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Towards a plastic-free ocean: Green TiO_2-based photocatalysts for mitigation of micro- and nanoplastic marine pollution

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The presence of plastics in the ocean is currently one of the most pressing environmental issues that our society faces. Big items cause entanglement and asphyxia of the biota. The smaller debris, known as microplastics (MPs, ⌀ = 1 μm – 5 mm) or nanoplastics (NPs, ⌀ < 1 μm), cause health issues to the biota that consumes them and are transferred throughout the tropic chain up to humans. Formerly, it was assumed that once plastics enter the ocean they remain there. Now, it is known that MPs are released from the marine environment into the atmosphere. Indeed, MPs cycle through the earth in a manner akin to global biogeochemical cycles. Currently, the most promissing technologies to fight MPs and NPs pollution are those based in their elimination from polluted effluents before their discharge into waterbodies. Photocatalysis is a water treatment process that can be adapted as tertiary treatment into wastewater treatment plants (WWTPs). By photocatalysis, MPs and NPs can be mineralized to CO_2 and H_2O or degraded into less toxic substances. Furthermore, if performed in Vis or solar light and if the photocatalyst is prepared using renewable feedstocks, the overall process respects the 6th, 7th and 9th principles of Green Chemistry. In this research, the Vis light photocatalysis of polyethylene (PE), polystyrene (PS) and polyethylene terephthalate (PET) MPs and NPs was investigated using N-TiO_2, C,N-TiO_2 and C,N-TiO_2/SiO_2. The photocatalysts were synthesized by two green routes: a bio-inspired route where proteins from *Mytilus edulis* mussels were used as renewable dopant agents and a biomineralization route using *Pteria sterna* oysters. Photocatalysis was performed in aqueous medium and the influence of pH, temperature, MPs' size and shape and the semiconductor's form (powders or films) on the removal process was tested. The removal was monitored by gravimetry, FTIR, OM, SEM-EDS, TG/DSC-FTIR and UHPLC-MS. It was found that MPs removal can reach values of up to 70% in 50 h of reaction. All the variables influenced degradation. The e^- plays an essential role in PE degradation, while h^+ and $O_2^{\bullet -}$ participates in the initiating step [1-3]. This information can guide the design of photocatalytic systems that enhance MPs' degradation.

[1] *Ariza-Tarazona et al*. Ceram. Inter 45 (2019) 9618. [2] *Ariza-Tarazona et al. J. Hazard. Mater. 395 (2020) 122632.* [3] *Vital-Grappin et al. Polymers 13 [7] (2021) 999.*

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