

# Removal of Pharmaceutical Compounds by a Sequential Treatment of Ozonation Followed by Fenton Process: Influence of the Water Matrix

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**Abstract**—A sequential treatment of ozonation followed by a Fenton or photo-Fenton process, using black light lamps (365 nm) in this latter case, has been applied to remove a mixture of pharmaceutical compounds and the generated by-products both in ultrapure and secondary treated wastewater. The scientific-technological innovation of this study stems from the *in situ* generation of hydrogen peroxide from the direct ozonation of pharmaceuticals, and can later be used in the application of Fenton and photo-Fenton processes. The compounds selected as models were sulfamethoxazol and acetaminophen. It should be remarked that the use of a second process is necessary as a result of the low mineralization yield reached by the exclusive application of ozone. Therefore, the influence of the water matrix has been studied in terms of hydrogen peroxide concentration, individual compound concentration and total organic carbon removed. Moreover, the concentration of different iron species in solution has been measured.

**Keywords**—Fenton, photo-Fenton, ozone, pharmaceutical compounds, hydrogen peroxide, water treatment

## I. INTRODUCTION

CURRENTLY, society is increasingly more aware of the environmental issues caused by the majority of human activities and has been adopting legislative measures to mitigate, at least partially, the situation. Among all the solutions being considered, the conservation of water resources presents a huge importance since they are limited and indispensable for our lives and the sustainability of the environment. As a result of the rapid human and economic development, excessive use and contamination, water supply has suffered an alarming deterioration in almost every region of the world. One frequent case of contamination comes from the organic material dissolved in water that can generally be eliminated using conventional biological oxidation. Nevertheless, in the last decade a series of compounds, called “emergent contaminants”, have been identified in waters and the study of their removal is between the lines of priority research of main organizations dedicated to the protection of public and environmental health, such as the OMS, the EPA, and the European Commission.

The list of emergent contaminants includes an extensive variety of products used on a daily basis with both domestic and industrial applications, including pharmaceuticals, pesticides, hormones, beauty products, flame retardants, polycyclic aromatic hydrocarbons (PAHs), and surfactants [1]. Between all of these contaminants, those that most likely raise the most cause for concern and study in recent years are pharmaceutical compounds, considering their consumption in the European Union [2]. Previously, these compounds were not considered to be dangerous, thus they were neither regulated nor included under parameters for water quality control. However, thanks to the development of analysis methods with lower limits of detection, they have been found in distributaries channels of potable and superficial water and wastewater all over the world [3]-[6]. The long-term consequences of these misuses are unknown, but in the short-term they have already caused serious harm to the environment and present a growing risk for a number of species [7]-[8]. On the other hand, different studies indicate that the conventional processes applied in water treatment plants, such as coagulation, sedimentation, or filtration reach minimum levels of the elimination of pharmaceutical compounds [9]-[10]. Accordingly, there is a need to remove these compounds from water and tertiary treatment technologies are recommended for this purpose. Among these technologies ozonation and advanced oxidation processes (AOPs) have already been reported as the most appropriate ones for this task. Thus, the specialized literature presents numerous examples on the use of ozone and other advanced chemical oxidation processes [11]. However, during advanced oxidation of pharmaceuticals, metabolites are formed and they can also be harmful compounds [12]-[13]. As a consequence, generated intermediates should also be removed from water. Therefore, mineralization should be the main aim of these processes.

In the present work, a sequential treatment of ozonation followed by a Fenton or photo-Fenton process, using black light lamps (365 nm), has been applied to remove a mixture of pharmaceutical compounds and the generated by-products both in ultrapure and secondary treated wastewater.

