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Influence of Fenton Reagent Ratios and of Hydrogen Peroxide Dosage on the Photo-Fenton Process Efficiency

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Abstract

The present study addresses the role of Fenton reagent ratios (H_2O_2:PCT, H_2O_2:Fe(II)) and the influence of H_2O_2 dosage in the performance of the photo-Fenton process. Paracetamol (PCT), the most widely used antipyretic, was adopted as model contaminant.Design of experiments was used to first test the most suitable H_2O_2:PCT ratio so to fix the PCT concentration to be used in the subsequent study of the H_2O_2:Fe(II) ratio. In all cases, PCT total remediation was attained, but the highest mineralization rate (≈75%) was obtained when 378 mg L^{-1} of H_2O_2 and 5 mg L^{-1} of Fe(II) were used. The mineralization increased by increasing both the H_2O_2:PCT and the H_2O_2:Fe(II) ratio, and the more efficient values were 10 and 40, respectively (for higher values a plateau was reached). Hence, the total amount of H_2O_2 and Fe(II) was fixed to 378 and 5 mg L^{-1}, and a dosage protocol, involving an initial release of H_2O_2 ($[H_2O_2]^{t0}$) and the time at which the dosage begins (t_{in}), was studied. Preliminary results revealed that assays performed with an initial release of at least 20% of the total amount of H_2O_2 can lead to higher mineralization rates (≥5%), showing that the H_2O_2 dosage can enhance photo-Fenton performance.

Keywords: photo-Fenton, pharmaceuticals, Fenton reagents ratios, H_2O_2 dosage.

1. Introduction

In the last years, in parallel with the increasing sensitivity of analytical instruments, a growing number of new organic substances has been detected, in different concentrations, in wastewater, natural water and groundwater. Apart from the so-called priority contaminants, whose environmental risks are well known, most of these substances are considered to be potentially hazardous since data regarding their impact onto the aquatic environment and human health are not available. In particular, special attention has recently been given to what are called Contaminants of Emerging Concern (CECs) (Klamerth *et al.*, 2009), including pharmaceuticals and personal care products. Directive 2013/39/EU of the European Parliament, apart from updating the list of priority substances, states the importance of CECs monitoring as well as of the reinforcement of the risk assessment of pharmaceuticals. The main characteristic of the CECs is that they are hardly biodegradable and they consequently resist treatment by conventional sewage treatment plants. Hence, alternative processes must be employed for their treatment. For this purpose, Advanced Oxidation Processes (AOPs) have been widely investigated. AOPs rely on the formation of highly reactive chemical species (hydroxyl radicals $^{\bullet}OH$) that can oxidize almost any organic contaminant (Andreozzi *et al*. 1999). Among these, the photo-Fenton process has shown to be highly efficient for the removal of CECs (Miralles Cuevas *et al*., 2012).The photo-Fenton process is a photochemical process based on the Fenton reaction between a catalyst, the ferrous iron Fe(II), and an oxidant, the hydrogen peroxide, leading to the formation of hydroxyl radicals.

An important experimental effort has been made for an overall understanding of the photo-Fenton process as well as for determining the experimental conditions that can enhance the treatment performance (Pignatello *et al.*, 2006). As a result, the Fenton reagent ratio (H_2O_2:Fe(II)) was proved to be one of the most significant factors (Gulkaya *et al*., 2006). Several studies also pointed out the importance of the H_2O_2 dosage (Nilsun H. I., 1999) in the improvement of the process performance, since it can avoid or reduce the activation of inefficient reactions scavenging hydrogen peroxide. As pointed out by Yamal *et al*. (2012), due to the lack of a convenient model and of related experimental data, the H_2O_2 dosage has not been addressed in a systematic way. Moreover, to the best knowledge of the authors, the simultaneous study of the Fenton reagent ratios and of hydrogen peroxide dosage on the photo-Fenton process efficiency, has not yet been addressed. This work uses Design of Experiments (DOE) to first study both the H_2O_2:PCT and H_2O_2:Fe(II) ratio in order to find out the Fenton reagent loads that enable a more efficient use of the hydroxyl radicals formed during the process, which in turn increases TOC reduction. In this way it was possible to determine the best experimental conditions ensuring the highest mineralization rate. Then, a DOE based on the variation of the initial release of H_2O_2 and the time at which the dosage begins, was carried out with the aim of studying the influence of the H_2O_2 dosage. The goal was also to demonstrate the necessity of combining the experimental and the modelling approach so to propose a systematic procedure for the selection of the optimal dosage profile.

