

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

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## Introduction

The use of wastewater in agriculture is limited by the presence 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 [1]. 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 [2].

## Aim of work

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 & Methods

TiO<sub>2</sub> 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<sup>2</sup>) 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 a ToF/ToF-MS system (AB-Sciex) through an ESI source operating in positive ion mode.

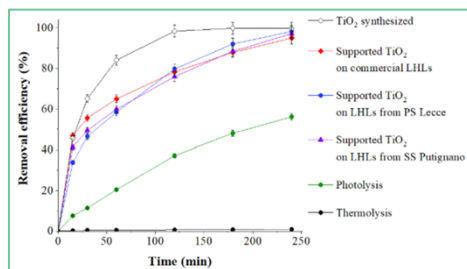


Figure 1. Kinetics studies on the photocatalytic degradation of organic pollutants in Milli-Q water by using TiO<sub>2</sub>-based photocatalysts.

## 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.

### The case of irbesartan

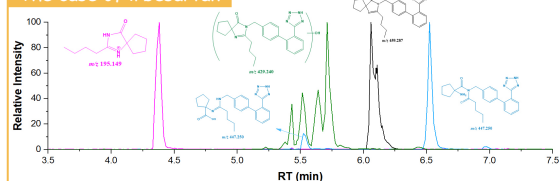


Figure 2. Multi-extracted ion current chromatograms (MULTI-EICC) derived from RPC chromatogram of irbesartan and its by-products.

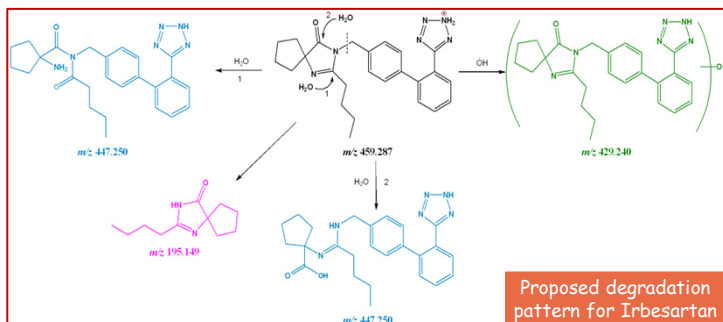


Figure 3. Proposed degradation mechanism for irbesartan.

## Conclusions & future perspectives

TiO<sub>2</sub>-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 [4].

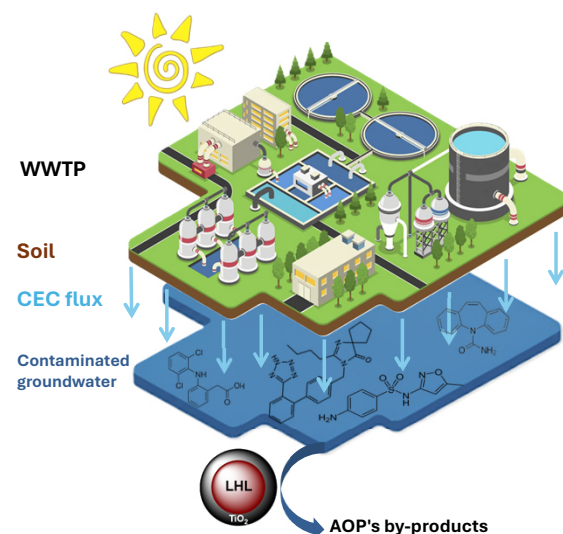


Table 1. Tabular characterization of target CECs and their degradation products found using commercial-LHL-based PPs. Proposed structures, accurate *m/z* values, collisional energies, elemental compositions, corresponding exact *m/z* values and mass accuracies are reported.

