

EMERGING PHOTOCHEMICAL PROCESSES INVOLVING IRON FOR WASTEWATER TREATMENT

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Abstract

Being the world facing water scarcity as a global consequence of Climate Change and freshwater excessive use, smarter water management procedures (i.e. use of reclaimed water) are urgently demanded. Pharmaceuticals, pesticides, flame retardants and many other substances used in households, industries or farms, are present in urban wastewater in trace concentrations (ng – µg/L). These substances, denominated Contaminants of Emerging Concern (CECs) are generally non-biodegradable, exhibiting low or incomplete degradation against actual wastewater treatment plants (WWTP) technology (typically, activated sludge) ending up in the natural environment where effluents are discharged. The plausible issues associated with CECs are toxicological effects (acute and bioaccumulation) towards aquatic biota, ecosystem damage, proliferation of antibiotic-resistant bacteria, among others. In consequence, so-called Advanced Oxidation Processes (AOPs) are required to couple to WWTP to obtain the enough quality required for the future wastewater effluents directives. For this PhD Thesis, we have mainly focused on Fenton, (solar-)photo Fenton and zerovalent iron (ZVI) based Fenton.

Dark Fenton and photo-Fenton were employed to degrade Fluoroquinolones (FQs) (a class of synthetic antibiotics considered CEC) as model pollutants under different conditions: pH (3 – 8), pollutant concentration (3 – 300 µM), number of present FQs (1, 3 and 5), and water matrix (ultra-pure, salty and simulated wastewater). Experiments were performed at bench and pilot plant scales, employing sunlight (simulated and real) and ultraviolet light irradiations. Obtained pollutant abatement rates with Fenton-related processes were compared with photolysis, heterogeneous photocatalysis and H₂O₂/UV. At equal conditions, only through photo-Fenton process significant FQs mineralization were achieved. In those cases where total organic carbon had not exhibited a considerable decrease, the reason was attributed to the release of oxidation by-products.

Since FQs are fluorescent, we decided to employ fluorescence excitation-emission matrices (EEM) in combination with the chemometric tool, Parallel Factor Analysis (PARAFAC), to track their degradations. Although EEM-PARAFAC related studies are usually focused towards the characterization and monitoring of dissolved organic matter (DOM) in natural waters and wastewater effluents (work also included in this PhD Thesis following the DOM along the different stages of a drinking water plant), it is barely the first time that it is used for the purposes we have here proposed. The objective is demonstrating that EEM-PARAFAC could be a feasible complementary methodology for the study of fluorescent CECs degradations, avoiding the use of expensive and sophisticated techniques (e.g mass spectrometry), not always available.

EEM-PARAFAC has demonstrated to be an economical, reagentless and non-time-consuming way for simultaneously follow the removal of several fluorescent CECs degradation in a sample, in presence of non-calibrated interferences, and allowing to gain further insights into the by-products molecular structures. Results indicated that irradiation alone is not able to produce important changes in the FQs's core structure, in sharp contrast with (solar-photo-)Fenton, where decrease of the PARAFAC components scores associated to the FQ-like compounds were observed. Zone of inhibition assays employing *E. coli* showed that the antibiotic activity

decreased in parallel with the overall decay of PARAFAC components related to parent pollutants and generated FQ-like by-products.

Iron is chelated by FQs, generating coordination complexes. For Enrofloxacin (ENR), one of the FQs most frequently used and detected in water bodies, it was observed that the complex with Fe^{3+} , stoichiometry $\text{ENR}:\text{Fe}^{3+} = 3:1$, was stable within a pH range from 3.0 to 7.5. Half-life time ($t_{1/2}$) of ENR alone under sun simulated conditions was around 22 min, whereas iron complexation enhanced its photostability, leading to a $t_{1/2}$ of 2.1 h. Moreover, reactive oxygen species generation and formed photoproducts were also iron dependent. Noteworthy, in presence of H_2O_2 , photo-Fenton takes place, being efficient even at neutral pH, also able of enhancing the degradation of other present CECs. We have therefore confirmed that FQ-iron interaction, usually downplayed, should always be considered when performing related photo-Fenton studies. In addition, FQs photolytic rate constants were always higher at neutral pH for every tested compound since their zwitterionic form is the most photolabile one.

The other important aspect of the PhD Thesis was the use of ZVI-based Fenton processes. Some CECs such as nitroaromatic compounds, exhibit slow degradation rates even with AOPs. The development of new and more efficient ZVI treatment trains for pollutant degradation has been attracting great interest in the last few years. This approach consists of a first pre-treatment only with ZVI (i.e. reduction, dehalogenation), followed by a Fenton oxidation taking advantage of the released iron ions from the first step. In order to analyse the strategy's plausible advantages and potential drawbacks within wastewater treatment applications, reductive/oxidative treatment train based on commercial ZVI microparticles (mZVI) has been studied. The effect of the initial amount of mZVI, H_2O_2 , pH, conductivity, anions, dissolved oxygen were analysed using p-nitrobenzoic acid (PNBA) as model pollutant. 83% reduction of PNBA 6 μM into p-aminobenzoic acid (PABA) was achieved in natural water at initial pH 3.0 and 1.4 g/L of mZVI under aerobic conditions in 2 h. An evaluation of the convenience of removing mZVI after the reductive phase (before the Fenton oxidation one) was investigated together with mZVI reusability. The Fenton step against the more reactive PABA required 50 mg/L of H_2O_2 to achieve more than 96% removal in 15 min at pH 7.5 (final pH from the pre-reductive step). At least one complete reuse cycle (reduction/oxidation) was obtained with the separated mZVI. This approach might be interesting to treat wastewater containing pollutants initially resistant to hydroxyl radical (HO^\bullet), but easily reduced, being able to decrease its toxic load as well as increasing its reactivity for a subsequent oxidation step.