Degradation of Sulfamethazine by Means of an Improved Photo-Fenton Process Involving a Hydrogen Peroxide Systematic Dosage

Despite being acknowledged as an emerging contaminant, Sulfamethazine (SMT) degradation has received scarce attention in the Advanced Oxidation Processes field. Thus, this work addresses the degradation of SMT in water solutions (12 L of 25 mg L^{-1} samples) by means of a photo-Fenton process and a systematic H_2O_2 dosage protocol that enhances its performance. A conventional photo-Fenton process led to 86% mineralization after 120 minute treatment when adding the Fenton reactants at once (initial concentrations were 10 mg L^{-1} Fe(II) and 200 mg L^{-1} H_2O_2). Conversely, the process achieved the total mineralization of the samples in less than 75 minutes when the same amount of H_2O_2 was continuously dosed according to a conveniently tuned dosage protocol. In both cases, total SMT degradation was achieved within 10 minutes. Hence, this work's aim is to determine the efficient dosage conditions of H_2O_2. The results show that a significant improvement of the photo-Fenton mineralization of SMT solutions is possible by adjusting the dosage of H_2O_2.

Keywords: sulfamethazine, emerging contaminants, photo-Fenton process, hydrogen peroxide dosage

Introduction

Antibiotics have been detected in worldwide ecosystems during the last three decades. However, interest in them as contaminants has grown only recently because of their persistent character and their increasing concentration levels in ground water, surface water, and even in drinking water [1-3]. The presence of antibiotics in natural ecosystems is acknowledged to alter normal flora and causes live organisms to develop resistance [1].

Antibiotics and other pharmaceuticals have been detected in sewage treatment plants. Martínez-Bueno et al. [4] have analyzed the persistence of organic emerging contaminants in Spain, and data from five plants for over two years of monitoring show

that sulfamethazine is among those compounds detected at concentrations above 1 µg/L whose removal efficiency was rated as low (<50%).

Sulfamethazine (SMT) or sulfamidine (4-amino-N-(4,6-dimethylpyrimidin-2-yl) benzenesulfonamide) is an antibacterial sulfonamide used in veterinary and human medicine. According to García-Galán et al. [5], SMT and its metabolites have been detected in waters, from which it is uncertain whether they can be remediated by conventional water treatments. Thus, research is required for alternative processes that could ensure mineralization of solutions of this emerging contaminant.

Advanced oxidation processes (AOPs), based on the generation of highly oxidant hydroxyl radicals ($^{\bullet}OH$), have been used as an alternative to remediate persistent contaminants from conventional water treatment plants influents and effluents: in the first case they are used to prevent the inactivation of the microorganisms used in the biological process, while in the second case they are used to refine the effluent before its final disposal [6].

Among the alternatives to remove recalcitrant contaminants, photo-Fenton and photolytic processes have demonstrated to be an efficient way to remediate antibiotics and other pharmaceuticals. Photolysis consists of the chemical decomposition of the contaminant by the absorption of energy at a given wavelength, while photo-Fenton process is an advanced oxidation process that consists of the reaction between an Fe(II) salt and H_2O_2 to generate hydroxyl radicals in the presence of irradiation of an appropriate wavelength [7].

There is copious literature exploring Fenton, photo-Fenton, and UV/H_2O_2 alternatives for the treatment of industrial effluents, mostly connected to pulp and paper and dyes and tannery applications. More recently, research in this field has also deepened into the effect of the effect and toxicity of reaction intermediates [8, 9].

The treatment of pharmaceuticals and personal care products (PPCP) in water solutions has also received attention. Photolysis of antibiotics has been addressed in the literature, as reviewed by Canonica et al. [10]. The photodegradation of sulphonamides such as sulphamethoxazole [11, 12] and sulfadiazine [13] has been reported. In particular, Kim and Tanaka [14] and Kim et al. [15] have investigated the photo degradation of SMT and other sulfa antibiotics at 254 nm and different experimental conditions. Ozonation [16] and UV/persulfate oxidation [17] have also proven to be effective for the degradation of SMT and other antibiotics. However, only the research by Pérez-Moya et al., [18, 19] has addressed SMT degradation by means of the photo-Fenton process.

The photo-Fenton process, which involves the presence of the hydroxyl radical as a highly oxidant species, offers a more efficient way to degrade recalcitrant contaminants. However, the hydroxyl radical is very unstable and non-selective, so it is frequently scavenged by undesired secondary reactions, some of them involving H_2O_2 consumption, which reduce the efficiency of the process [20]. A lot of research has been dedicated to improving the process performance, and the continuous batch-wise dosing of H_2O_2 has been revealed as a very promising option [21-24].

Very recently, Yamal-Turbay et al. [25] proposed a systematic H_2O_2 dosage protocol based on an initial reagent release (y_0) and a continuous inlet flow starting at a given time (t_{ini}) and finishing after a defined time span (ΔT_{add}). Given a fixed amount of H_2O_2 to be dosed ($Q^{H_2O_2}$) and the dosage time (ΔT_{add}), the appropriate combination of two factors, namely t_{ini} and y_0, showed improvement in the mineralization of model samples of commercial instant coffee. Thus, this work's goal is to improve the performance of the photo-Fenton process in remediating and mineralizing SMT sample solutions by applying this dosage protocol.

Experimental

Materials

12 L of 25 mg L^{-1} SMT samples were prepared in tap water using 99% Sigma-Aldrich SMT. pH was set at 3.0±0.1 by adding HCl 1 M (J.T. Baker). 7-hydrated Fe(II) sulfate (Merck) and H_2O_2 30% w/v (Panreac) were used as received. HPLC gradient grade acetonitrile and filtered milli-Q grade water were used for HPLC determinations. A stock of ammonium metavanadate (Riedel-de-Haën) 0.062 M in H_2SO_4 (Panreac) 0.58 M was used for the determination of H_2O_2 concentration.

Pilot Plant

An automated pilot plant was used in this study. It includes two main units, namely a Pyrex reservoir and a tubular photo-reactor provided with a PL-L-55W low pressure Hg lamp in a quartz envelope, emitting mostly at 254 nm. The plant is provided with a pumping system that guarantees perfect mixing for a recirculation flow above 7.7 L min^{-1} and it was operated at 11.3 L min^{-1}. The plant is equipped with a SCADA system that allows programming the inlet flow of H_2O_2 to the reactor through a peristaltic pump. The experiments were carried out at pH = 3.0±0.5 and temperature 24±5°C.