Structures	Accurate <i>m/z</i> values	CE (eV)	Major product ions	Elemental composition	Exact <i>m/z</i> values	Mass accuracy (ppm)
	237.1030	30	237.1030	[C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O] <sup>+</sup>	237.1022	3
			194.0967	[C <sub>12</sub> H <sub>12</sub> N] <sup>+</sup>	194.0964	2
			193.0892	[C <sub>12</sub> H <sub>11</sub> N] <sup>+</sup>	193.0886	3
			192.0814	[C <sub>12</sub> H <sub>10</sub> N] <sup>+</sup>	192.0808	3
	253.0975	30	253.0975	[C <sub>13</sub> H <sub>13</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>+</sup>	253.0972	1
			236.0743	[C <sub>13</sub> H <sub>13</sub> NO] <sup>+</sup>	236.0706	16
			210.0941	[C <sub>12</sub> H <sub>12</sub> NO] <sup>+</sup>	210.0913	13
			182.0981	[C <sub>12</sub> H <sub>11</sub> N] <sup>+</sup>	182.0964	9
	194.0969	30	194.0969	[C <sub>12</sub> H <sub>10</sub> NO] <sup>+</sup>	194.0964	2
			193.0919	[C <sub>12</sub> H <sub>9</sub> NO] <sup>+</sup>	193.0886	17
			179.0756	[C <sub>12</sub> H <sub>9</sub> N] <sup>+</sup>	179.0730	15
			167.0785	[C <sub>12</sub> H <sub>8</sub> N] <sup>+</sup>	167.0730	33
		165.0720	[C <sub>12</sub> H <sub>8</sub> N] <sup>+</sup>	165.0573	89	
	254.0589	30	254.0589	[C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S] <sup>+</sup>	254.0594	2
			188.0837	[C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O] <sup>+</sup>	188.0818	10
			156.0140	[C <sub>8</sub> H <sub>10</sub> NO <sub>2</sub> S] <sup>+</sup>	156.0114	17
			108.0453	[C <sub>8</sub> H <sub>8</sub> NO] <sup>+</sup>	108.0444	8
		92.0505	[C <sub>7</sub> H <sub>8</sub> N] <sup>+</sup>	92.0495	11	
	270.0540	30	270.0540	[C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S] <sup>+</sup>	270.0543	1
			172.0085	[C <sub>8</sub> H <sub>10</sub> NO <sub>2</sub> S] <sup>+</sup>	172.0063	13
			124.0411	[C <sub>8</sub> H <sub>8</sub> NO <sub>2</sub> ] <sup>+</sup>	124.0393	15
			109.0536	[C <sub>7</sub> H <sub>8</sub> NO] <sup>+</sup>	109.0522	13
		108.0455	[C <sub>7</sub> H <sub>8</sub> NO] <sup>+</sup>	108.0444	10	
	296.0241	30	296.0241	[C <sub>12</sub> H <sub>12</sub> Cl <sub>2</sub> NO] <sup>+</sup>	296.0240	0.3
			278.0278	[C <sub>12</sub> H <sub>10</sub> Cl <sub>2</sub> NO] <sup>+</sup>	278.0134	51
			250.0214	[C <sub>12</sub> H <sub>10</sub> Cl <sub>2</sub> N] <sup>+</sup>	250.0185	12
			215.0520	[C <sub>12</sub> H <sub>10</sub> ClN] <sup>+</sup>	215.0496	11
		214.0441	[C <sub>12</sub> H <sub>9</sub> ClN] <sup>+</sup>	214.0418	11	
		180.0811	[C <sub>12</sub> H <sub>10</sub> N] <sup>+</sup>	180.0808	2	
	266.0142	30	266.0142	[C <sub>12</sub> H <sub>10</sub> Cl <sub>2</sub> NO] <sup>+</sup>	266.0134	3
			230.0394	[C <sub>12</sub> H <sub>8</sub> ClNO] <sup>+</sup>	230.0367	12
			195.0716	[C <sub>12</sub> H <sub>8</sub> NO] <sup>+</sup>	195.0679	19
			167.0679	[C <sub>12</sub> H <sub>8</sub> N] <sup>+</sup>	167.0730	30
	429.2390	30	429.2390	[C <sub>25</sub> H <sub>28</sub> N <sub>4</sub> O] <sup>+</sup>	429.2397	2
			401.2355	[C <sub>25</sub> H <sub>26</sub> N <sub>4</sub> O] <sup>+</sup>	401.2336	4
			207.0923	[C <sub>14</sub> H <sub>17</sub> N] <sup>+</sup>	207.0917	3
			195.1505	[C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O] <sup>+</sup>	195.1492	6
		180.0819	[C <sub>14</sub> H <sub>16</sub> N] <sup>+</sup>	180.0808	6	
	445.2332	30	445.2332	[C <sub>25</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> ] <sup>+</sup>	445.2347	3
			417.2275	[C <sub>25</sub> H <sub>26</sub> N <sub>4</sub> O <sub>2</sub> ] <sup>+</sup>	417.2285	2
			402.2231	[C <sub>25</sub> H <sub>26</sub> N <sub>4</sub> O] <sup>+</sup>	402.2176	14
			223.0901	[C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O] <sup>+</sup>	223.0866	16
		180.0805	[C <sub>14</sub> H <sub>16</sub> N] <sup>+</sup>	180.0808	2	
	251.0938	30	251.0938	[C <sub>13</sub> H <sub>16</sub> NO] <sup>+</sup>	251.0927	4
			208.0792	[C <sub>13</sub> H <sub>14</sub> NO] <sup>+</sup>	208.0757	17
			180.0825	[C <sub>13</sub> H <sub>14</sub> N] <sup>+</sup>	180.0808	10
			152.0644	[C <sub>12</sub> H <sub>12</sub> ] <sup>+</sup>	152.0626	15
	195.1495	30	195.1495	[C <sub>11</sub> H <sub>16</sub> NO] <sup>+</sup>	195.1492	2
			167.1572	[C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> ] <sup>+</sup>	167.1543	18
			84.0822	[C <sub>8</sub> H <sub>10</sub> N] <sup>+</sup>	84.0808	17

The SS approach required the use of the Biotransformer 3.0 [3] software, through which abiotic TPs were predicted.

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[4] Beate I. Escher and Kathrin Fenner *Environmental Science & Technology* (2011), Volume 45, Issue 9, 3835-3847.