



## Enhancement of pesticide photo-Fenton oxidation at high salinities

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### ABSTRACT

The performance of the photo-Fenton reaction under high salinity conditions (up to 50 mS cm<sup>-1</sup>) has been tested regarding the oxidation of two pesticides, imidacloprid and methomyl, in the shape of their commercial formulations. In opposition to what is commonly outlined in the literature, an enhancement in pesticides depletion has been found due to the positive participation of halogen radicals, Cl<sup>•</sup>. However, this beneficial effect does not improve organic carbon elimination but rather displays worse total organic carbon (TOC) depletion. This effect is most likely due to the hydroxyl radicals scavenging and the complexation of Fe<sup>3+</sup> by chloride salts, which reduce the availability of reagents. Although salts/Fe<sup>3+</sup> interaction was observed, Fe<sup>3+</sup> interaction with the organic content was revealed as more relevant, especially for imidacloprid.

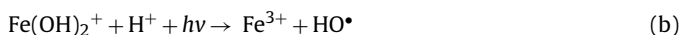
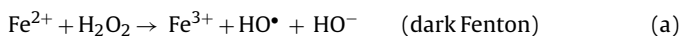
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## 1. Introduction

### 1.1. Photo-Fenton process

Advanced oxidation processes (AOPs), which are based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been reported to be powerful oxidative techniques [1]. Among these processes, the homogeneous photo-Fenton reaction and the titanium dioxide-mediated heterogeneous photocatalytic treatment have recently shown great promise for the treatment of industrial wastewater [2,3] and the prevention of groundwater contamination of [4,5]. HO<sup>•</sup> is a highly reactive transient specie that can rapidly oxidize most organic substances [6]; furthermore, catalytic behavior and light enhancement can improve its potentialities.

In the photo-Fenton reaction, the generation of hydroxyl radicals is achieved by the decomposition of hydrogen peroxide by means of the oxidation of dissolved ferrous ions, reaction (a), in the presence of UV light, which photo-reduces Fe<sup>3+</sup>, reaction (b), thereby recovering Fe<sup>2+</sup> and contributing to an additional pathway leading to a greater generation of free radicals in comparison to the dark Fenton reaction [7–9].



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Photo-catalytic processes present several drawbacks in practical applications, such as the amount of chemicals needed and the pH 3 requirement (to prevent Fe(OH)<sub>3</sub> precipitation). However, photo-Fenton also has some advantages over heterogeneous catalysis. For instance, the employed reagents are harmless once the process is complete, and if Fe<sup>2+</sup> working conditions meet reuse standards, there is no need for catalyst separation and recovery. In addition, solar light could also be a suitable source of radiation for the process, which makes it optimum for outdoor installation, especially in rural areas, which in turn reduces both costs and risks [10–12].

Extensive work has addressed the photo-Fenton reaction as applied to pesticides decontamination [8,13–17]. Studies have established this process as a suitable treatment for bio-recalcitrant pollutants. Most of this research has been performed in countries with rural regions under high hydric stress where the reuse of even agricultural water is required. The most important characteristics of this water are their content of salts, mainly chlorides, nitrates and sulfates, a certain amount of BOD and COD, traces of pesticides, and inert ingredients that comprise commercial products and their degradation by-products.

The photo-Fenton reaction has been widely studied from all possible perspectives; although notable contributions can be found [18–20], a weakness of the extant research is the scarce study of two important aspects that the present work addresses: this reactions' performance with commercial formulations versus moderate/high salinities. In the recycling hydroponic system envisaged in this study the effluents might function under either condition.

## 1.2. Hydroponics scenario

Hydroponics is a culture method conducted in a soil-less environment that is usually installed inside greenhouses of varying sophistication. The nutrient source is provided directly to the roots by means of a flowing solution. These systems allow for the control of nutrients given to the plants, thereby assuring the nutrient sources' nutritive and sanitary qualities [21]. Their advantages include their high production per unit area compared to soil cultures and the independence of external climate conditions. Both of these factors are particularly interesting for extreme climate regions, which are often present in developing countries in need of higher productivity.

Hydroponics typically work as closed systems, preventing the leaching of chemicals into ground or surface water and enabling the recycling of the nutrient effluent as many times as needed; while the increasing concentration on salts and pesticides does not harm the crops. It is considered an efficient technique of saving water from which regions such as Spain, where water scarcity provokes the overexploitation of wells and their consequent salinization by seawater intrusions [22] can benefit. In particular, an area that may take profit of is Spanish struggling South Basin, where the use of protected agriculture [23] is already extensive and where technification by hydroponics has not yet been widely utilized as a way of economizing water.

Despite the positive aspects of recycling after a number of rounds, the effluent cannot be directly discharged to the environment due to its enriched salt content and pesticide-derived products. Treatment is necessary to recondition the effluent prior to sending it back to the system or for it to meet the sewage system's standards.