Yamal-Turbay et al. [25] proposed a characterization of the dosage of the total load ($Q^{H_2O_2}$) based on the addition of a fraction of this load (y_0) at the process startup (t_0=0) and the subsequent addition of the rest of the load by a ramp defined by its initial time (t_{ini}) and its duration (ΔT_{add}). Hence, the amount $q(t)$ and the fraction $y(t)$ added at each time t is given by:

$$y(t) = \frac{q(t)}{Q^{H_2O_2}} = \begin{cases} 0 & \text{if } t > 0 \\ y_0 & \text{if } 0 \leq t < t_{ini} \\ y_0 + m(t - t_{ini}) & \text{if } t_{ini} \leq t < t_{ini} + \Delta t_{add} \\ 1 & \text{if } t \geq t_{ini} + \Delta t_{add} \end{cases} \tag{1}$$

Therefore, the slope of the ramp is given by:

$$m = (1 - y_0)/\Delta t_{add} \tag{2}$$

Given $Q^{H_2O_2}$ and ΔT_{add}, this dosage protocol allows a 2^2 factorial experimental design with t_{ini} and y_0 as factors, from which the enhancement of the process can be derived. Yamal-Turbay et al. [25] showed the potential of this approach by addressing the mineralization of model coffee samples. In a similar way, this work studies the influence of dosage in SMT degradation following an equivalent protocol that allows designing a 2^2 factorial scheme with star points.

Hydrogen peroxide loads will be referred to as the amount to be dosed $Q^{H_2O_2}$ (mg). For comparative purposes with the true H_2O_2 initial concentration in the pure batch mode (no dosage), $C_0^{H_2O_2}$, the equivalent concentration $C_{eq,\infty}^{H_2O_2} = Q^{H_2O_2} V_R^{-1}$ (mg/mL) will also be used. This is the concentration that would be obtained after the addition of this amount to a reactor of fixed volume V_R.

Analytical Methods

Total organic carbon (TOC), SMT, and H_2O_2 concentrations were measured at regular time intervals throughout the process span as indicators of process evolution and effluent quality.

TOC was determined by means of a Shimadzu $V_{CHS/CSN}$ TOC analyzer, with a detection limit of 1 mg L^{-1}. H_2O_2 concentration was measured using the

spectrophotometric method proposed by Nogueira et al. [26] based on the reaction with ammonium metavanadate.

For measuring SMT concentration, 20 µL samples were manually injected into an Agilent 1200 series, provided with a UV-DAD array detector set at 274 nm (Agilent Chem-Station (Rev.B.04.06 SP1[647]) software) and a C18 5 µm 150x4.6 mm Zorbax Eclipse XDB-C18 column (Agilent Technologies), and operated at 25ºC. The mobile phase was a mixture of acetonitrile:water (45:55) flowing at 1.5 mL min^{-1}; a six-level calibration curve ranging from 0-50 mg L^{-1} was used for SMT quantification; and the retention time for SMT under these conditions was 1.2 minutes.

Results and Discussion

Fenton Reagent

For comparative purposes, SMT concentrations and Fenton reagent loads were established according to concentrations reported elsewhere [18], which are also in agreement with the detection limit of the available equipment. In that reference work, 1 L of 50 mg L^{-1} SMT solutions were used; Fe(II) initial concentrations ranged from 12 to 68 mg L^{-1}; and H_2O_2 concentrations ranged from 176 to 1024 mg L^{-1}.

Conversely, in this work Fe(II) concentration was set at 10 mg L^{-1}, the legal limit for liquid effluents in Spain [27]. As a consequence of this reduction in the iron load and taking into account the detection limit of the TOC analyzer, the SMT concentration was fixed at 25 mg L^{-1}, despite being higher than actual concentrations detected in wastewaters, usually in the range of µg-ng L^{-1}. Different initial H_2O_2 concentrations were tested (12, 20, 40, 60, and 200 mg L^{-1}) including conditions below and above theoretical stoichiometric H_2O_2 (equal to 140.5 mg L^{-1} for 25 mg L^{-1} SMT).

Given iron concentration (10 mg L^{-1}), a set of experiments were conducted to select a convenient Fenton reagents ratio. First order rate constants for TOC degradation (k_{TOC}) were estimated and compared to identify the range of most promising H$_2$O$_2$ loads (those producing higher initial reaction rates). Results (Fig. 1) show that initial H$_2$O$_2$ concentrations below 200 mg L^{-1} can increase initial reaction rate, which would confirm the benefit of H$_2$O$_2$ dosage. Accordingly, the following conditions were selected for investigating the effect of H$_2$O$_2$ dosage on the mineralization process:

- SMT initial concentration: 25 mg L^{-1}

- Fe(II) initial concentration: 10 mg L^{-1}

- Total H$_2$O$_2$ load to be dosed: $Q^{H_2O_2}$ = 2400 mg (8.0 mL, 30% w/v), meaning $C_{eq,\infty}^{H_2O_2}$ = 200 mg L^{-1}.

Blank Assays

A preliminary set of blank assays was performed in order to characterize the influence of different factors (reagents and irradiation) on the evolution of SMT degradation. 25 mg L^{-1} SMT samples in tap water were used. Table 1 shows the SMT degradation results, which can be summarized as follows:

- 200 mg L^{-1} of H$_2$O$_2$ yields up to 98% SMT degradation; irradiation alone leads to 90% SMT degradation, which is in accordance with observations reported elsewhere [15]; and combined Fe(II)/UV achieves only 69% (this is more than the scarce 13% obtained with only 10 mg L^{-1} Fe(II), but less than the outcome of UV alone; the Fe(II) absorption of part of the energy irradiated explains such an efficiency decrease [28, 29]).

- Regarding mineralization, all blank assays produced less than 30% TOC reductions, from 8.9% in the case of H_2O_2 to 23.4% in the case of Fe(II)/UV. Thus, the reverse performance obtained by mineralization with respect to SMT degradation confirms the need for the combined use of Fe(II)/UV and H_2O_2.

The blank assays confirmed that long reaction times are required to yield a significant reduction of SMT concentration. Hence, new assays were proposed for the UV/H_2O_2, Fenton and photo-Fenton processes.

