



POLYANILINE/TiO₂ COMPOSITES: GREEN PHOTOCATALYTIC SYNTHESIS AND APPLICATION IN WASTEWATER REMEDIATION

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In recent years, polyaniline (PANI) composites and nanocomposites with metal and metal-oxide materials have received growing attention for electrochemical and photoelectrochemical applications (Gu 2013). Among them, PANI/TiO₂ composites are probably the most interesting systems due to synergistic effects between the conductive polymer and the oxide photocatalyst in terms of photogenerated charge separation and photocatalytic efficiency (Bae 2011). Moreover, polyaniline has been reported to possess favourable sorption properties, which can be exploited for pollutant remediation (Alcaraz-Espinoza 2015, Janaki 2012). PANI/TiO₂ composites are thus promising candidates for wastewater treatment combining different pollutant remediation approaches.

Polyaniline is classically synthesised via oxidative polymerization (Tran 2011), which involves noxious reagents (aniline and peroxydisulfates) and leads to toxic and carcinogenic byproducts (such as benzidine and trans-azobenzidine). In recent years, greener alternatives have been reported, such as a synthetic process starting from aniline dimer ((4-aminophenyl)aniline) and using Fe³⁺ as catalyst and H₂O₂ as oxidant (Della Pina 2018). Unfortunately, this alternative procedure does not offer any control over the polymer morphology, leading to compact materials with low surface area and, as a consequence, poor dye-sorption capability.

Very recently, we proposed a new photocatalytically induced green synthesis leading to stable polyaniline/TiO₂ composites with porous morphology, wide surface area, high crystallinity and, most important, excellent dye removal performance and reusability (Cionti 2018). The reaction is carried out in two steps: at first, the aniline dimer is dissolved in a HCl aqueous solution and TiO₂ is added while starting UV irradiation. In the second step, H₂O₂ is added in the dark, leading to the final product.

In this work, we shed light on the photocatalytic nature of the synthetic mechanism, highlighting the different roles of TiO₂ and of H₂O₂ on the composite structural and morphological features as well as on the composite performance for pollutant abatement.

The reaction mechanism was investigated by a combination of spectrometric techniques, radical scavenger tests, and surface characterizations (**Fig.1**). By sampling the reaction mixture at different irradiation times, we demonstrated that under UV irradiation the growth of the oligomers occurs at the TiO₂ particle surfaces. The same experiment carried out without UV irradiation showed the intrinsic photocatalytic nature of the process: in the dark, only short oligomers without appropriate chain conjugation were produced. However, even after prolonged UV irradiation, the final green product could be obtained only upon addition of H₂O₂, showing that, while oligomer formation is initiated by radicals produced by TiO₂ photocatalysis, small amounts of an oxidant (H₂O₂) are still needed for the polymer chain growth.

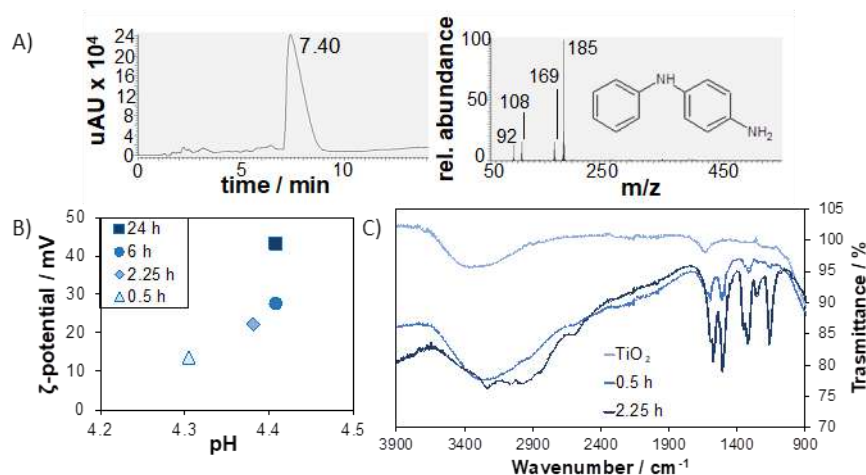


Figure 1. A) LC-MS analyses of the liquid phase showing the only presence of unreacted dimer in solution. B) ζ -potential measurements of the solid phase sampled at different irradiation times: the potential increase is attributed to positively charged oligomers at the TiO₂ surface. C) FT-IR spectra of bare TiO₂ and the solid fraction sampled after different irradiation times.

The role of the H₂O₂ amount proved to be especially crucial with respect to the composite properties. Increasing the H₂O₂ amount together with that of TiO₂ led to composites with low surface area and reduced dye removal capability (**Fig.2 a**) due to a faster polymerization step. On the other hand, when only the photocatalyst amount was increased, neither the product morphology, nor its dye-removal ability were affected. This enables to increase the TiO₂ content within the composite with the aim of enhancing its photocatalytic performance. In this respect, the composite stability was tested in water under prolonged UV irradiation, showing that the material optical, structural and morphological properties remained unchanged.

The composite was tested towards the removal of anionic azo dyes in aqueous solution, evaluating the effect of the matrix composition and the composite reusability (**Fig.2 b**), showing promising results.

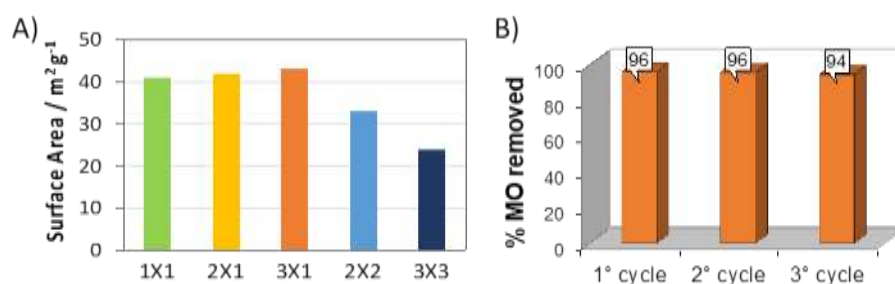


Figure 2. A) BET surface area of composites with double and triple amount of TiO₂ and unchanged H₂O₂ (samples 2x1 and 3x1, respectively) and double and triple amount of both TiO₂ and H₂O₂ (2x2 and 3x3). B) Recycle tests of PANI/TiO₂ towards sorption and release of methyl orange (MO).

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