Kinetic modeling of solar photo-Fenton process for micropollutant removal from municipal WWTP effluents in low-cost reactors

Abstract:

The reuse of effluents from wastewater treatment plants (WWTPs) is becoming an increasingly widespread and necessary alternative to conventional water sources in regions of the world with water scarcity. Conventional treatment plants are not designed to remove certain organic compounds, which are usually at low concentration and also biorecalcitrant. Despite being found at very low concentrations of the order of $\mu g\ L^{-1}$ – $ng\ L^{-1}$ (and therefore named as micropollutants), their accumulation in ecosystems can cause negative effects on crops (when using water for irrigation), in water and aquatic organisms and, consequently, on human health as well. Although there is still no legislation shared by European countries, some countries have started regulating their treatment and discharge. As such, there is a growing interest in the development of tertiary treatments for micropollutant removal. In this regard, the solar photo-Fenton process stands out as being one of the most efficient and environmentally sustainable advanced oxidation processes (AOPs). However, further research is needed to reduce operating costs as well as to scale up the process.

This Ph.D. thesis is aimed at the development of mechanistic models which allow the operation of the low-cost raceway pond reactors (RPRs) as tertiary treatment in municipal WWTPs (MWWTPs) to be designed and optimized.

Section 4.1 focuses on the development of a model at the optimum pH of the photo-Fenton reaction (pH 2.8) for micropollutant removal from secondary effluents. For this, the effect of temperature and photon absorption on the kinetics of the process was studied. The assays were carried out at lab-scale in synthetic secondary effluent with 0.1 mM Fe^{2+} and 1.47 mM H_2O_2 varying the temperature (10 - 40 ºC), the ultraviolet A (UVA) irradiance (10 - 40 W m^{-2}) and the liquid depth in the reactor (5 and 15 cm). The pesticide acetamiprid (ACTM) was used as a model pollutant at an initial concentration of 100 μg L^{-1}, similar to that of the total load of micropollutants detected in MWWTP effluents. This compound was selected as it is a highly recalcitrant neonicotinoid included on the EU watch list of priority hazardous substances. The results showed a double contribution by temperature to the process, namely, the Fenton reaction being accelerated, and the Fe^{3+} light absorption coefficient being increased. Concerning the effect of photon absorption,

the ACTM degradation rate increased with the volumetric rate of photon absorption (VRPA) up to VRPA values of 866 μE m^{-3} s^{-1}. Nonetheless, at higher VRPA values the process became photosaturated. To explain this phenomenon, the formation of an activated state of iron was proposed. Once Fe^{3+} is photoactivated, it is reduced to Fe^{2+}, with a fraction of the absorbed radiation being converted into heat. Consequently, a fraction of iron remains in its initial state as Fe^{3+}. From these observations, a mechanistic model consisting of a set of 8 reactions was proposed, and the parameters were estimated from the results obtained at lab-scale. The model was successfully validated outdoors in RPRs of 5 and 15 cm of liquid depth (120 and 360 L capacity). Moreover, its relevance in terms of variations in the catalyst concentration was demonstrated. In terms of mass of pollutant removed per reactor surface area unit and unit of time, high treatment capacities (135 mg m^{-2} h^{-1}) were achieved with 0.18 mM Fe^{2+} and 15 cm liquid depth.

Certain economic and environmental drawbacks related to the operation at acidic pH hinder the scaling of the process. The wastewater acidification to reduce pH to 2.8 implies an increase in its salinity as well as the operating costs. To avoid this, other alternatives such as the operation at neutral pH with iron complexes are being investigated. Among iron chelating agents, the biodegradable [S,S]-ethylenediamine-N,N'-disuccinic acid ([S,S]-EDDS) is gaining a growing interest due to the high photochemical efficiency of Fe^{3+}-EDDS.

With this aim in mind, Section 4.2 focuses on the phenomenological study of the process at neutral pH with the Fe^{3+}-EDDS complex. The assays were conducted at lab-scale with 0.1 mM Fe^{3+} at Fe^{3+}:EDDS molar ratio of 1:1. Firstly, the reactions involved in the photolysis of Fe^{3+}-EDDS as well as the effect of H_2O_2 concentration (0.74, 1.47 and 2.94 mM) were studied. No effect by the initial H_2O_2 concentration on Fe^{3+}-EDDS decomposition was observed, meaning the use of an H_2O_2 concentration of 0.88 mM H_2O_2, lower than that used previously (1.47 mM), was proposed. Once Fe^{3+}-EDDS had decomposed, a small fraction of the total amount of iron remained in solution, which could be explained by the presence of oxidized Fe^{3+}-EDDS species.