SMT Degradation Performance

Three different AOP alternatives were analyzed and compared in terms of the reduction of the concentrations of SMT (degradation) and TOC (mineralization). Figure 2 summarizes these results. Regarding SMT, UV/H_2O_2 requires 30 minutes to reduce 95% of its initial concentration. On the other hand, Fenton and photo-Fenton processes achieve similar performance only within 7.5 minutes. The three studied AOPs noticeably improve SMT degradation with respect to the blank assays discussed in the previous section.

Regarding mineralization, Fenton process reduces 55% of the initial TOC during the first 45 minutes of reaction. No further mineralization is observed even though there still remains some residual amount of H_2O_2; this is consistent with the drop of the cycling rate of Fe(III) into Fe(II) in the absence of irradiation [7]. The UV/H_2O_2 process stops as H_2O_2 is exhausted; still, it leads to a TOC reduction (67%) higher than that obtained by the Fenton process within the same time span. For the photo-Fenton process, H_2O_2 exhaustion occurs within 30 minutes, and TOC reduction reaches 86%. This mineralization clearly contrasts with the maximum 30% reached with blank assays.

All assays were replicated and the average absolute deviation of the measurements was always below 1.5 mg L^{-1}. In particular, Figure 3 plots the data

obtained for the central assay of the Design of Experiments introduced next, and includes the corresponding error bars to illustrate the variability of data.

Once the higher outcome of the photo-Fenton treatment is demonstrated, the next step is to study the effect of H_2O_2 dosage on the performance of the process.

Influence of dosage on process performance

The design of experiments (DOE) in Table 2 was undertaken to characterize the process performance as a function of the variables of the dosage protocol [25]. Given the total duration of the treatment (120 minutes), the length of the dosage interval (Δt_{add}) was decided on the basis of the preliminary assays and set to 60 minutes in order to limit the alternatives only to a couple of variables of interest. These variables are:

- y_0: defined as the fraction of the total H_2O_2 dose released at $t = 0$ min. The minimum and maximum values of this variable were taken as 10 and 30% (centered in 20%).
- t_{ini}: the time when the rest of the H_2O_2 starts to be continuously added at a constant flow during Δt_{add}. DOE considers 0 and 30 minutes as minimum and maximum values for this variable, centered in 15 minutes.

Accordingly, from this point on, experiments are referred to as follows: $code\_y_0\_t_{ini}$, where "*code*" is a correlative letter. Thus, a unique identifier is coupled to each operating condition.

Given these two factors, the system's response was assessed in two different ways. On the one hand, it is analyzed by the earliest sample time at which SMT is not detected (t_{SMT}). This indicator is given by the detection limit of the analytical method (0.5 ppm), which corresponds to more than 95% degradation of the initial SMT concentration. Obviously, the precision in determining this indicator is given by the

sample time, which is 2.5 minutes. On the other hand, the system performance is also assessed by the time at which mineralization occurs. The precision of this second indicator is given by the TOC detection limit (1 ppm) and the sample time, which in this case is higher: 10 minutes.

Hence, this study addresses the improvement of the process efficiency. Rigorous optimization is not intended. The factorial design employed is just a means for systematically exploring the region of interest and the study only shows how improved operational conditions may be found and identified. Thus, the characterization of the dual response will be later presented as a function of these two objectives that may be conflicting (Fig. 5).

Two reference assays were carried out: one with a total release of reagent at the initial reaction time, t = 0, (Ref_100), and the other one with a continuous inlet of H_2O_2 during the first 60 minutes assay (L_0_0). These experiments are compared to the central experiment of the DOE (Central_20_15) in Figure 4. The improvement of the process is shown to be clear for both dosage protocols, and total mineralization is achieved in less than a 90 minute treatment, when compared to 86% in 120 minutes when no dosage is applied. This observation conforms to the idea that gradual addition of H_2O_2 reduces the scavenging of hydroxyl radicals [20-23, 25, 30].

Regarding SMT, elimination in less than 15 minutes was observed in all cases, except the central assay (Central_20_15), which needed almost 30 minutes to degrade more than 95% of initial SMT.

As a summary of the DOE results, Figure 5 shows the relation between the time necessary to degrade 95% of initial SMT (t_{SMT}) and the time to degrade at least 92% of initial TOC (t_{TOC}) for all the DOE assays and the two reference ones. Only assay R_100 (86.1% TOC reduction) does not achieve 92% mineralization within a 120 minute

treatment, as it is obtained in all the cases where systematic dosage is applied. As indicated by Yamal-Turbay et al. [25] both factors, y_0 and t_{ini}, are related: the combination of low y_0 with low t_{ini} is the one that leads to a better performance. When a low initial release is provided, it is necessary to start continuous dosage sooner to avoid reagent exhaustion, as may be observed in experiment B_10_0 and J_6_15.

As previously mentioned, the DOE provides evidence of the cross-effect between the factors of the dosage protocol. Process performance for different y_0 and t_{ini} are compared in Figure 6 with the aim to visualize this effect. In experiment B_10_30, for instance, TOC reduction is particularly slow after the first 10 minutes, as H_2O_2 is exhausted, while it accelerates after reagent dosage starts after 30 minutes. Something similar occurs in experiment D_30_30, although y_0= 30% appears to be enough to keep the process running until continuous dosage starts. Experiment A_10_0 exhibits a slower behavior compared to experiment C_30_0, but both are faster than B_10_30 and D_30_30 due to the early presence of H_2O_2.

Therefore, results show that, when conveniently tuned, hydrogen peroxide dosage accelerates the degradation of SMT and increases (up to 100%) the mineralization obtained at the end of the treatment span. This is achieved through an efficient process which uses the same amount of hydrogen peroxide, but reduces the treatment cost significantly.

Conclusions

The photo-Fenton treatment has proved to be effective in totally degrading 12 L of a 25 mg L^{-1} SMT sample by using 10 mg L^{-1} iron and 200 mg L^{-1} H_2O_2 initial concentrations. After the 120 minute treatment employed in this work, only 86% mineralization of the sample was achieved by adding the entire Fenton load at once. This represents an initial improvement of 30 percentage points with respect to previous

works that use larger amounts of reagents (Fe(II): 12-68 mg L^{-1}, H_2O_2: 176-1024 mg L^{-1}). However, further enhancement was next shown to be possible via H_2O_2 dosage.