2. Materials and methods

2.1 Reagents and chemicals

Paracetamol (PCT) 98% purity purchased by Sigma-Aldrich was used as model pollutant. To perform the photo-Fenton experiments, reagent-grade H_2O_2 33 % w/v by Panreac and iron sulfate ($FeSO_4 \cdot 7H_2O$) by Merck, adopted as the Fe(II) source, were used. HPLC gradient grade methanol (MeOH) purchased by J.T. Baker and filtered milli Q grade water were used as HPLC mobile phases. Hydrogen chloride HCl 37% by J.T. Baker was used to adjust the initial pH to 2.8±0.1. All experiments were carried out by using distilled water as water matrix.

2.2 Analytical determinations

Total Organic Carbon (TOC) concentration was measured with a Shimadzu VCHS/CSN TOC analyzer and samples were taken each 15 minutes.In order to determine PCT concentration an HPLC Agilent 1200 series with UV-DAD was used. The measurement method is the one described by Yamal *et al.* (2014). All the samples, taken at 0-1.5-2.5-5-7.5-10-15 min, were treated with 0.1 M methanol (in proportion 50:50) to stop reaction and further degradation of PCT. Finally a spectrophotometric technique described by Nogueira *et al.* (2005), based on the measurement of the absorption at 450 nm of the complex formed after reaction with ammonium metavanadate, was used to determine the hydrogen peroxide concentration. Samples were taken each 5 min until a reaction time of 30 min and then each 15 min until the end of the assay (120 min).

2.3 Pilot plant

The pilot plant is a 15-L system composed by a glass reservoir (13.5-L) and an annular photo-reactor (1.5-L) equipped with an Actinic BL TL-DK 36 W/10 1SL lamp (UVA-UVB). The recirculation flow rate is set to 12 L min^{-1} to ensure perfect mixing conditions. Moreover, the pilot plant is equipped with sensors for continuous measurements (online data) of pH, temperature, dissolved oxygen concentration, conductivity, Oxidation-Reduction Potential (ORP), and flow-rate recirculation. Online data acquisition is managed through a programmable logic controller (PLC) connected to a SCADA system. For more specifications about the pilot plant, refer to Yamal *et al.* (2014).

2.4 Experimental procedure

Preliminary photo-Fenton assays were performed in batch mode with recirculation. The glass reservoir was first filled with 10 L of distilled water and then, the remaining 5L of distilled water, in which PCT was previously dissolved, were added. After 10 min of recirculation, a sample was taken to measure the initial concentrations of PCT ($[PCT]^0$) and TOC ($[TOC]^0$). Once pH was adjusted to 2.8±0.1, Fe(II) was added as $FeSO_4 \cdot 7H_2O$ and the light was switched on. Finally, after other 10 min of recirculation, H_2O_2 was added to start the experiment. The reaction time was fixed to 120 min.Further experiments were next performed with H_2O_2 dosage. The procedure and the conditions were the same ones described above, with the only difference that the hydrogen peroxide wasn't added all at once but according to a specific dosage protocol, described by Yamal *et al.* (2012). For these experiments, reaction time was extended to 150 min.

2.5 Design of Experiments (DOE)

First, a set of photo-Fenton experiments was carried out to study the role of the H_2O_2:PCT ratio in the process performance. Such experiments are based on a central composite design where the initial concentrations of PCT ($[PCT]^0$) and H_2O_2 ($[H_2O_2]^0$) were varied while the initial concentration of Fe(II) ($[Fe(II)]^0$) was maintained constant to 10 mg L^{-1} (see Table 1).

Table 1. Design of experiments performed to investigate the role of H_2O_2:PCT ratios in the photo-Fenton performance

$[PCT]^0$ mg L^{-1}	$[H_2O_2]^0$ mg L^{-1}	$[Fe(II)]^0$ mg L^{-1}
11.7	378	10
20	189	10
20	567	10
40	110.7	10
40	378	10
40	645.3	10
60	189	10
60	567	10
68.3	378	10

Then, a further set of photo-Fenton experiments was performed by changing $[H_2O_2]^0$ and $[Fe(II)]^0$ for a same value of $[PCT]^0$, set to 40 mg L^{-1}, to investigate the role of the H_2O_2:Fe ratio (see Table 2).