Afterwards, the effect of photon absorption on the kinetics of the photo-Fenton process was investigated. The experiments were carried out at 25 ºC (the annual average temperature of the wastewater in the MWWTP located in Almería city) in synthetic effluent doped with 100 μg L^{-1} ACTM. The effect of photon absorption was evaluated by varying both the liquid depth (5 and 15 cm) and the UVA irradiance on the reactor surface

(10 W m^{-2} – 50 W m^{-2}). Reaction rates of micropollutant removal and reactant consumption linearly increased with the initial VRPA up to VRPA values of 1547 µE m^{-3} s^{-1} (first order reaction with regard to VRPA), in other words, the process was photolimited. At higher VRPA values, the reaction rates remained constant (zero order reaction with regard to VRPA), pointing out that the process was photosaturated. The fact that photosaturation takes place at higher VRPA values than at acidic pH is due to the higher absorptivity of Fe^{3+}-EDDS in comparison with Fe^{3+}. Finally, the effect of light path length on treatment capacity was studied. It was found that, even under photolimiting conditions, treatment capacity can be increased by increasing liquid depth.

To scale up the process, it is necessary to evaluate its efficiency when applying the optimum operating conditions found with synthetic effluents to real effluents of very different composition. As such, Section 4.3 addresses the micropollutant removal in real effluents from 5 different MWWTPs located along the Mediterranean cost of Spain. The assays were developed outdoors in an RPR of 5 cm liquid depth (19 L capacity). Liquid chromatography-triple quadrupole-linear ion trap-mass spectrometry (LC-QqLiT-MS/MS) was used to detect and quantify the micropollutants, in collaboration with the Environmental Analysis and Water Treatment research group at the Solar Energy Research Center (CIESOL). The results showed that the mild oxidation conditions previously studied are suitable for treatment in real conditions. Regardless of the origin and composition of the effluents, more than 80% of the total load of micropollutants was removed in less than 15 min reaction time. Regarding salinity, in spite of the large number of works that pointed out a negative effect on the degradation of micropollutants by photo-Fenton of chlorides and sulfates, it was not observed when treating real effluents. Indeed, the results showed faster removal rates in the effluent with the highest concentration of anions.

In Section 4.4, the modeling of the process at neutral pH with the Fe^{3+}-EDDS complex is addressed for the first time. During a three-month research stay with Professor Orlando Alfano´s research group in Santa Fe (Argentina), an in-depth study on the coupling of the modeling of photochemical kinetics with the radiation field in RPRs was carried out. The two components of solar radiation were considered: direct radiation, which comes directly from the sun, and diffuse component, which is the scattered radiation. The effect of diffuse radiation, not previously considered, could be significant especially in winter, when the solar zenith angle may be greater than 50º at noon. The VRPA corresponding

to this component of radiation was estimated assuming the hypothesis of azimuthal symmetry, that is, propagation of rays in one spatial coordinate (the liquid depth) and one angular coordinate. From the previous kinetic studies as well as the hypotheses deduced from the experimental results, a complex mechanistic model of 16 reactions was proposed. The experimental data of ACTM removal in synthetic effluent, discussed in Section 4.2, were used to estimate the kinetic parameters. The model was successfully validated outdoors in an RPR of 5 cm liquid depth both in winter and summer.

Once the efficiency of the process to treat real effluents was demonstrated and a mechanistic model was developed, Section 4.5 deals with the application of the model to design and optimize the operation of the RPRs. To this end, the reactions corresponding to the removal of the three most abundant compounds detected in the five effluents studied in Section 4.3 (gabapentin, O-desmethyltramadol and O-desmethylvenlafaxine) were included in the model. The kinetic parameters were estimated from the experimental data of the removal of each compound, being of the same order of magnitude in all the effluents. Afterwards, the performance of the model for being applied to the operation of RPRs in continuous flow mode was validated, and the effect of liquid depth and hydraulic residence time on treatment capacity was simulated. The simulation results are of relevance for RPR design, since the reactor area could be estimated as a function of the hydraulic residence time and liquid depth. This maximizes the treatment capacity as a function of solar irradiation conditions.

In short, the work presented in this Ph.D. thesis is of relevance in terms of extending the use of the low-cost and highly efficient RPRs to a large scale. From the phenomenological study of the photo-Fenton process at lab-scale, mechanistic models of the process both at acidic pH with Fe^{3+} and neutral pH with Fe^{3+}-EDDS have been proposed. These models can be fine-tuned as a function of the operating conditions (radiation power, wastewater composition, reactor geometry, etc.) for the design and optimization of the operation of RPRs when treating real effluents from MWWTPs.