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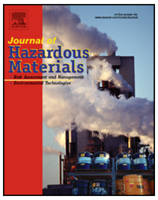

Fosetyl-Al photo-Fenton degradation and its endogenous catalyst inhibition

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HIGHLIGHTS

- Fosetyl-Al degradation generates phosphate ions that interfere in its own oxidation precipitating iron.
- Iron precipitation is not as rapid as expected due to the intervention of intermediate phosphate species.
- Interferences caused by iron precipitation also take place in the case fosetyl-Al is present in a mixture of pesticides.
- Photo-Fenton process increases biodegradability of fosetyl-Al solutions.
- Solar photo-Fenton seems to be more efficient for pesticide degradation in the tested conditions.

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ABSTRACT

Interferences from many sources can affect photo-Fenton reaction performance. Among them, catalyst inhibition can be caused by the complexation and/or precipitation of iron species by the organic matter and salts present in the reaction media. This is the case of the oxidation of effluents containing organophosphorous fosetyl-Al. The degradation of this fungicide generates phosphate anions that scavenge iron and hinder Fe(II) availability. Experimental design was applied to artificially enlighten photo-Fenton reaction, in order to evaluate fosetyl-Al degradation. The performed experiments suggested how iron inhibition takes place. The monitoring of photo-Fenton reaction over a mixture of fosetyl-Al with other two pesticides also showed the interferences caused by the presence of the fungicide on other species degradation. Solar empowered photo-Fenton was also essayed for comparison purposes. Artificial and solar light photo-Fenton reactions were revealed as effective treatments for the elimination of tested fungicide. However, the phosphate ions generated during fosetyl oxidation decreased iron availability, what hampered organic matter degradation.

1. Introduction

Light empowered advanced oxidation processes (AOP), such as photo-Fenton reaction or photo-catalysis, are based on the light enhancement of the production of highly reactive radical species. They has been proven as efficient processes for the decontamination of waters polluted with emergent pollutants of different origin [1,2] such as endocrine disruptors [3,4], pharmaceuticals [5,6], pesticides [7–9], etc. They have recently shown to be promising for the treatment of industrial wastewater [2,3] and the prevention of groundwater contamination [4,5]. One of the main advantages of these techniques among other AOPs has to do the versatility of their light/energy source. Although most studies are performed in artificial UV light reactors, very positive results have been obtained in the last two decades from works on solar light empowered devices [1,10–13], which makes them optimum for outdoor installation, especially in rural areas, with high insolation rates.

This work is specially focused on the photo-Fenton reaction and certain factors influencing the efficiency of this process. It faces a new perspective of the study of photo-Fenton applied over pesticide polluted water due to the fact that takes into account the direct interferences that the target contaminant to treat can exert over the process.

As said before, photo-Fenton reaction is based on the generation of highly reactive transient species, mainly hydroxyl radical, $HO^{\bullet}$, which can rapidly oxidize most organic substances [6]. Reaction (a) shows how hydroxyl radical is obtained from the decomposition

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of hydrogen peroxide by means of the oxidation of dissolved ferrous ions. The presence of UV light photo-reduces Fe^{3+}. Reaction (b) recovers Fe^{2+} and contributes to an additional pathway that leads to a greater generation of free radicals in comparison to the dark Fenton reaction [7,9].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad \text{(dark Fenton)} \tag{a}$$

$$Fe(OH)_2{}^{+} + H^{+} + h\nu \rightarrow Fe^{3+} + HO^{\bullet} \tag{b}$$

Literature reports diverse sources of interferences in these reactions that can be classified into HO• scavenging effects and precipitation and/or complexation of iron species:

1.1. HO• scavenging

One of the most reported sources of influence are halide salts. According to Pignatello and colleagues [14] Cl^- and Br^- consume hydroxyl radicals in detriment of the target organic matter, according to the pH dependent reversible reaction (c) [15]. However, there are some cases in which the halide radical generated in the middle of the reaction can contribute enhancing the depletion of certain species from the organic load [9,16].

$$HO^{\bullet} + X^{-} \rightleftharpoons HOX^{\bullet -} \underbrace{\rightleftharpoons}_{H^{+}(-H_2O)} X^{\bullet} \underbrace{\rightleftharpoons}_{X^{-}} X_2{}^{\bullet -} \tag{c}$$

An excess of hydrogen peroxide in comparison to the organic matter content can also act as a hydroxyl radical sink itself [17,18].

Fe complexing or precipitation:

Organic substances and their degradation by-products can complex Fe(III); some of them compose labile complexes which undergo thermal or photochemical reduction to Fe(II) [19,20]. Nevertheless, certain ligands could stabilize the Fe(III), inactivate its recycling [9,21] and jeopardize organic matter oxidation.

