Hydrogen Peroxide Continuous Dosage in the Photo-Fenton Process: Comparative Study between Lab-Scale and Solar Reactor

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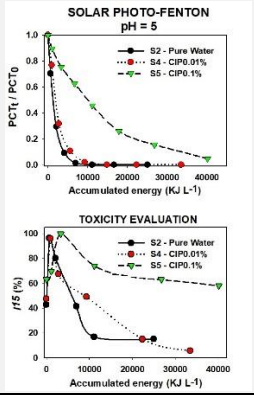

The role of continuous hydrogen peroxide (HP) dosage in the ferrioxalate-assisted photo-Fenton process is crucial for optimizing its efficiency. This study aims to compare the effectiveness of HP continuous dosage between lab-scale and solar reactor experiments in the abatement of paracetamol (PCT) at circumneutral pH. The effects of an initial pulse of HP and dosing time, as well as HP concentration, were studied in the lab experiments with ultrapure water. The conditions in which the best results were obtained were tested in a simulated industrial wastewater, but only 18.9% of conversion was reached. On the other hand, PCT was almost completely destroyed (95.4%) when the solar reactor was used with the same complex matrix. However, despite the great accumulated energy, a high toxicity level remained at the end of the reaction.

Introduction

The growing concern over Emerging Contaminants is evident, particularly with substances such as pharmaceuticals and personal care products, pesticides, dyes, antibiotics, and antibiotic-resistant genes [1]. Advanced Oxidation Processes, with a particular focus on the Fenton and photo-Fenton systems, have gained attention and are widely utilized for treating both, natural and wastewater.

When evaluating the cost of the process, the oxidizing agent can be one of the most expensive reagents, especially when the system operates at natural pH and relies on solar radiation [2]. The pursuit of automating the photo-Fenton process is driven by the goal of impring its performance, with a focus on decreasing hydrogen peroxide (HP) consumption compared to manual operation. This objective is directed at lowering both the economic cost and process time, ultimately enhancing resource use efficiency.

The current research work aims to study the effect of continuous HP dosing strategy to remove paracetamol (PCT) from different water matrices. The approach centers on the application of the solar photo-Fenton reaction at a near neutral pH, incorporating ferrioxalate.

Material and Methods

Experiments were conducted in two different photoreactors. Firstly, a batch lab-scale reactor irradiated by a solar simulator was used [3]. The local radiation flux averaged over the reactor window (q_w) was 92.80 W m^{-2} (300 to 500 nm). The total volume of the treated solution was 3 L. The second reactor was a pilot-plant non-concentrating solar photoreactor designed to capture UV/Vis and near-IR solar radiation. The irradiated volume was 6.1 L, while the total volume was 35 L [4]. Both experimental setups were equipped with a diaphragm dosing pump (Acquatron® MA-CP series).

For all tests, pH was 5, initial PCT concentration was 40 mg L^{-1}, Fe^{3+} concentration was 3 mg L^{-1} and oxalate (Ox) concentration was 47.5 mg L^{-1}. The dosing of HP involved its automated addition at a constant flow rate (0.35 L min^{-1}). The concentration of the oxidant in the reservoir from which the pump is fed was established based on the mass of HP desired to be added within a defined dosing time.

The treated samples consisted of: a) ultrapure water, and b) synthetic industrial wastewater coming from a pharmaceutical plant, formulated using CIP300®, a neutral pH detergent, and PCT pharmaceutical drug, which contains several excipients (pre-gelatinized starch, stearic acid, and povidone K30).

Finally, A Microtox Model 500 Toxicity Analyser was utilized to assess acute toxicity of the samples. Toxicity was computed as the percentage of light emission inhibition (*I%*) by the *Vibrio fischeri* NRRL-B-11177 bacteria following a 15-minute incubation period.

Results and Discussion

Lab and pilot plant scale reactors were employed to assess the scalability and efficiency of hydrogen peroxide dosage in PCT photo-Fenton degradation.

A total of 10 experiments were carried out in the lab-scale reactor. Nine of them were assessed in ultrapure water, in order to study the effect of radiation (ON or OFF), HP final concentration (47.25 to 756 mg L^{-1}), dosing time (75 or 150 min), and the application of an initial HP pulse of 47.25 mg L^{-1}.

