Photocatalytic degradation of emerging organic pollutants in waters by nanocomposite materials

Sapia Murgolo

University of Bari Aldo Moro, Department of Chemistry, Faculty of Science

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Extended abstract

The research activities in the field of water treatment technologies have demonstrated that the conventional wastewater treatment plants (WWTPs), typically based on biological processes, are not able to efficiently remove a wide variety of persistent, toxic and/or non biodegradable organic pollutants as well as pharmaceuticals and personal care products (PPCPs). Therefore, most of the aforementioned organics end up in receiving water bodies and, consequently, WWTPs are nowadays considered as secondary sources of micropollutants in the environment. Most current research in the field of wastewater treatment is therefore oriented towards the development of novel depollution technologies with enhanced performance in terms of efficiency and applicability.

In this perspective, the research activity of this PhD thesis aimed at investigating the efficiency of novel TiO_2-based nanocomposite materials obtained by combining different types of catalytically active nanoparticles (NPs) with potential synergy within a suitably designed host polymers, such as hybrid organic inorganic and fluorinated polymers, for photocatalytic degradation of pollutants in aqueous solutions. Particularly, they included:

- nano-sized TiO_2 supported on single wall carbon nanotubes,
- nano-sized TiO_2 film supported on stainless steel,
- TiO_2 based photocatalytic dual layer hollow fibre membrane,
- metallic meshes coated with 10wt% TiO_2 at the surface of the polymer particles,
- nano-size TiO_2 magnetic catalytic particles.

A mixture of organic pollutants of emerging concern, including PPCPs and EDCs, was used to evaluate the performance of the innovative TiO_2-based nanocomposite catalysts in term of degradation of micropollutants present at low concentration ($\mu g\ L^{-1}$ range) in different water matrix i.e. distilled water, groundwater and secondary effluent (biologically treated wastewater) of a WWTP. All matrices tested were spiked with the investigated organic pollutants.

Photolytic and photocatalytic experiments were performed in presence of UV light as well as in presence of simulated solar light (SolarBox device). The simulated solar light was used in order to

evaluate any potential increase of the photocatalytic properties associated with the new nanocomposite materials, which might allow the use of solar energy to activate the process in order to reduce operating costs and facilitate the implementation of large-scale systems.

Reactors with different geometries and light intensities were investigated: bench scale systems equipped with Hg-UV lamp, simulated-solar light and excimer UV lamp as well as pilot scale systems equipped with Hg-UV lamp.

The methodology was based on the comparison of the kinetics of degradation of the target contaminants obtained with the developed nanocomposite catalysts with the ones obtained with various controls, including hydrolysis, UV (photolysis) as well as with respect to photocatalysis using the conventional TiO_2 Degussa P25 catalyst (non-porous anatase; surface area 50 m^2/g, average diameter 30 nm). In this context, an accurate evaluation of the electrical energy per order magnitude (EE/O) was also performed for each reactor configurations used.

The performance of the newly developed TiO_2-based nanocomposite catalysts was also investigated in terms of residual toxicity of treated solution. In order to monitoring changes in toxicity, several acute toxicity tests (Microtox assay, Daphnia acute toxicity assay, Green alga Selenastrum capricornutum test, AMES mutagenic test and Fish embryo acute toxicity) were performed. In addition, preliminary investigation of the transformation products formed under the oxidative conditions was performed using liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS) analyses, which provided insights on the degradation pathways of the target pollutants.

The main conclusions summarizing the results obtained in this work are as follows:

(i) among the investigated catalyst the nanostructured TiO_2 supported on stainless steel had the best performance in degrading the target pollutants in groundwater and it significantly surpassed the conventional TiO_2 Degussa P25 in the pilot scale reactor equipped with Hg-UV lamp.
The evaluation of the electrical energy per order magnitude of removal (EE/O) confirmed the better performance of the new catalyst with respect to Degussa P25 and that the performance in degrading the target pollutants is compound-dependent;

(ii) results clearly demonstrated that in real wastewater, both suspended catalysts and supported catalysts showed a low performance in degrading the target pollutants probably due to a matrix effect that a real effluent can exercise against the catalyst;

(iii) under simulated solar light irradiation, despite the detrimental effect of the real wastewater matrix on the degradation efficiency, such an effect was found moderate for nano-sized TiO_2

supported on SWCNTs. Therefore, the obtained results showed that the new photocatalyst has proved to be a promising candidate to be used in a photocatalytic based-AOP;

(iv) for the new catalyst, a reduction of toxicity was observed based on all the toxicity tests performed except for the FET (Fish embryo acute toxicity) for which the toxicity remains unchanged. The different trends observed in the suite of ecotoxicological tests can be due to the different mode of action of the chemical substances present in the mixture or the possible synergic specific effects (e.g. mutagenic and embryotoxic) of the mixture.