Preliminary assays confirmed that an excess of H_2O_2 during the first stages of the process reduces TOC degradation performance, which can be attributed to the scavenging of hydroxyl radicals. After that, dosage was investigated by applying a dosage protocol that permits a subsequent two-factor design of experiments. Hence, the systematic exploration of a set of dosage alternatives led to conditions yielding total mineralization of the problem sample in less than a 75 minute assay.

Relative to the performance obtained without the dosage, the dosage alternative yielded an improvement of 14 percent points in the timing of the process. Regarding SMT, total degradation is achieved in less than a 10 minute treatment with the appropriate combination of the dosage protocol variables.

Concerning the tuning of the dosage parameters, the design of experiments reveals that low y_0 requires low t_{ini} in order to achieve both aims: fast mineralization and fast degradation. When higher y_0 values are used, t_{ini} influence on SMT degradation diminishes, but more time is necessary to reach total mineralization.

Concerning the effect of the dosage parameters, the assays performed reveal that both fast degradation and fast mineralization are achieved when low y_0 is paired with low t_{ini} (reducing initial load and starting the dosage sooner). Conversely, for higher y_0 values, the influence of t_{ini} is lower, and the time to reach total mineralization is increased. However, determining the best pair of conditions (y_0 and t_{ini}) requires defining specific performance indices (or costs), and the results presented should not be taken as optimal. Such an investigation would be a particular application that could be addressed with the same approach presented.

Nonetheless, further work regarding different ranges of SMT concentrations should be considered. The value 25 mg L^{-1} was set according to the capacity of both the analytical methods and the dosage equipment, but lower concentrations of emerging contaminants can be expected in water and wastewaters, as well as matrices of different species also affecting water quality. Scaling is beyond the scope of this work and it is still an issue to be addressed in each particular situation.

Acknowledgements

References

1. Homem, V. and Santos, L., Degradation and removal methods of antibiotics from aqueous matrices - A review. *J. Environ. Manage.,* **92,** 2304-2347 (2011).
2. Klavarioti, M., Mantzavinos, D. and Kassinos, D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.,* **35**, 402-417 (2009).
3. Kasprzyk-Horderna, B., Dinsdale, R.M. and Guwy, A.J., The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Water Res.,* **42**, 3498–3518 (2008).
4. Martínez Bueno, M.J., Gomez, M.J., Herrera, S., Hernando, M.D., Agüera, A. and Fernández-Alba, A.R., Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. *Environ. Pollut.,* **164**, 267-273 (2012).
5. García-Galán, M.J., Díaz-Cruz, M.S. and Barceló, D., Kinetic studies and characterization of photolytic products of sulfamethazine, sulfapyridine and their acetylated metabolites in water under simulated solar irradiation. *Water Res.,* **46**, 711-722 (2012).

6. Oller, I., Malato, S. and Sánchez Pérez, J.A., Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. *Sci. Total Environ.*, **409**, 4141–4166 (2011).

7. Pignatello, J.J., Oliveros, E. and MacKay, A., Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Technol.,* **36:1**, 1-84 (2006).

8. Nagel-Hassemer, M.E., Carvalho-Pinto, C.R.S., Matias, W.G. and Rubens Lapolli, F. Removal of coloured compounds from textile industry effluents by UV/H_2O_2 advanced oxidation and toxicity evaluation. *Environ. Technol.*, **32(16)**, 1867-1874 (2011).

9. Borba, F.H., Módenes, A.N., Espinoza-Quiñones, F.R., Ricieri Manenti, D., Bergamasco R. and Diaz Mora, N. Toxicity assessment of tannery effluent treated by an optimized photo-Fenton process. *Environ. Technol.*, **34(5)**, pages 653-661 (2013).

10. Canonica, S., Meunier, L. and von Gunten, U., Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Res.,* **42**, 121-128 (2008).

11. Lester, Y., Avisar, D. and Mamane, H. Photodegradation of the antibiotic sulphamethoxazole in water with UV/H_2O_2 advanced oxidation process. *Environ. Technol.*, **31(2)**, 175-183 (2010).

12. Ngouyap Mouamfon, M.V., Li, W., Lu, S., Qiu, Z., Chen, N. and Lin, K. Photodegradation of sulphamethoxazole under UV-light irradiation at 254 nm. *Environ. Technol.*, **31(5)**, 489-494 (2010).

13. Zhang, Y and Ma, L. Photodegradation mechanism of sulfadiazine catalyzed by Fe(III), oxalate and algae under UV irradiation. *Environ. Technol.*, **34(12)**, 1617-1623 (2013).

14. Kim, I. and Tanaka, H., Photodegradation characteristics of PPCPs in water with UV treatment. *Environ Int* **35**, 793–802 (2009).

15. Kim, I., Yamashita, N. and Tanaka, H., Photodegradation of pharmaceuticals and personal care products during UV and UV/H_2O_2 treatments. *Chemosphere*, 77, 518–525 (2009).

16. Ikehata, K., Jodeiri, Naghashkar, N., Gamal El-Din M. Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone-Sci. Eng,* **28:6**, 353-414 (2006)

17. Gao, Y-q., Gao, N-y., Deng, Y., Yang, Y-q. and Ma, Y., Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chem. Eng. J.,* **195–196**, 248–253 (2012).

18. Pérez-Moya, M., Graells, M., Castells, G., Amigó, J., Ortega, E., Buhigas, G., Pérez, L.M., and Mansilla, H.D., Characterization of the degradation performance of the sulfamethazine antibiotic by photo-Fenton process. *Water Res.,* **44,** 2533-2540 (2010).

19. Pérez-Moya, M., Mansilla, H.D., Graells, M., A practical parametrical characterization of the Fenton and the photo-Fenton sulfamethazine treatment using semi-empirical modeling. *J. Chem. Technol. Biot*, **86:6**, 826-831 (2011)

20. Gulkaya, I., Surucu, A. and Dilek, F., Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater. *J. Hazard. Mater. B,* **136**, 763-769 (2006).

21. Zazo, J.A., Casas, J.A., Mohedano, A.F. and Rodríguez, J.J., Semicontinuous Fenton oxidation of phenol in aqueous solution. A kinetic study. *Water Res.,* **43**, 4063-4069 (2009).

22. Chu, W., Chan, K.H., Kwan, C.Y. and Choi, K.Y., Degradation of atrazine by modified stepwise-Fenton's processes. *Chemosphere,* **67**, 755-761 (2007).