Table 2. Design of experiments performed to investigate the role of H_2O_2:Fe ratios in the photo-Fenton performance

$[PCT]^0$ mg L^{-1}	$[H_2O_2]^0$ mg L^{-1}	$[Fe(II)]^0$ mg L^{-1}
40	94.5	5
40	189	5
40	378	5
40	94.5	7.5
40	189	7.5
40	378	7.5
40	94.5	10
40	189	10
40	378	10

A specific code was used for each experiment: $[PCT]^0$_$[Fe(II)]^0$_$[H_2O_2]^0$. Finally, in order to investigate the role of the H_2O_2 dosage, a central composite design was performed. This was based on the variation of the initial amount of hydrogen peroxide, $[H_2O_2]^{t0}$, added to the reactor (at time t_0=0 min), expressed as a percentage of the total amount of hydrogen peroxide to be dosed during the whole process ($[H_2O_2]^{TOT}$=378 mg L^{-1}), and the time at which the dosage begins, t_{in} (see Table 3). In all cases, $[PCT]^0$=40 mg L^{-1} and $[Fe(II)]^0$=5 mg L^{-1}.

Table 3. Central composite design performed to study the role of hydrogen peroxide dosage in the photo-Fenton performance for $[PCT]^0$=40 mg L^{-1}, $[Fe(II)]^0$=5 mg L^{-1} and $[H_2O_2]^{TOT}$=378 mg L^{-1}

$[H_2O_2]^{t0}$	t_{in}
%	**min**
10	0.00
30	0.00
10	20.00
30	20.00
20	10.00
20	10.00
20	10.00
5.9	10.00
34.1	10.00

3. Results and discussion

In all cases, PCT total remediation was attained (results not shown), while TOC decrease reached a plateau (a mineralization rate between 70% and 80%; Fig. 1a). Process performance cannot be further improved for values of the H_2O_2:PCT ratio beyond 10.Moreover, Figure 1b shows that the same mineralization rate (≈74%), which was also the highest, was obtained when an initial concentration of H_2O_2 of 378 mg L^{-1} was fixed and for all the tested initial concentrations of Fe(II) (5,7.5, and 10 mg L^{-1}). So, in this case, the plateau is reached starting from values of the H_2O_2:Fe ratio of about 40. Hence, since an increase in the initial concentration of Fe(II) does not significantly improve the TOC mineralization, the lowest value can be selected, or rather $[Fe(II)]^0$ = 5 mg L^{-1} that, for an initial concentration of H_2O_2 of 378 mg L^{-1}, corresponds to a H_2O_2:Fe ratio of about 80. In this way, the highest mineralization rate can be attained by using the lowest amount of Fe(II).Consequently, the H_2O_2 dosage was tested for the best values of H_2O_2:PCT and H_2O_2:Fe ratios that, according to the results above described, were 10 and 80 respectively. Hence, different dosage protocols, summarized in Table 3, were tested in the case of $[PCT]^0$=40 mg L^{-1}, $[Fe(II)]^0$=5 mg L^{-1} and $[H_2O_2]^{TOT}$=378 mg L^{-1}. The best performance was attained when 20% of the total amount of H_2O_2 was dosed starting from the beginning of the process (t_{in}=t_0). Even though a slight increase in the TOC mineralization was obtained (5%), the dosage protocol, prevents the mineralization to reach a plateau, as observed in the case without dosage. For this reason, the reaction time was extended to 150 minutes. Hence, it could be concluded that the H_2O_2 dosage can help to improve the process performance but a more detailed study is required in order to find out the optimal H_2O_2 dosage profile in a systematic way.

