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HUMIC ACID COATED MAGNETIC PARTICLES AS HIGHLY EFFICIENT HETEROGENEOUS PHOTO-FENTON MATERIALS FOR WASTEWATER TREATMENTS

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Contaminants of emerging concern (CECs) are increasingly being detected at low levels in surface water, groundwater and drinking water [1]. Despite their low concentration there is a real concern on their impact on aquatic life and human health due to their toxicity [2]. As a consequence of their incomplete removal in the traditional wastewater treatment plants (WWTPs), considerable efforts have been devoted to develop purification methods able to destroy these contaminants.
Advanced oxidation processes (AOPs) have been attracting wide attention, since they are efficient in the degradation/mineralization of organic contaminants through the production of oxidizing species (mainly hydroxyl radicals, $^{\bullet}OH$) [3].
Among AOPs there is increasing interest in Fenton, photo-Fenton and Fenton-like processes that can generate highly reactive species [4] through the reaction between recyclable iron and H_2O_2 or other alternative oxidants (e.g. $S_2O_8^{2-}$). Heterogeneous photo-Fenton reaction with iron-based materials has been proposed as a promising alternative to the homogeneous process due to the easy recovery of the catalyst. In particular, different iron-based materials (morphologically controlled hematite, nanometric magnetite, passivated zero valent iron) has been tested in the recent years with the aim to give insights into the mechanism of transformation of CECs at the surface of these catalysts in Fenton or Fenton-like conditions. [5,6,7] In this light, the analysis of the catalyst composition (e.g. speciation of the active species) and of the species released in solution plays a crucial role.
In this work, magnetic particles (MPs) coated with different amount of humic acid (HA), synthesized by co-precipitation method under anoxic and oxygenated conditions, were characterized by different techniques (XPS, XRD spectroscopy, TGA, SEM and FTIR).
The ability of these materials to promote heterogeneous Fenton- and photo-Fenton-like processes was investigated using 4-chlorophenol as target pollutant. The HA coating induced an enhancement on the catalyst efficiency both in the dark and under irradiation, showing the best performance at pH below 4 under simulated sunlight irradiation.
The comparison between the XPS experimental data (Figure 1) and the observed reactivity suggested an active role of the more defective iron species at the surface which could promote a higher photo-dissolution with an increment of the reactive iron, both at the surface and in solution. Even if the iron ions leached in solution could have a remarkable influence on the oxidation process, a relevant role can be imputed to processes at the solid/liquid interface (heterogeneous reactivity).

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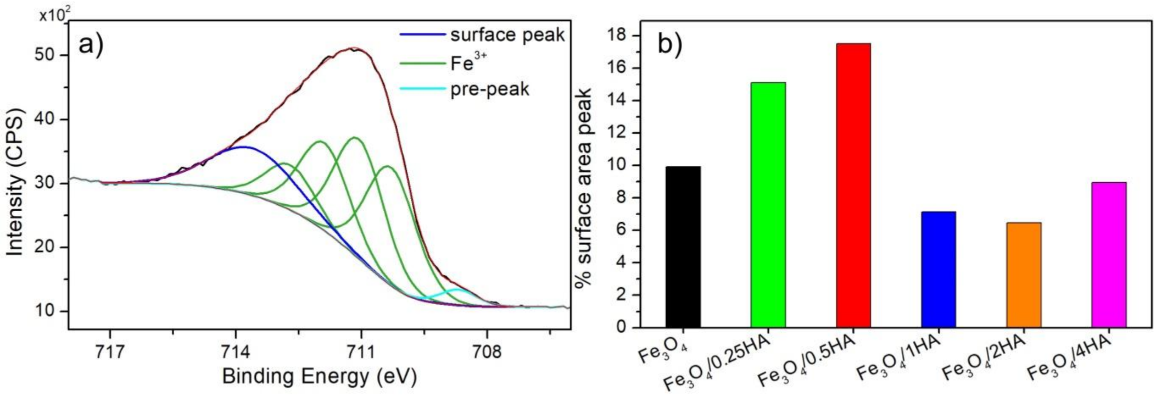

Figure 1. High-resolution spectrum of Fe 2p region of Fe_3O_4/0.5HA (MPs synthesized with HA solution 0.5%) prepared under anoxic conditions (a). Spectrum is charging corrected. Percentage of the surface peak in all samples prepared in anoxic conditions (b).

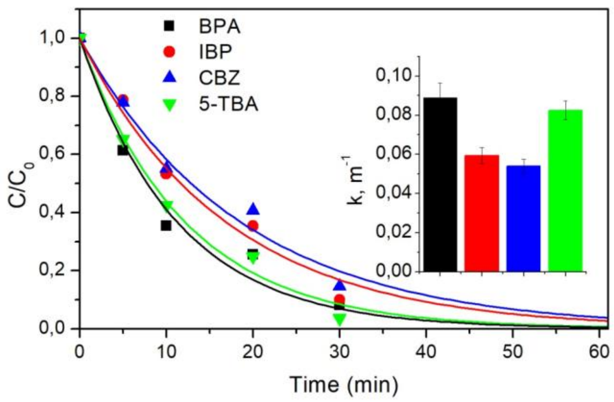

Figure 2. Photo-Fenton-like degradation of CEC mixture (20 μM) in real wastewater. Conditions: pH 3, H_2O_2 1.0 mM, Fe_3O_4/0.5HA 100 mg dm^{-3} (MPs synthesized with HA solution 0.5%). Inset: first-order kinetic constants of the process.

The best performing MPs/HA (Fe_3O_4/0.5HA) showed high efficiency for the abatement of CECs, namely Carbamazepine, Ibuprofen, Bisphenol A and 5-Tolylbenzotriazole also in real wastewater (Figure 2) demonstrating that this material can be successfully employed in advanced tertiary treatments for the removal of CECs from urban wastewater by employing cheap and environmental friendly materials and reagents (e.g. H_2O_2) and activating the process through the widely diffused and inexpensive solar irradiation.

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