The model compounds selected were sulfamethoxazol and acetaminophen. Sulfamethoxazole (SMT) is a sulphonamide type synthetic antibiotic used for the elimination of bacteria causing different illnesses [14]. Acetaminophen (ACT) is a common analgesic and anti-inflammatory which is widely used for humans and animals [15]. The ozonation was applied as the initial process that permits the generation of hydrogen peroxide and the removal of the initial contaminants. In a second process, as a result of the low mineralization yield reached by the exclusive application of ozone, the efficacy of the degradation of total organic carbon was studied by applying Fenton or photo-Fenton processes.

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The hydrogen peroxide generated *in situ* in the previous ozonation was taken advantage of in this process.

## II. EXPERIMENTAL

### A. Secondary Effluent and Chemicals

Both ultrapure and wastewater were doped with the two selected pharmaceuticals (SMT and ACT). Ultrapure water was obtained from a Milli Q Milli water system while the biologically treated wastewater was collected from the effluent of the municipal wastewater treatment plant of Badajoz (Spain). This effluent, of pH 7.7, contains, in average values, 19 mg·L<sup>-1</sup> TOC, 24 mg·L<sup>-1</sup> IC, 46.5 mg·L<sup>-1</sup> COD and 14 mg·L<sup>-1</sup> BOD as main characteristics.

Pharmaceuticals (SMT and ACT) were purchased from Sigma-Aldrich and used as received. Iron (II) sulphate 7-hydrate was obtained from Panreac (Spain).

### B. Experimental Setup

Experiments were carried out in 1 L cylindrical reactor equipped with mechanical agitation and an inlet for measuring temperature.

For the ozone processes, other inlets for feeding the gas (oxygen or ozone-oxygen) through a porous plate situated at the reactor bottom, sampling and one outlet for the non absorbing gas were used.

In photo-Fenton experiments, the reactor was situated in the middle of a wooden box (45 cm x 35 cm each wall) where four 15 W black light lamps, emitting mainly 365 nm radiation, were placed in each of the corners inside the box. Ferrioxalate actinometry [16] was used to determine the incident photon flux,  $I_0$ , in the photoreactor, that was found to be  $5.4 \times 10^{-8}$  Einstein·min<sup>-1</sup> with four lamps simultaneously working.

Steadily, samples were withdrawn from the reactor and analysed for parent compound, total organic carbon (TOC), chemical oxygen demand (COD) and hydrogen peroxide concentration. In addition, in ozonation experiments it was also determined ozone gas and dissolved ozone concentrations. When Fenton or photo-Fenton processes were applied it was also quantified Fe(II) and total iron concentrations. In some cases, experiments were carried out in triplicate for experimental errors determination.

### C. Analytical Procedure

SMT and ACT were analysed by high-performance liquid chromatography (Elite La Chrom) with a GEMINI 5U C18 110R column. Elution of samples was initially made with a mixture of acidified water (1% phosphoric acid) and methanol (90/10 v/v) that was gradually changed to reach 40/60 v/v acidified water/methanol after 7 min.

The flow rate was 0.5 mL·min<sup>-1</sup>. Detection was made with L-2455 Hitachi Diode Array detector at 267 nm for SMT and 245 nm for ACT.

Dissolved ozone was measured following the method of Bader and Hoigné [17]. Ozone in the gas phase was monitored by means of an Anseros Ozomat ozone analyser. The analysis was based on the absorbance at 254 nm.

Hydrogen peroxide concentration was determined through the cobalt-bicarbonate method [18].

Total iron concentration was analyzed by the ferrozine method [19], Fe(II) concentration by the phenantroline method [20]. Total organic carbon was monitored by a TOC-V<sub>SCH</sub> Shimadzu carbon analyser. Chemical Oxygen demand (COD) was determined in a Dr. Lange spectrophotometer, the method based on the standard dichromate reflux method [21]. Finally, biological oxygen demand (BOD) was measured following the procedure of the Warburg respirometer [22]. For this purpose, activated sludge from the secondary sedimentation unit of Badajoz wastewater treatment plant was used.