The existence of strong interactions between Fe(II) and Fe(III) with major and minor inorganic ligands $SO_4{}^{2-}$, OH^-, $HCO_3{}^-$, $CO_3{}^{2-}$ and HS^- is well known [22]. In the case of sulfate salts, they can hinder organic matter oxidation [23–25], even though they are poor HO• scavenger, and sulfate iron complexes are soluble. However, the $SO_4{}^{2-}$coordinated iron species inhibit the ulterior previously to (a) required complexation with H_2O_2, so they have to be taken into account if sulfate concentration is considerable.

Halide anions can also exert certain complexing effect over Fe(III). Nonetheless, they can be considered as relatively weak ligands of ferrous ion [14].

Among other inorganic salts, photo-Fenton process seems to be quite sensitive to the presence of phosphate [4]. In the presence of $H_2PO_4{}^{2-}$ (predominant specie at pH~3) ferric ions undergo a complex reaction with this salt, causing Fe(III) to lose the ability to be recycled to Fe(II) and to catalyze hydrogen peroxide decomposition into HO• radicals [26,27].

Regarding to the target compound, due to its simple structure, fosetyl-Al is easy to produce and cheap to sell; therefore it is widely used as systemic fungicide against oomycetes (mainly root-attacking *phytophthora* and downy mildews) in a variety of crops, both in agricultural environments and in gardening. The possibility of interfering in photo-Fenton reaction due to its phosphate group components makes it interesting for the study of the aforementioned endogenous inhibition.

According to all this, the main aim of this study is to evaluate the degradation of the fungicide fosetyl-Al by means of photo-Fenton reaction, and its role as catalyst inhibitor affecting its oxidation and the oxidation of other pesticides coexisting in the same mixture. For the accomplishment of the first purpose, experimental design in an artificially enlightened reactor was used, followed with biodegradability tests. In order to complete the picture, solar photo-Fenton experiments were carried out in relation to the results obtained from the experimental design, and in the presence of other two structurally different pesticides.

2. Experimental

2.1. Photo-Fenton reaction

The photo-Fenton reaction was carried out in different devices depending on the radiation source. For artificially enlightened reaction, a 2 L jacketed stirred vessel with three 8 W black light lamps (λ_{max} = 365 nm) axially arranged to the reactor were used. The photon flow was measured by o-Nitrobenzaldehyde actinometry, being 5.05×10^{-6} Einstein s^{-1} at 365 nm. The 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 [5]. The pH was set at the beginning of the reaction to 2.7 (optimum for the equilibrium $[Fe^{2+}]/[Fe^{3+}]$ to achieve its highest ratio) with H_2SO_4 (Panreac) diluted solution. No interference is expected from this sulfate due to its low concentration in the final mixture [14]. pH was monitored during the process and kept constant between 3 and 2.5 by the reaction itself. All the trials were carried out until reaching the total consumption of hydrogen peroxide.

In the case of solar-photo-Fenton, the experiments were performed in two different locations. The smaller device consisted on a bench-scale plant located in University of Barcelona (latitude 41°28′ N, longitude 2°06′ E, sea level). The photo-reactor comprises a module of 6 parallel CPCs (theoretical concentration factor of 1, C_{CPC} = 1) made of polished aluminum, with a total mirror's area of solar irradiation caption-reflection of 0.228 m^2, tubular quartz receivers, attached to a galvanized surface angled 41°. The irradiated volume was 0.95 L from a total reaction volume of 5 L allocated in a mechanically stirred reservoir tank of 10 L. The solution was continuously recirculated employing a pump (peristaltic pump Ecoline VC-380, ISMATEC) through the photo-reactor piping and the reservoir tank. Temperature was not controlled and it could vary from 20 to 30 °C. A scheme of the device is included as Fig. A1 in Appendix A.

The bigger pilot photo-reactor was sited in Tabernas, Almería (Spain), at Plataforma Solar de Almería. Based also in CPC's [28], it is made up of two twin systems of three collectors. Each collector (1.03 m^2 each) consists of eight series-connected tubes, mounted on a fixed platform tilted 37° (local latitude). The 22 L of a total of 35 L was the irradiated volume. More details of this device can be found elsewhere [2,29].

2.2. Chemicals

Fosetyl-Al or aluminum ethylphosphonate was chosen as the target compound of this study due to its possible source of interference during its degradation owing to its phosphorous derived structure, Fig. 1. It is a pesticide with systemic fungicide activity. Fosbel 80 (Probelte S.A.) was the source of fosetyl-aluminum. The commercial formulation is a wettable product with 80% of the active principle and around a 19% of kaolin.

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