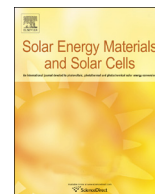




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Solar photodegradation of antipyrine in a synthetic WWTP effluent in a semi-industrial installation



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ABSTRACT

The aim of this work was to study the continuous mineralization of antipyrine present in a synthetic municipal wastewater effluent (SE) in a semi-industrial UV/solar compound parabolic collector (CPC) plant using a homogeneous photo-Fenton oxidation assisted with ferrioxalate. Under the selected continuous operating conditions ($[\text{H}_2\text{O}_2]=750$ ppm, $[\text{Fe}]=12$ ppm, $\text{pH}=2.7$, and $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]=66.2$ ppm, flowrate=1200 L/h, 77% of TOC is removed when treating an aqueous synthetic effluent containing 50 ppm of antipyrine. The use of artificial UV lamps together with solar radiation increases mineralization up to 88%.

Determination of the hydrogen peroxide consumed and remaining in the water revealed that 4.7 mol of H_2O_2 were consumed per each mol of total organic carbon removed from solution.

The operational costs due to the consumption of reagents and catalysts were calculated from the optimal conditions. The results showed that the ferrioxalate-assisted solar photo-Fenton process was economically feasible with no electric consumption due to the use of photovoltaic panels. Under optimal conditions, a total cost of 2.78 cent €/g TOC removed (1.56 €/m³) was calculated.

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1. Introduction

A recent research showed the regular presence of over seventy anthropogenic individual pollutants, some of which are encountered in relatively high amounts in a Sewage Treatment Plant (STP) receiving urban wastewater [1]. The efficiency of removal of pharmaceutical and personal care products (PPCP) in STP was roughly dependent on its hydrophobicity expressed as apparent octanol–water distribution coefficient [2]. Among them, antipyrine ($\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$), which is a common analgesic and anti-inflammatory medication, was present in both influent and effluent from STP showing a low 32.8% of removal efficiency. The presence of small concentration of PPCP has been associated to chronic toxicity, endocrine disruption and the development of pathogen resistance. The consequences are particularly worrying in aquatic organisms as they are subjected to multigenerational exposure [3]. The presence of micropollutants also endangers the reuse of treated wastewater, a generally proposed solution to achieve a sustainable water cycle management [4].

An effective tertiary treatment technology is thus required to ensure a safe use for reclaimed wastewater. The available technologies include oxidation processes alone or combined with nanofiltration or

reverse osmosis [5]. Many advanced oxidation processes have been described for the removal of organic compounds in wastewater, especially in the treatment of water containing pharmaceuticals [6–9]. 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, $\text{HO}\cdot$, as already reported [10,11].

In a previous research, the mineralization of an aqueous solution of antipyrine using a solar photocatalytic oxidation process assisted with ferrioxalate was evaluated in a small (2 m^2) compound parabolic collector (CPC) pilot plant [12]. Under the selected operating conditions ($[\text{H}_2\text{O}_2]=250$ ppm, $[\text{Fe}]=14$ ppm, $\text{pH}=2.7$, and $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]=80$ ppm), 60% of TOC was removed in just 5 min after treating an aqueous solution containing 50 ppm of antipyrine. The addition of oxalic acid up to a maximum concentration of 80 ppm significantly increased the mineralization rate during the first 15 minutes of the reaction. Results showed that the ferrioxalate-assisted solar photo-Fenton process was economically feasible, being able to achieve up to 60% mineralization with a total cost of 4.5 cent €/g TOC removed (1.1 €/m³).

The aim of this paper is to study the industrial applicability of this technique. To this end, the operation was carried out continuously and treating a synthetic municipal wastewater effluent (SE) in a semi-industrial UV/solar compound parabolic collector (CPC) plant. Optimal conditions were found based on experimental tests performed using a factorial design and neural networks (NNs)

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fittings. Finally, true operation costs were calculated to test if the process could be competitive on an industrial scale.

The synergistic effect between the individual processes and the consumption of H_2O_2 during mineralization were also studied.

Finally, the use of artificial UV radiation was tested in order to improve the mineralization process and also to study the viability of the industrial application of this process in cloudy days (with low UV-A solar power).

2. Experimental

2.1. Materials

Antipyrine (99%) was obtained from Acros. Although 50 ppm is a value significantly higher than the environmental concentration, it was chosen for better evaluation of the kinetics [12].

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 synthetic municipal wastewater treatment plant effluent (SE) was adapted of OECD Guidelines for Testing of Chemicals [13]: peptone (32 ppm), meat extract (22 ppm), urea (6 ppm), K_2HPO_4 (28 ppm), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (4 ppm), NaCl (7 ppm) and $\text{Mg}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (2 ppm), $\text{TOC}=20$ ppm. All reagents were purchased from Panreac.

