Rare-earth metal oxides nano-dispersed onto ligno-humic-like support derived from sewage sludge for waste wates treatment

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Introduction

The new European Directive on the water 2024/3019 set innovative challenging objectives for water depuration which include the removal of contaminants of emerging concerns (CECs), a particular class of compounds not yet fully regulated whose presence can cause toxic effects on human health and the environment (Feng *et al* (2024)). For these reasons, research is underway into low-impact methods aimed at their complete elimination. Wastewater treatment plants (WWTPs) aim to remove exogenous contaminants through various processes. Photocatalytic processes (PPs) offer the advantage of high CECs removal in a sustainable manner with the possibility of easy integration into existing wastewater treatment systems (Murgolo *et al* (2024)). The photocatalytic degradation of CECs is promoted by the presence of specific catalysts (semiconductors).

The performances of semiconductor photocatalysts, like titania or ceria, can be tuned by appropriately doping with heteroatoms, like noble metals, which significantly decrease the band gap to visible light range. Another strategy to improve semiconductor properties is the ligand-to metal charge transfer with aromatic compounds. The use of naturally occurring aromatic, like lignocellulose recovered from specific biomasses, has recently been investigated for titania. This work deals with the preparation of carbon-activated CeO_2 and TiO_2 as photocalysts for the removal of water contaminants. As source of aromatic dopants were used ligno-humic like compound (LHLs) obtained by sewage sludge treatments which lead to a double benefits, namely recovery of resources and containment of the final waste to be disposed of, in coherence with “circular economy” principles.

In this scenario, the development of photocatalytic systems supported on ligno-humic-like (LHL) compounds derived from sludge used in WWTPs for the degradation of the main organic contaminants present in wastewater has been implemented as well as the removal efficiency and the nature of the degradation products evaluated. This study focuses on investigating the outcomes of photocatalytic processes using high-resolution mass spectrometry (HRMS) coupled to liquid chromatography (LC), with particular attention to the degradation products of the targeted compounds.

Materials and Methods

TiO_2 was supported onto commercial and extracted ligno-humic-like (LHL) compounds from sewage sludge up-taken from WWTPs of Lecce (primary sludge) and Putignano (sewage sludge). In a typical experimental test, 400 mL of contaminated aqueous solution (Milli-Q water or groundwater) containing the selected organic pollutants were irradiated with simulated solar light (250 W/m^2) in presence of 100 ppm of supported catalyst. Samples (1 mL) were collected at 0, 15, 30, 60, 120 and 240 min, appropriately diluted in Milli-Q water and analyzed for the determination of residual content of organic contaminants by using an Acquity chromatography system (Waters) coupled with an ToF/ToF-MS system (AB-Sciex) thorugh an ESI source operating in positive ion mode.

Results

Among the catalysts supported on LHLs, they proved particularly active in removing contaminants, achieving an overall removal rate of 95% after 4 hours of reaction. Furthermore, compared to commercial Degussa catalysts, the catalysts were easily recoverable at the end of the reaction cycle and reused without loss of catalytic activity. LC-HRMS/MS analysis enable the separation and contextual identification of the monitored CECs and their degradation products allowing us to propose hypothetical structures for the latter.

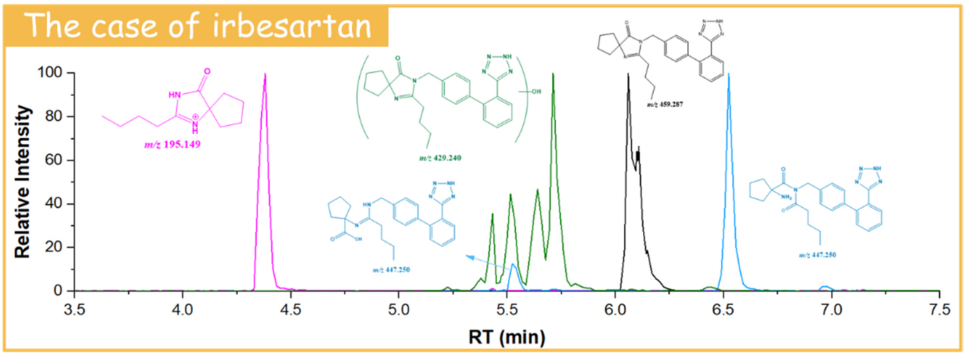

Figure 1. Kinetics studies on the photocatalytic degradation of organic pollutants in Milli-Q water by using TiO_2-based photocatalysts.

Four organic CECs were specifically investigated, namely Diclofenac, Carbamezapine, Irbesartan and Sulfamethoxazole. The investigated catalytic systems were found active in promoting the photodegradative removal of CECs considered.

Conclusions

TiO_2 –based-PPs allowed the degradation of each of the compounds under study. LC enables the separation between precursor-related DPs. Putative structures, particularly oxidation products, were assigned to some by-products on the basis of accurate *m/z* values, retention time agreement with standard injections, and MS/MS spectral data. Further studies will be carried out in order to quantify the different process intermediates and carry out scale-up. Given the limited knowledge on the environmental fate and toxicity of TPs, additional investigations on this drug and its transformation products, including in vitro and in silico toxicity assessments, are recommended (Beate *et al* (2011)).

References

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