## 1.3. Objectives

The aim of this work is to study the suitability and performance of the photo-Fenton reaction for degrading a mixture of two commercial pesticide formulations based on methomyl and imidacloprid in the presence of high salinity. The working scenario is a simulated hydroponic greenhouse where the effluents can be reused several times as a semi-closed system until they reach a conductivity threshold, at which point the flows are diverged to treatment once they have high concentrations of salts, pesticides and related organics.

## 2. Experimental

### 2.1. Photo-Fenton reaction

The photo-Fenton reaction was carried out in a 2 L jacketed stirred vessel with three 8W black light lamps ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) axially arranged to the reactor. This device was connected to a thermostatic bath that permitted the experiments to evolve at a controlled temperature of 21 °C. A more detailed description of the device and the procedure can be found elsewhere [7]. The pH was set to 2.7 (optimum for the equilibrium  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$  to achieve its highest ratio) at the beginning of the reaction with  $\text{H}_2\text{SO}_4$  (Panreac) diluted solution. This value was monitored during the process and kept constant between 3 and 2.5. Except for the 60 min experiments, all of the trials were carried out until reaching the total consumption of hydrogen peroxide. Every set and every sample was withdrawn and then quenched with  $\text{NaHSO}_3$ , 40% (w/v) (Panreac) to remove the remaining hydrogen peroxide.

### 2.2. Chemicals

Methomyl and imidacloprid were chosen as target compounds due to their extended application in horticulture. They present different chemical structure and properties. While methomyl is an N-carbamate (Fig. 1a), imidacloprid is a neonicotinoid (Fig. 1b), a third-generation pesticide. Commercial formulations of both products were used with no further purification. Tomilo-20 L was the carbamate source and Kohinor the neonicotinoid's; 200  $\text{g L}^{-1}$  of active principle in each product. Both were obtained from Aragonesas Agro S.L. (Spain).

$\text{KNO}_3$  with no antipackaging,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$ ,  $\text{NaCl}$ , and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  were used for simulating the salinity content.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was the source for ferrous ions, and hydrogen peroxide was dispensed as a commercial solution of 30% (w/v). All of these substances were purchased from Panreac. Deionized water was used to prepare every solution.

### 2.3. Chemical analyses

Pesticides depletion in each experiment was monitored using high performance liquid chromatography with a photodiode array detector. The column used was a Mediterranean Sea18, 5  $\mu\text{m}$  25  $\text{cm} \times 0.46 \text{ cm}$  (Teknokroma). The mobile phase, composed of a mixture of water and acetonitrile (both from Merck) (60:40), was delivered at a flow rate of 1  $\text{mL min}^{-1}$ . In the cases with higher salinity content, a peak related to a NaCl-masked methomyl peak; therefore, another method was used, having a mobile phase composed of 2.5 mL of 80%  $\text{H}_3\text{PO}_4$ , 25 mL of methanol diluted to 500 mL with milli-Q water. In this case, the flow was 0.7  $\text{mL min}^{-1}$ . The wavelength of the UV maximum absorbance was 232.5 nm for methomyl, while for imidacloprid, it was 269 nm. Dissolved organic carbon was also monitored in the shape of TOC, total organic carbon, by a Shimadzu TOC-VCSN TOC analyzer. Dissolved ferrous ion (together with total iron) and hydrogen peroxide were followed by spectrophotometric methods [24,25]. 1,10-Phenanthroline was purchased from Aldrich, while sodium acetate, acetic acid, and ascorbic acid were purchased from Panreac, as were  $\text{NH}_4\text{VO}_3$  and  $\text{H}_2\text{SO}_4$ .

### 2.4. Experimental plan

The photo-Fenton reaction was tested with different salinity conditions, from no salts to a concentration of 42.13  $\text{g L}^{-1}$ . Table 1 shows the averaged parameters of each type of effluent, grouped in Set A, before chemical treatment. The added salts were determined according to the previous literature regarding the typical minerals needed by crops and soilless cultures [26–28]. In the case of A1, only the essential salts for crop nutrition were added, while in A2, A3, and A4, the principal species that caused salinity problems (NaCl and  $\text{CaSO}_4$ ) were also added. While the conductivities of A1 and A2 represent intermediate points of conductivity that could be still used in the hydroponic system, A3 accounts for the threshold salinity limit, the extent to which plants can be forced, according to Fornes and Montesano [29,30]. A4 represents a highly saline effluent closed to the conductivity of seawater. The aim of this experiment was to analyze the extension of the salinity effect under extreme conditions.

The photo-Fenton reaction was carried out with initial reagents concentrations of 10  $\text{mg L}^{-1}$  of ferrous iron ( $\text{FeSO}_4$ ) and 100  $\text{mg L}^{-1}$  of hydrogen peroxide. These values were chosen according to previous experiments in which these concentrations enabled the total depletion of 20  $\text{mg L}^{-1}$  of imidacloprid without any salt [8]. All experiments, except otherwise is noted, were carried out until hydrogen peroxide was totally consumed.

Samples of the photo-Fenton reactor were withdrawn along the reaction for this set, and successive experiments and the following

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