23. Prato-Garcia, D. and Buitrón, G., Evaluation of three reagent dosing strategies in a photo-Fenton process for the decolorization of azo dye mixtures. *J. Hazard. Mat.,* **217–218**, 293–300 (2012).

24. Carra, I., Ortega-Gómez, E., Santos-Juanes, L., Casas López, J.L. and Sánchez Pérez, J.A., Cost analysis of different hydrogen peroxide supply strategies in the solar photo-Fenton process. *Chem. Eng. J.,* **224**, 71-81 (2013).

25. Yamal-Turbay, E., Graells, M. and Pérez-Moya, M., Systematic Assessment of the Influence of Hydrogen Peroxide Dosage on Caffeine Degradation by photo-Fenton Process. *Ind. Eng. Chem. Res,.* **51:13**, 4770-4778 (2012).

26. Nogueira, R.F.P., Oliveira, M.C. and Paterlini, W.C., Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate. *Talanta,* **66**, 86-91 (2005).

27. DOGC núm. 3894, DECRET 130/2003, de 13/05/2003, (29.5.2003). Available at http://www.gencat.cat/diari/3894/03127147.htm.

28. Braun, A.M., Maurette, M.T. and Oliveros, E., Photochemical Technnology. John Wiley & Sons, Inc. London, 1991.

29. Ferraudi, G., Elements of Inorganic Photochemistry. John Wiley & Sons Inc. London, 1988.

30. Huston, P.L. and Pignatello, J.J., Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. *Water Res.,* **33:5,** 1238-1246 (1999)

Table 1. SMT degradation and mineralization achieved with blank assays at the end of the treatment span (120 min.).

Table 2. Assays carried out according to the DOE. $C_{eq,\infty}^{H_2O_2} = 200$ mg L^{-1}.
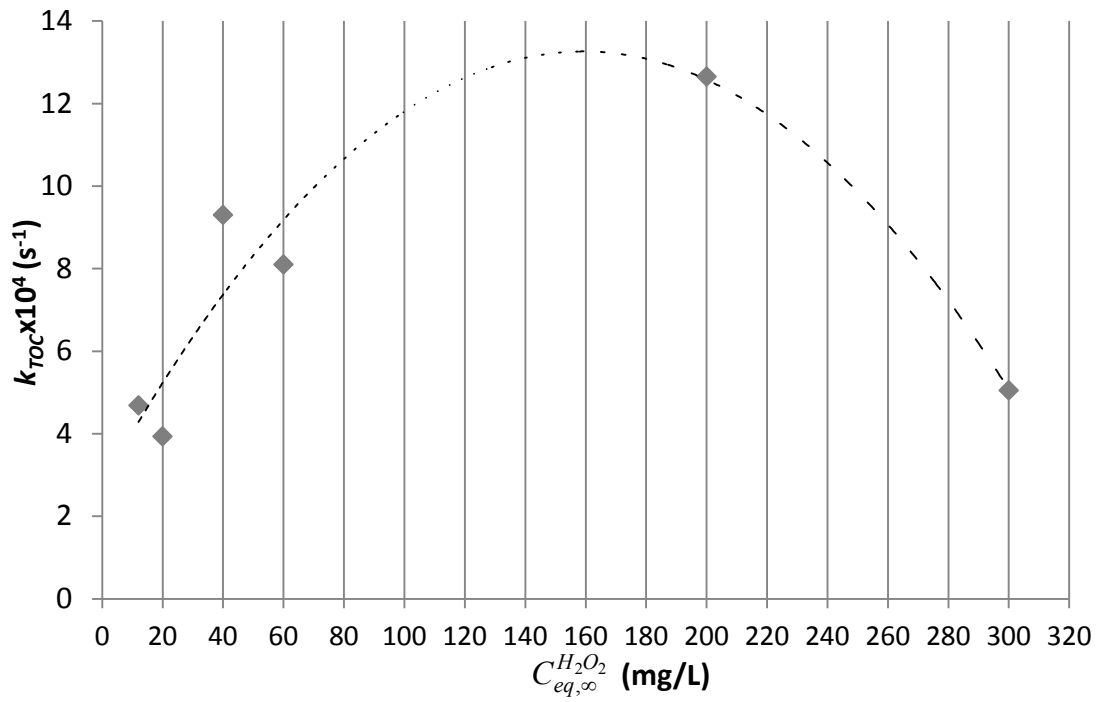
Figure 1. *First order rate* constants for TOC degradation (k_{TOC}) versus $C_{eq,\infty}^{H_2O_2}$ for a 25 mg L^{-1} SMT concentration and 10 mg L^{-1} iron concentration.

Figure 2. TOC, SMT and H$_2$O$_2$ normalized concentration profiles for different AOPs. $C_0^{SMT} = 25$ mgL^{-1}; $C_0^{Fe(II)} = 10$ mgL^{-1}; $C_0^{H_2O_2} = 200$ mgL^{-1}

Figure 3. TOC, SMT and H$_2$O$_2$ normalized concentration profiles for the central assay of the design of experiments. $C_0^{SMT} = 25$ mgL^{-1}; $C_0^{Fe(II)} = 10$ mgL^{-1};

Figure 4. TOC, SMT and H$_2$O$_2$ normalized concentration profiles for different dosage protocols compared to reference experiment. $C_0^{SMT} = 25$ mgL^{-1}; $C_0^{Fe(II)} = 10$ mgL^{-1}; $C_{eq,\infty}^{H_2O_2} = 200$ mgL^{-1}

Figure 5. Relation between the time necessary to degrade 95% of initial SMT (t_{SMT}) and the time necessary to achieve total mineralization (t_{TOC}) for all of the DOE and reference assays. Final TOC conversion is indicated in brackets in the case when mineralization (100%) is not achieved (Assay R_100)

Figure 6. TOC, SMT and H$_2$O$_2$ normalized concentration profiles for different y_0 where $t_{ini} \geq 30$ min. $C_0^{SMT} = 25$ mgL^{-1}; $C_0^{Fe(II)} = 10$ mgL^{-1}; $C_{eq,\infty}^{H_2O_2} = 200$ mgL^{-1}

