



Short communication

Solar photo-degradation of a pharmaceutical wastewater effluent in a semi-industrial autonomous plant



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HIGHLIGHTS

- The applicability of the process has been proved at a semi-industrial scale.
- Up 79% of TOC can be removed in 2 h ($[TOC]_0 = 20\text{--}400$ ppm).
- The ferrioxalate complex is the responsible for enhanced mineralization.
- Acetate and formate (more resistant to treatment) comprise 60% of the remaining TOC.

ARTICLE INFO

Article history:

Received 12 January 2016

Received in revised form

7 February 2016

Accepted 9 February 2016

Available online xxx

Handling Editor: Shane Snyder

Keywords:

Industrial treatment

Solar

Photo-Fenton

ABSTRACT

An industrial wastewater effluent coming from a pharmaceutical laboratory has been treated in a semi-industrial autonomous solar compound parabolic collector (CPC) plant. A photo-Fenton process assisted with ferrioxalate has been used. Up to 79% of TOC can be removed in 2 h depending on initial conditions when treating an aqueous effluent containing up to 400 ppm of initial organic carbon concentration (TOC). An initial ratio of Fe(II)/TOC higher than 0.5 guarantees a high removal.

It can be seen that most of TOC removal occurs early in the first hour of reaction. After this time, mineralization was very slow, although H_2O_2 was still present in solution. Indeed it decomposed to form oxygen in inefficient reactions. It is clear that remaining TOC was mainly due to the presence of acetates which are difficult to degrade.

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1. Introduction

An effective tertiary treatment technology is required to ensure a safe use for industrial wastewater. Many advanced oxidation processes have been described for the removal of organic compounds in wastewater, especially in the treatment of water containing pharmaceuticals (Dalrymple et al., 2007; Malato et al., 2010). Among the different advanced oxidation processes, the homogeneous solar photo-Fenton reaction is one of the most environmentally benign and cost-effective systems used to generate hydroxyl radicals, $\cdot OH$, as already reported (Monteagudo et al., 2010; Jiménez et al., 2011).

An increase in degradation of organic pollutants when using ferrioxalates under sunlight has already been demonstrated (Nogueira et al., 2002; Lucas and Peres, 2007). Two facts account for

these increased efficiencies: i) a higher portion of the solar spectrum can be used and ii) the photolysis of ferrioxalate generates Fe(II) in acid solutions so that extra $\cdot OH$ radicals can be used to improve the degradation rate (Selvam et al., 2005; Monteagudo, 2009).

The degradation of pharmaceuticals in wastewater using a photo-Fenton process has been largely studied in literature (Radjenović et al., 2009; Gimeno et al., 2016). However, studies of real industrial effluents is limited and restricted to laboratory scale (Adishkumar et al., 2012) or to 40 L pilot plant scale (Sirtori et al., 2009). To the best of our knowledge, no study with an industrial effluent from the pharmaceutical industry has been published before using a semi-industrial autonomous plant under a photo-Fenton process assisted with ferrioxalate.

The aim of this paper is then to study the industrial applicability of this technique at a big scale. To this end, the operation was carried out continuously and treating an industrial wastewater effluent in a semi-industrial autonomous solar compound parabolic

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collector (CPC) plant.

2. Material and methods

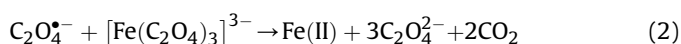
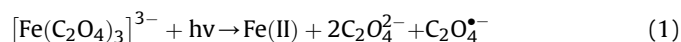
Analytical grade ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ and 30% w/v hydrogen peroxide (H_2O_2) were purchased from Merck and used as received. The pH was adjusted to 2.7 with H_2SO_4 and NaOH solutions.

The chemical composition of the industrial wastewater is summarized in Table 1 (TOC = 1914 ppm). The wastewater was diluted to obtain an initial TOC between 20 and 400 ppm.

The CPC consisted of a continuously stirred tank solar reactor (1500 L), a centrifugal pump, and a solar collector unit with an area of 60 m² in an aluminum frame mounted on a fixed south-facing platform tilted to 39° in Ciudad Real (Spain) with connecting tubing and valves (Fig. 1). The solar unit had borosilicate glass tubes connected by plastic joints, and the total illuminated volume inside the absorber tubes was 350 L. The installation is provided with 200 W mono crystalline photovoltaic panels and thermal collectors and is able to treat 0.7 m³/h of aqueous effluent operating under a continuous mode.

