018). Both systems were modelled by using kinetic power-law equations, following a methodology presented previously (Diaz de Tuesta *et al.*, 2017).

All the CNT samples revealed catalytic activity in the CWPO of 2-NP when compared with the results obtained in the non-catalytic run (*i.e.*, H_2O_2 and 2-NP conversions lower than 15 % after 24 h without catalyst). Additionally, the CNTs did not show significant adsorption of the pollutant in runs carried out in the absence of H_2O_2. In water, the highest activity was observed for E30 (with a complete removal of 2-NP after 24 h, whereas conversions of 2-NP lower than 95 % were obtained with the other CNT). E30 also yielded the best CWPO performance, ascribed to the best efficiency in the consumption of H_2O_2 (*i.e.*, higher TOC conversion for lower H_2O_2 conversion). This behaviour could be explained by a higher hydrophobic character of the sample (assessed by contact angle determination), as consequence of the absence of N-containing groups in the structure. However, amphiphilic A20E20, A20E10 and E10A20 samples presented the highest catalytic activity for the removal of 2-NP from biphasic media. This catalytic activity was ascribed to the formation of Pickering emulsions, enabling the decomposition of H_2O_2 into hydroxyl radicals at the hydrophilic section of the catalyst, and the adsorption and further reaction of 2-NP with hydroxyl radicals at the lipophilic section. In addition, the stabilization of the emulsion leads to an increase of the interfacial area between the phases, increasing the transfer of 2-NP from the oil phase to the aqueous one. Under biphasic conditions, the lower catalytic activity of the most lipophilic sample (E30) was explained by its distribution in the organic phase and a negligible H_2O_2 conversion. On the other hand, the highest conversion of H_2O_2 was achieved using the most hydrophilic CNT (A30), which was preferentially distributed in the aqueous phase.

The biphasic oxidation was modelled as follows:

$$-\frac{dC_{H_2O_2}}{dt} = k_{H_2O_2} \cdot C_{H_2O_2}^2$$

$$-\frac{dC_{2\text{-}NP,oil}}{dt} = k_{A,2\text{-}NP,transfer} \cdot \left(C_{2\text{-}NP,oil} - P_{OW} \cdot C_{2\text{-}NP,aq}\right)$$

$$\frac{dC_{2\text{-}NP,aq}}{dt} = k_{2\text{-}NP,transfer} \cdot \left(C_{2\text{-}NP,oil} - P_{OW} \cdot C_{2\text{-}NP,aq}\right) - k_{2\text{-}NP,ox} \cdot C_{2\text{-}NP,aq} \cdot C_{H_2O_2}$$

The coefficient of distribution (P_{OW}) of 2-NP between the phases was 32.4. Table 1 summarizes the parameters of the model obtained for the biphasic oxidation of 2-NP under the following operating conditions: initial pH 3, 50 ºC, catalyst load = 2.3 g L^{-1}, starting concentration of 2-NP = 5 g L^{-1} in the oil phase and 0 g L^{-1} in the aqueous phase, and stoichiometric dose of H_2O_2 needed for the complete mineralization of 2-NP.

Table 1. Kinetic constants ($k_{H_2O_2}$ and $k_{2\text{-}NP,ox}$), transfer constant (considering a constant interfacial area) and determination coeficient (R^2) of the developed kinetic model

Material	$k_{H_2O_2}$ (M^{-1} h^{-1})	$k_{2\text{-}NP,transfer}$ (h^{-1})	$k_{2\text{-}NP,ox}$ (M^{-1} h^{-1})	R^2
E30	0.000	0.63	0.008	0.969
A20E20	0.041	1.68	0.045	0.979
E10A20	0.050	0.90	0.054	0.971
A20E10	0.080	1.03	0.039	0.974
A30	0.258	0.79	0.034	0.972

The results obtained put in evidence the superior properties of amphiphilic CNT for the oxidation of lipophilic organic compounds present in biphasic systems due to the formation of Pickering emulsions.

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