Figure 1. First order rate constants for TOC degradation (k_{TOC}) versus $C_{eq,\infty}^{H_2O_2}$ for a 25 mg L^{-1} SMT concentration and 10 mg L^{-1} iron concentration.
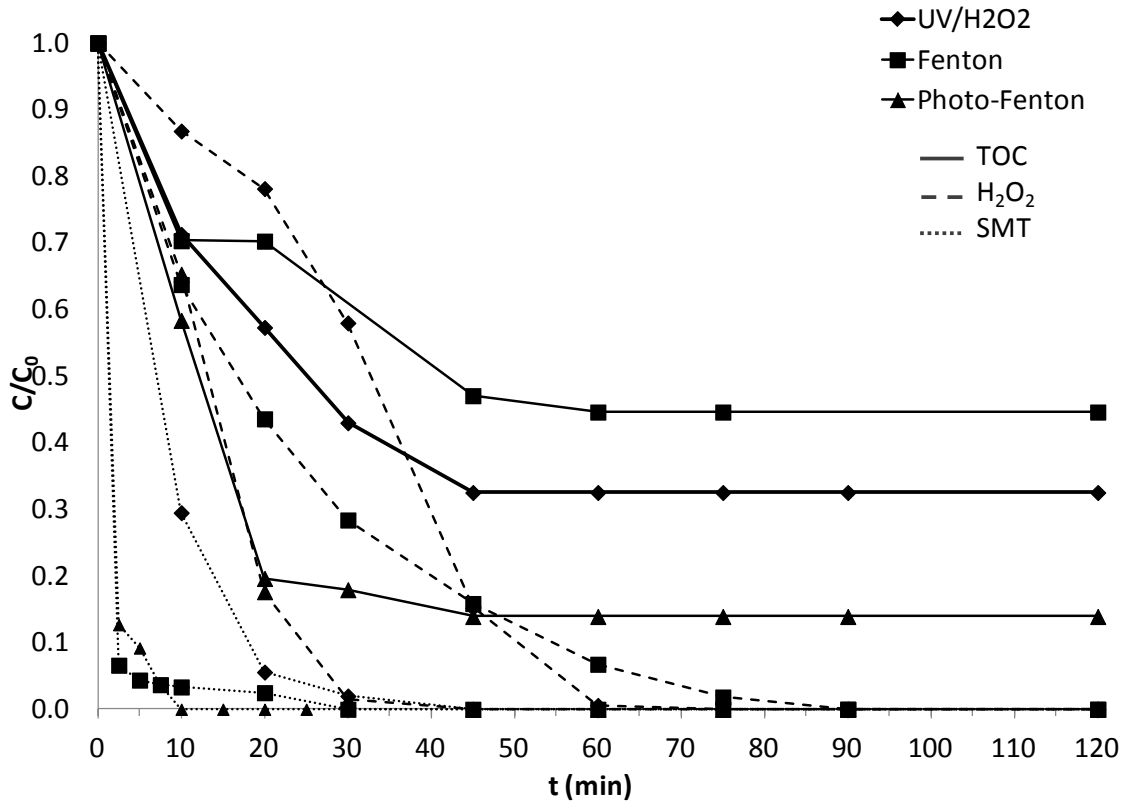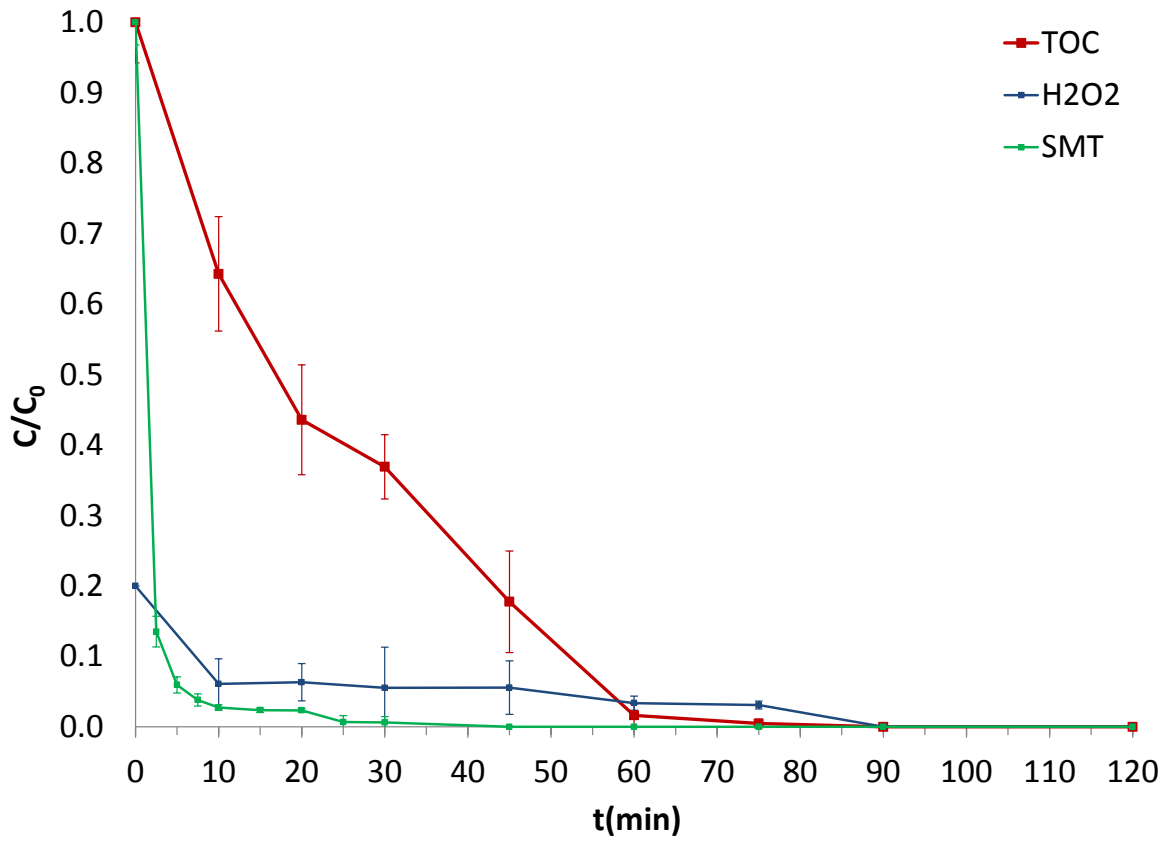
Figure 2. TOC, SMT and H_2O_2 normalized concentration profiles for different AOPs.
$C_0^{SMT} = 25 \ mgL^{-1}$; $\quad C_0^{Fe(II)} = 10 \ mgL^{-1}$; $\quad C_0^{H_2O_2} = 200 \ mgL^{-1}$