Firstly, the influence of radiation was noticeable. Under dark conditions and total added HP=378 mg L^{-1}, PCT conversion only reached 3.5%, meanwhile a minimum conversion of 79% was obtained for irradiated conditions. Secondly, the effects of the initial pulse of HP and dosing time of 75 min *vs*. 150 min, were not significant in the achieved contaminant conversion levels (data not shown). Based on these results, the experiment with synthetic industrial wastewater was carried out with continuous addition of HP until 75 min (total HP=378 mg L^{-1}),

without initial punctual dosage. In this assay, PCT was poorly degraded (18.9% at 180 min).

Table 1 presents the operating conditions of the runs performed in the solar reactor. The dosing time was 75 min, considering the results obtained in the laboratory tests.

Firstly, it's important to note that for each of the tests outlined in Table 1 (Runs S1 to S5), variable values of accumulated energy and temperature increase were recorded due to the environmental conditions encountered during each experimental test. Therefore, the accumulated radiation ($Q_{300\text{-}550nm}$, KJ L^{-1}) was calculated according to Eq. (1):

$$Q_{300-550nm,t} = Q_{300-550nm,t-1} + \Delta t_t \overline{RAD}_{300-550nm,t} \frac{A_r}{V_t} \quad (1)$$

where $Q_{300\text{-}550nm,t}$ is the total accumulated radiation (KJ L^{-1}), Δt represents the time interval (s), $RAD_{300\text{-}550nm,t}$ is the average total radiation (W m^{-2}), A_r is the irradiated area (0.24 m^2), and V_t is the total volume (35 L).

The results presented in Table 1 illustrate the efficacy of the examined process. Firstly, complete conversion of PCT was attained within just 60 minutes of reaction for ultra pure water conditions (S1 to S3). However, when employing low doses of oxidizing agent (S1), a notable decrease in the rate of contaminant degradation was evident. Up to 200% more accumulated energy was needed to achieve complete conversion of the contaminant compared to an intermediate oxidant concentration of 378 mg L^{-1} (S2). Secondly, dosing an excess of HP (S3) did not lead to any benefit in PCT degradation. Remarkably, high contaminant conversions (up to 98%) were achieved within just 60 minutes of reaction for low detergent concentrations in the simulated effluent (S4). However, when a higher detergent percentage was introduced under the same HP level (S5), a conversion of 95.4% was attained but at 180 minutes, indicating the significant influence of the real matrix. Finally, the toxicity in the system was evaluated. The evolution of *I%* in the system was closely linked to the appearance and disappearance of Hydroquinone (HQ), one of the main transformation by-products. It was observed that 0.01% of CIP300 did not represent a great addition of toxicity to the system. However, a slight slowdown of the reaction was observed, since HQ disappeared at a higher $Q_{300\text{-}550nm,t}$ than in the run without CIP300, so the toxicity in the medium also lasted longer. On the other hand, when the detergent was used at a concentration of 0.1%, there was an extra addition on toxicity of 23.71% caused by only CIP300 (blank test). Furthermore, the presence of a low amount of HQ at the end of the reaction, despite the great accumulated energy, caused that *I%* remained high (as shown in the Graphical Illustration).

Table 1. Experimental conditions in the pilot plant solar reactor.

Run	HP (mg L^{-1})	ΔT^{180} (°C)	T^{180} (°C)	$Q_{300\text{-}550nm,t}$ (KJ L^{-1})	Flow (mgHP min^{-1})	Matrix[a]	X_{PCT}[b] (%)
S1	47.25	15.1	38.9	5.23E+04	21.88	UW	98.9 (60 min)
S2	378	10.1	35.9	2.50E+04	175	UW	98.7 (60 min)
S3	756	15.7	41.9	4.97E+04	350	UW	98.9 (45 min)
S4	378	11.9	39.9	3.35E+04	175	IW0.01	97.9 (60 min)
S5	378	15.2	44.2	4.02E+04	175	IW0.1	95.4 (180 min)

[a] UW: ultra pure water; IW0.01: simulated wastewater with 0.01% CIP300; IW0.1: simulated wastewater with 0.1% CIP300.
[b] Between parenthesis: time (min) at which the conversion value was reached.

Conclusions

The effectiveness of continuous HP dosing in the ferrioxalate assisted solar photo-Fenton process, even under conditions simulating industrial effluent, was demonstrated. Despite the complexity introduced by real matrices and detergent additives, the solar reactor exhibited superior performance compared to lab-scale tests. The combined effect of UV/Vis and thermal sunlight was able to almost completely degrade PCT in the simulated wastewater. However, the persistence of high toxicity levels underscores the need for continued research on mitigation strategies for harmful by-products, such as hydroquinone, to ensure the environmental sustainability of wastewater treatment processes.

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