However, in the presence of K_2HPO_4 , Fe(II) added to the system precipitates as shown in Fig. 1 until a high concentration of iron is added (> 15 ppm). This fact would complicate the process at industrial level, so that either a high Fe concentration should be added to have a photocatalytic effect or a previous precipitation step should be made to remove phosphates if they are present in the effluent. In this work, SE has been prepared without adding K_2HPO_4 to study the photocatalytic process.

2.2. Semi-industrial CPC plant

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 m^2 (concentration factor=1) in an aluminum frame mounted on a fixed south-facing platform tilted to 39° in Ciudad Real (Spain) with connecting tubing and valves (Fig. 2). The solar unit had borosilicate glass tubes connected by plastic joints, and the total illuminated volume inside the absorber tubes was 350 L. Visible solar radiation (400–600 nm) and UV radiation (200–400 nm) were measured using two Ecosystem model ACADUS radiometers, which provided data for the incident UV-A solar power (W m^{-2}) and the accumulated solar power (W h). The installation is provided with 200 W mono crystalline photovoltaic panels and thermal collectors

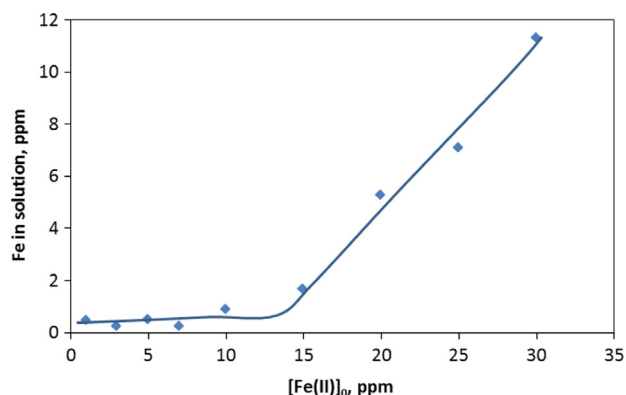


Fig. 1. Precipitation of Fe (II) as a function of initial Fe(II) concentration.

and is able to treat $1.2 \text{ m}^3/\text{h}$ of aqueous effluent operating under a continuous mode.

For the combined experiment, a 152 L reactor (1464 mm \times 300 mm \times 390 mm) with 35 UV-C lamps (36 W each one, but just 12 W of UV-C radiation), was operated in series with the solar CPC plant. A complete installation scheme is shown in Fig. 1b.

2.3. Water analysis

The evolution of the H_2O_2 concentration in solution was monitored by titration with an aqueous solution of potassium permanganate (0.02 mol L^{-1}) using an automatic Titrimo SET/MET 702 (Metrohm). The total organic carbon concentration was determined using a TOC analyzer (TOC-5000 A Shimadzu). The ferrous, ferric and total iron concentrations were obtained via photometric measurement with 1,10-phenanthroline (according to ISO 6332) using a UV-vis spectrophotometer (Zuzi 4418PC). UV absorption spectra were recorded using a UV-vis spectrophotometer (HACH-LANGE, model DR5000).

Before data analysis was done, all samples were withdrawn from the reactor for H_2O_2 analysis and immediately treated with excess Na_2SO_3 solution to prevent further oxidation (this procedure was performed to prevent overestimating the degradation).

2.4. Flow study in the CPC reactor

The residence time distribution (RTD) curve can be used as a diagnostic tool for ascertaining features of flow patterns in reactors [14]. These include the possibilities of bypassing and/or regions of stagnant fluid (i.e., dead space). Since these distributions can cause unpredictable conversions in reactors, they are usually detrimental to reactor operation.

In this work RTD has been calculated for different flow rates using a dye as a tracer. Methylene blue was injected into the CPC reactor as a step function, and the outlet stream was monitored as a function of time using an UV spectrophotometer. From the results of these experiments, RTD and mean residence time were determined for different flow rates (Fig. 3).

The curves obtained in our system, especially at high flow rates, are quite similar to ideal flow with a slightly dead volume. These data allow design calculations for the system and also help us to conduct a series of experiments and find the right time for sample analysis.

2.5. Experimental design

A central-composite experimental design was applied to investigate the effects of three variables: the initial concentrations of H_2O_2 and Fe(II) and flow rate. The molar ratio Fe/oxalic acid was kept in 3, assuming that due to ferrioxalate chemistry, $[\text{Fe(III)}(\text{C}_2\text{O}_4)_3]^{-3}$ is the main photoactive specie formed in the system [15].

The response function was the degree of mineralization at the outlet. The design process consisted of three series of experiments:

- (i) a factorial design with 2^k trials (all possible combinations of codified values +1 and -1), which in the case of $k=3$ variables consisted of 8 experiments.
- (ii) selection of the axial distance of the star points (codified values $\alpha=2^{k/3} = \pm 2$) consisting of $2k=6$ experiments; and
- (iii) replicates of the central point (three experiments).

The complete experimental design and additional experiments performed to obtain the optimal conditions are shown in Table 1.

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