## III. RESULTS AND DISCUSSION

### A. Determination of maximum concentration of hydrogen peroxide

It is well known that when ozone is applied in water, hydrogen peroxide is formed [23]-[24]. This reaction is particularly important when unsaturated compounds are present in water. Thus, ozone breaking of aromatic rings or carbon double bond breaking through Criegee mechanism [25]-[26] leads to saturated compounds and formation of hydrogen peroxide. The main objective of this research was the use of the hydrogen peroxide, produced during the single ozonation experiments, in a second process: Fenton or photo-Fenton processes. Then, appropriate experimental conditions to obtain the maximum possible concentration of hydrogen peroxide were first established. In so doing, the optimal conditions for ozone concentration, pharmaceuticals ratio (the total concentration was always 30 mg·L<sup>-1</sup>) and pH have been determined both in ultrapure water and secondary treated wastewater using an experimental response surface modeling (RSM) design. Concretely, these optimal conditions were as follows: inlet ozone gas concentration, 23.5 mg·L<sup>-1</sup>; SMT/ACT ratio, 0.2 (initial SMT concentration: 5 mg·L<sup>-1</sup>, initial ACT concentration: 25 mg·L<sup>-1</sup>) and pH 1.5. Thus, as can be seen in Figure 1, when the conditions mentioned above are applied in single ozonation experiments a hydrogen peroxide concentration of approximately  $1.3 \times 10^{-4}$  mol·L<sup>-1</sup> is reached in 20 minutes.

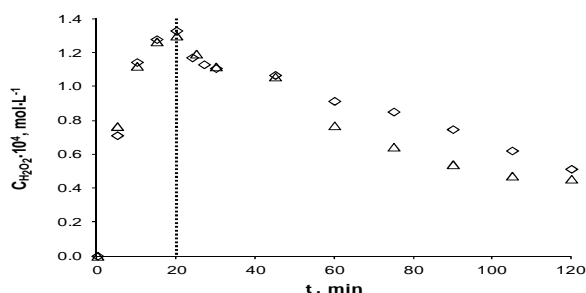


Fig. 1 Time evolution of hydrogen peroxide concentration formed in the ozonation of an aqueous solution of SMT and ACT. Experimental conditions: temperature: 20°C, pH 1.5 (perchloric/perchlorate), gas flow rate: 20 L·h<sup>-1</sup>, inlet ozone gas concentration: 23.5 mg·L<sup>-1</sup>, initial SMT concentration: 5 mg·L<sup>-1</sup>, initial ACT concentration: 25 mg·L<sup>-1</sup>, TiO<sub>2</sub> concentration: 1.5 g·L<sup>-1</sup>. Symbols: ◇: ultrapure water; △: biologically treated wastewater

### B. Removal of SMT and ACT Mixtures from water

Ozonation experiments of a SMT, ACT mixture was carried out both in ultrapure water and secondary treated wastewater to study the removal rates of target compounds and the influence of the water matrix.

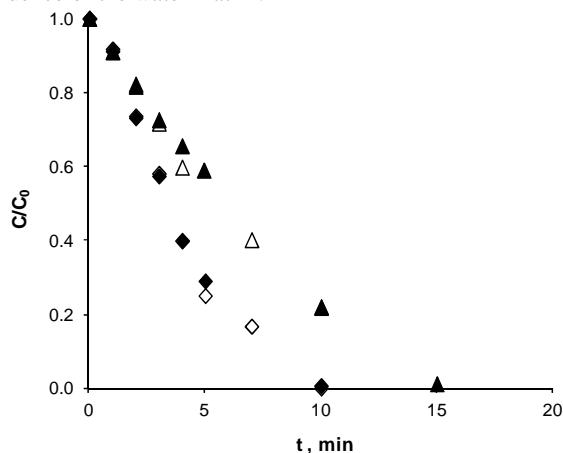
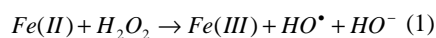