Figure 3. TOC, SMT and H_2O_2 normalized concentration profiles for the central assay of the design of experiments. $C_0^{SMT} = 25 \ mgL^{-1}$; $C_0^{Fe(II)} = 10 \ mgL^{-1}$; $C_{eq,\infty}^{H_2O_2} = 200 \ mgL^{-1}$
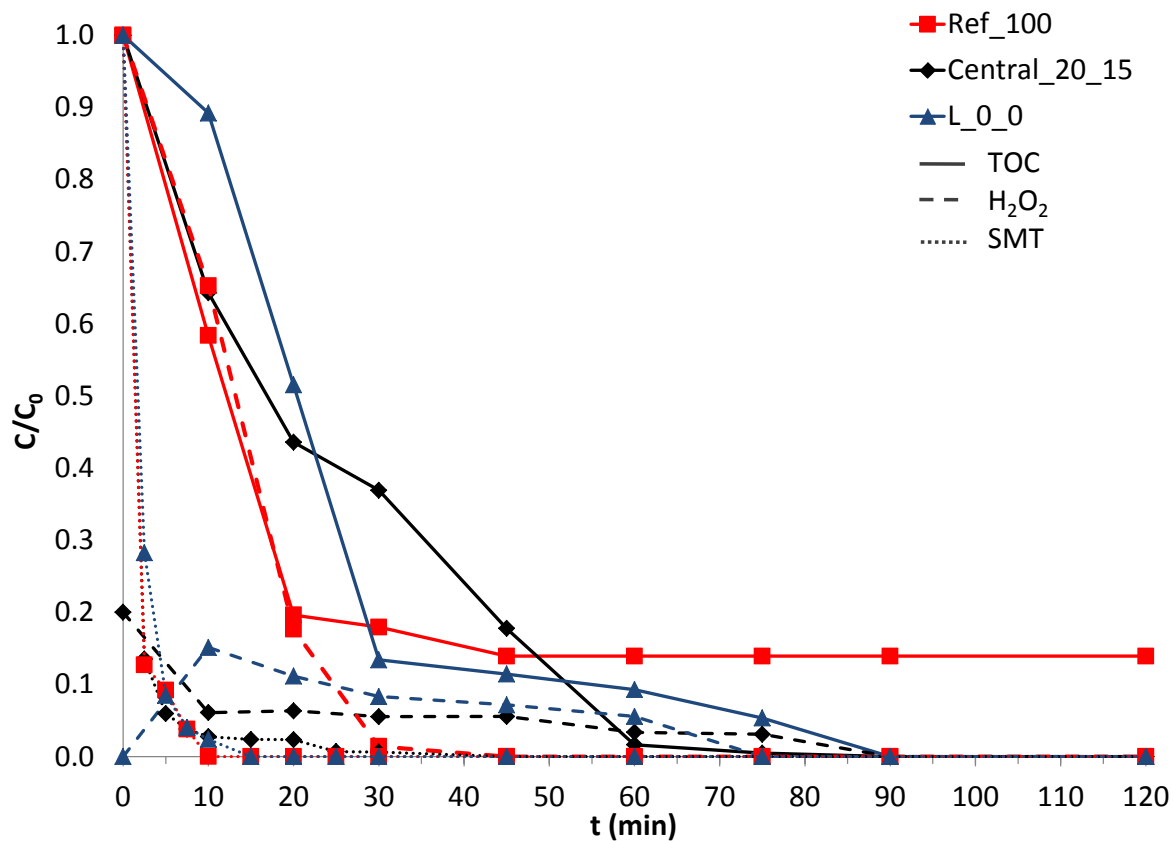
Figure 4. TOC, SMT and H_2O_2 normalized concentration profiles for different dosage protocols compared to reference experiment. $C_0^{SMT} = 25 \ mgL^{-1}$; $C_0^{Fe(II)} = 10 \ mgL^{-1}$; $C_{eq,\infty}^{H_2O_2} = 200 \ mgL^{-1}$
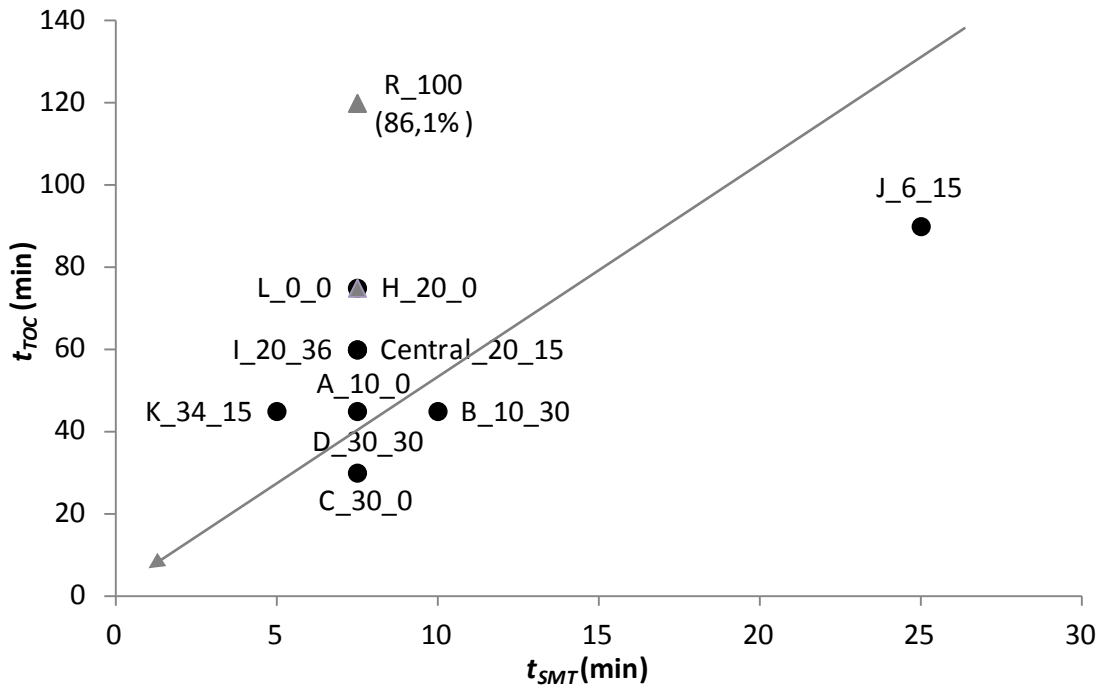
Figure 5. Relation between the time necessary to degrade 95% of initial SMT (t_{SMT}) and the time necessary to achieve total mineralization (t_{TOC}) for all of the DOE and reference assays. Final TOC conversion is indicated in brackets in the case when mineralization (100%) is not achieved (Assay R_100)
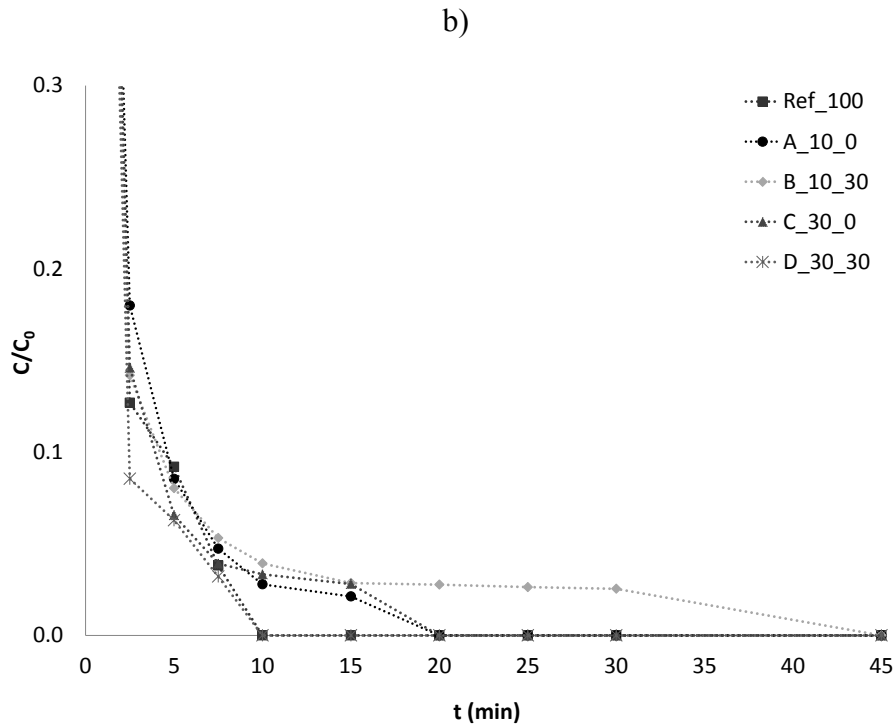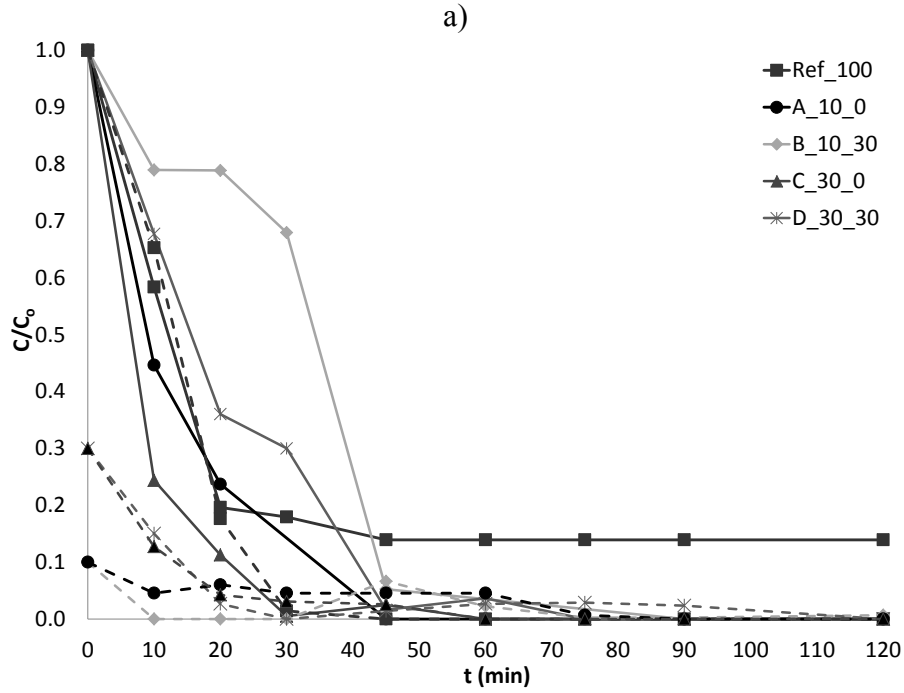