3. Results and discussion

The ferrioxalate-assisted kinetic photo-Fenton mechanism (Durán et al., 2008) implies the absorption of a photon by an Fe(III)-polycarboxylate species which initiates the formation of short-lived intermediates that ultimately yield Fe(II). The superoxide radical ($\text{O}_2^{\bullet -}$) is also formed, but quickly reacts to yield H_2O_2 . Thus, the addition of ferrioxalate in the presence of UV/ H_2O_2 is expected to improve mineralization rate due to formation of additional Fenton's reagent:



Different experiments were made changing the initial concentration of hydrogen peroxide and Fe(II). The molar ratio Fe/oxalic acid was kept in 3, assuming that due to ferrioxalate chemistry, $[\text{Fe}(\text{III})(\text{C}_2\text{O}_4)_3]^{-3}$ is the main photoactive specie formed in the system (Monteagudo et al., 2009). Fig. 2 shows that a high TOC removal close to 80% can be achieved after 120 min depending on initial $\text{H}_2\text{O}_2/\text{Fe}(\text{II})$ ratio. The initial TOC concentration also affect the process, although a ratio of Fe(II)/TOC higher than 0.5 guarantees a high removal in all the cases.

The evolution of a typical experiment with high initial TOC concentration ($[\text{TOC}]_0 = 274.1$ ppm) is shown in Fig. 3. It can be seen that TOC removal occurs early in the first hour of reaction. After this moment TOC removal was very slow, although H_2O_2 was still present in solution. Indeed it decomposed to form oxygen in inefficient reactions (5), (7) and (8) (Miralles et al., 2014):



The release of inorganic ions was confirmed by the experiments. Fig. 4 show the formation of inorganic ions as already found in previous works for other waters containing chlorfenvinphos and amoxicillin (Klamerth et al., 2009; Trovó et al., 2011). Organic acids (such as acetate, formate and oxalate) can be produced in a wide range of concentrations. Klamerth et al. (2009) found up to 0.21 mM acetate and 0.31 mM formate appearing during photo-Fenton decomposition of chlorfenvinphos (0.15 mM). Acetate and formate are the last stages prior to mineralization and more resistant to photo-Fenton treatment (Klamerth et al., 2009). In our case, acetate, formate and oxalate together accounted for 60% of the remaining TOC after 1 h (see Fig. 3). The plateau observed for TOC removal can be justified with the presence of these compounds and some other refractory specie present in wastewater.

The presence of intermediate and the competitive reactions induced in the photo-Fenton system assisted with ferrioxalate (including the consumption of $\cdot\text{OH}$ by H_2O_2) accounts for the null degradation of acetates.

On the other hand, in the Fenton and photo-Fenton systems, chloride ions can form complexes with iron (FeCl_2^+), which effectively compete with the $\cdot\text{OH}$ radical (Lores et al., 2013). Also undesirable chlorinated oxidation products can be formed thus competing with hydroxyl radicals. However, chloride ions in our tests remained constant (Fig. 5). This behaviour is consistent with that found by Poulopoulos et al. (2008) when studying the photo-Fenton treatment of 2-chlorophenol aqueous solutions. They found that the increase in Fe(III) amount added led to lower amounts of chlorinated intermediate formed. In our tests 95% of Fe(II) in converted into Fe(III) in less than 20 min. This means that the aryl-Cl bond present in a possible chlorinate intermediate undergoes cleavage very quickly, resulting in the release of inorganic Cl^- in the solution.

Another important point is the agreement between the TOC degradation rate and oxalate concentration. TOC clearly decreased with decreasing oxalate concentration and completely stops when oxalate was no longer present (Fig. 6). Enhancement of the photo-Fenton reaction by formation of the ferrioxalate complex, $[\text{Fe}(\text{III})(\text{C}_2\text{O}_4)_3]^{-3}$ is clear.

Table 1
Characterization of industrial wastewater.

Parameter	Value
Dissolved oxygen (ppm)	0.05
pH	6.57
Conductivity (mS/cm)	14.9
Fe^{2+} (ppm)	0.3
Fe overall (ppm)	0.42
Turbidity (NTU)	26.3
Antipyrine (ppm)	3.89
Overall solids (ppm)	10.468
Volatile solids (ppm)	2.952
Dissolved solids (ppm)	9.968
Volatile suspended solids (ppm)	1.356
COD (ppm)	3875
Acetate (ppm)	849.764
Formate (ppm)	41.471
Chloride (ppm)	683.129
Nitrate (ppm)	138.471
Sulfate (ppm)	250.502
TOC (ppm)	1914

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