Fig. 2 Evolution of remaining SMT and DCF dimensionless concentration corresponding to single ozonation experiments. Experimental conditions as in Figure 1. Symbols: ▲, △: SMT; ◆, ◇: ACT (empty symbols mean experiments carried out in secondary treated wastewater)

As can be inferred from Figure 2, the ozonation during 20 minutes (time to reach the maximum hydrogen peroxide concentration) permits the elimination of the initial contaminants. In addition, by comparing the experiments of single ozonation in ultrapure and secondary treated wastewater, no significant differences were observed regardless of the pharmaceutical compound treated which also suggests that direct ozonation is the predominant mechanism of SMT and ACT removal. On the other hand, in contrast to the high ozone reactivity with ACT and SMT, intermediates of simple ozonation react slowly with ozone. Thus, after 20 min ozone reactions, TOC only diminishes 10% when ultrapure water is used and 20 % when the contaminants are in secondary treated wastewater. End intermediates formed are usually saturated carboxylic acids that hardly react with ozone [27]. As a consequence, ozone direct reactions are unimportant and low TOC degradation observed is likely due to hydroxyl radical oxidation. Therefore, it should be remarked that the use of an advanced oxidation as second process is necessary because of the low mineralization yield reached by the exclusive application of ozone.

### C. Fenton and photo-Fenton processes

The scientific-technological innovation of this study rely on *in situ* generation of hydrogen peroxide from the direct ozonation of pharmaceuticals that can later be used in the application of Fenton and photo-Fenton processes, in which hydroxyl radicals are produced through reaction (1).



However, pH has a significant role in Fenton and photo-Fenton processes. Thus, the previous ozonation experiments were carried out at pH 1.5, and when ozone feeding was stopped, after 20 minutes, pH was raised to 3 using NaOH. Additionally, dissolved ozone was removed by bubbling nitrogen gas in the solution.

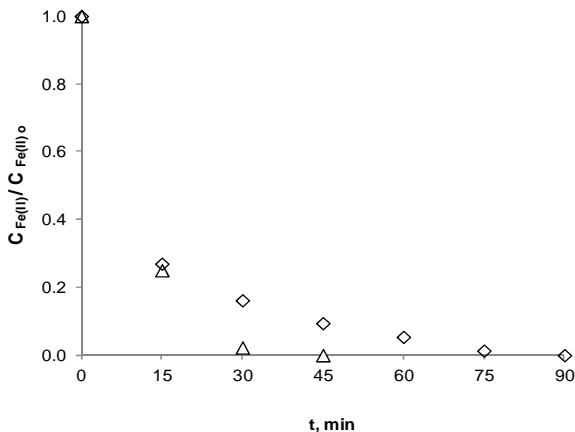
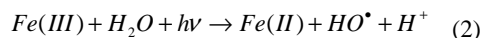


Fig. 3 Evolution of Fe(II) concentration with time during the Fenton process applied after a single ozonation experiment.

Experimental conditions: temperature: 20°C, pH 3 (perchloric/perchlorate),  $C_{H_2O_2}$ :  $1.3 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ,  $C_{H_2O_2}/C_{Fe(II)}$ : 10, total iron concentration:  $1.3 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ . Symbols: ◇: ultrapure water; △: secondary treated wastewater.

When ferrous ions were added to the aqueous solution containing hydrogen peroxide, no degradation of total organic carbon was obtained both in ultrapure water and secondary treated wastewater. This is likely the result of the rapid consumption of Fe (II), much more pronounced when experiments were performed in secondary treated wastewater (see Figure 3), when still exists in the reaction medium 65% and 85.5% of hydrogen peroxide generated in the previous ozonation process, in ultrapure water and wastewater, respectively.

With the aim of remove total organic carbon, photo-Fenton process was carried out by using black-light lamps (maximum wavelength: 365 nm). By applying UVA radiation, Fe(II) can be regenerated via photo-Fenton reaction as follows:



Reduction of Fe(III) to Fe(II) is helpful to regenerate radicals in several elementary steps of the reaction mechanism [28].