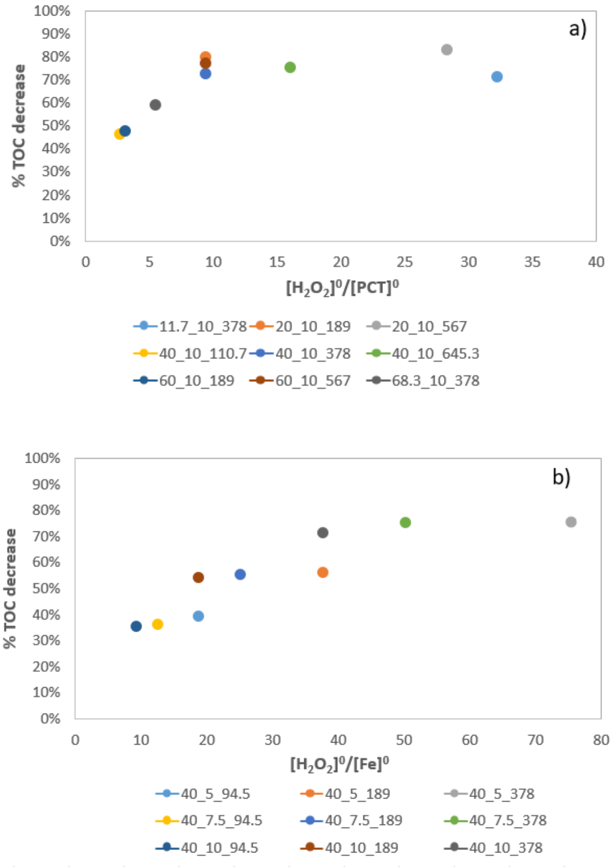

Figure 1. a) The photo-Fenton process performance (in terms of % of TOC decrease) is represented as a function of the H_2O_2:PCT ratio **b)** and as a function of the H_2O_2:Fe(II) ratio

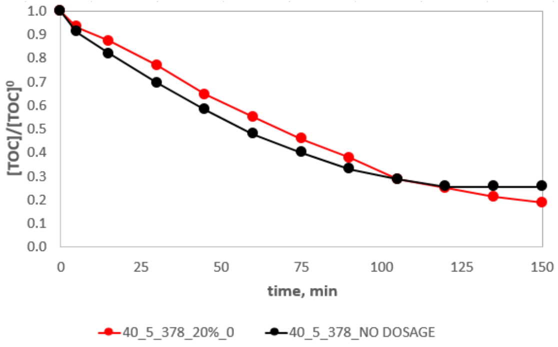

Figure 2. Normalized TOC decrease as a function of reaction time. The best dosage protocol found ($[H_2O_2]^{t0}$=20% and t_{in}=0 min, red line) is compared with the case with no dosage (black line). A specific code was used to refer to this experimental run: $[PCT]^0$_$[Fe(II)]^0$_$[H_2O_2]^0$_$[H_2O_2]^{t0}$_ t_{in}.

4. Conclusions

This study investigates the role of reagent and contaminant ratios on the performance of the photo-Fenton process. Moreover, the influence of H_2O_2 dosage was also investigated. Paracetamol was selected as model contaminant because it is highly used as antipyretic and analgesic. It was possible to observe that the mineralization rate increases by increasing the H_2O_2:PCT and H_2O_2:Fe ratios. However, a plateau is reached for values of these ratios greater than 10 and 40, respectively. Especially, it was noticed that the highest mineralization rate was obtained for the highest value of the initial concentration of H_2O_2 (378 mg L^{-1}), regardless the value of the initial concentration of Fe(II). A very slight decrease in the TOC mineralization was observed by changing the value of the initial concentration of Fe(II) from 10, to 7.5 and 5 mg L^{-1}. Hence, it was concluded that the H_2O_2:Fe ratio can be increased until a value of about 80 (that corresponds to $[H_2O_2]^0$=378 mg L^{-1} and $[Fe(II)]^0$=5 mg L^{-1}). Such ratio allows working with the lowest initial concentration of Fe(II) with no significant impact on process performance. Moreover, this work highlighted the important role of H_2O_2 dosage in the photo-Fenton process performance. By fixing the same total amount of H_2O_2 to be added to the reactor ($[H_2O_2]^{TOT}$=378 mg L^{-1}), it was possible to compare experiments with and without dosage, and it was shown that dosage improves the mineralization rate for the same total amount of H_2O_2. Nevertheless, further work is required to propose a proper and systematic procedure for determining the optimal hydrogen peroxide dosage and to explore the potentiality of H_2O_2 dosage. Especially, the combination of the experimental and modelling approach seems to be the only possible way to achieve this important goal.

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