Figure 6. a) TOC (continuous lines) and H_2O_2 (dotted lines) normalized concentration profiles and b) SMT normalized concentration profile for different y_0 where $t_{ini} \geq 30$ min. $C_0^{SMT} = 25 \ mgL^{-1}$; $C_0^{Fe(II)} = 10 \ mgL^{-1}$; $C_{eq,\infty}^{H_2O_2} = 200 \ mgL^{-1}$

Table 1. SMT degradation and mineralizations achieved with blank assays at the end of the treatment span (120 min.).

Assay	Final degradation (%)	Final mineralization (%)
Fe(II) / UV	68.6	23.4
UV	89.6	10.6
H_2O_2	98.4	8.9

Table 2. Assays carried out according to the DOE. $C_{eq,\infty}^{H_2O_2} = 200$ mg L^{-1}.

Assay*	Codified values		Variables levels	
	t_{ini}	y_0	t_{ini} (min)	y_0 (%)
A_10_0	-1	-1	0	10%
B_10_30	1	-1	30	10%
C_30_0	-1	1	0	30%
D_30_30	1	1	30	30%
Central_20_15	0	0	15	20%
H_20_0	-1	0	0	20%
I_20_36	1.414	0	36	20%
J_6_15	0	-1.414	15	6%
K_34_15	0	1.414	15	34%
L_0_0	-1	-2	0	0%
Ref_100	-1	8	0	100%

* Assay code corresponds to: X(correlative letter)_Y(y_0)_Z(t_{ini})