As can be observed from Figure 4, after the previous ozonation treatment, photo-Fenton process has a negligible effect when experiments were developed using secondary treated wastewater (only 8% mineralization in 2 hours), while in the case of ultrapure water the application of this second process lead to a 50% mineralization in 2 hours.

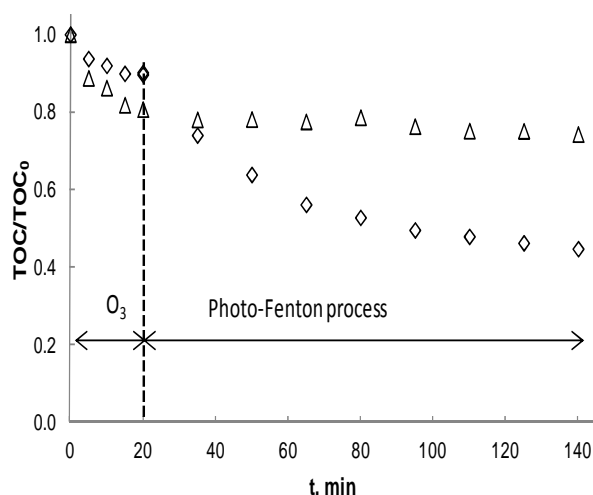


Fig. 4 Evolution of remaining TOC dimensionless concentration corresponding to sequential treatment of ozonation followed by a photo-Fenton process. Experimental conditions of ozonation experiments as in Figure 1. Experimental conditions in photo-Fenton processes as in Figure 3. Symbols: ◇: ultrapure water; △: biologically treated wastewater

This low mineralization when real wastewater was treated must be due to the fact that there are substances that act as hydroxyl radical scavengers.

#### IV. CONCLUSIONS

The optimal conditions determined for maximum hydrogen peroxide concentration during the ozonation process, both in ultrapure water and secondary treated wastewater, were: inlet ozone gas concentration, 23.5 mg·L<sup>-1</sup>; pharmaceuticals ratio: 0.2 (initial SMT concentration: 5 mg·L<sup>-1</sup>, initial ACT concentration: 25 mg·L<sup>-1</sup>) and pH 1.5.

Hydrogen peroxide concentration of approximately 1.3·10<sup>-4</sup> mol·L<sup>-1</sup> was reached in 20 minutes ozonation.

The ozonation during 20 minutes allows the removal of pharmaceutical compounds; however, TOC only diminishes 10% when ultrapure water was used and 20% when contaminants were in biologically treated wastewater.

When ferrous ions were added to the aqueous solution containing hydrogen peroxide, no degradation of total organic carbon was obtained both in ultrapure water and secondary treated wastewater.

Photo-Fenton process has a negligible effect when experiments were carried out using secondary treated wastewater, while in the case of ultrapure water the application of this second process lead to a 50% mineralization in 2 hours, after the previous ozonation treatment.

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#### REFERENCES

- [1] P. Westerhoff, Y. Yoon, S. Snyder, and E. Wert, "Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemical during Simulated Drinking Water Treatment Processes", *Environ. Sci. Technol.*, vol. 39, pp. 6649-6663, 2005.
- [2] S. Mompelat, B.L. Bot, and O. Thomas, "Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water", *Environ. Int.*, vol. 35, pp. 803-814, 2009.
- [3] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford, and S.A. Snyder, "Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters", *Water Res.*, vol. 41, pp. 1013-1021, 2007.
- [4] B. Kasprzyk-Hordern, R.M. Dinsdale, and A.J. Guwy, "The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK", *Water Res.*, vol. 42, pp. 3498-3518, 2008.
- [5] J.L. Santos, I. Aparicio, M. Callejón, and E. Alonso, "Occurrence of pharmaceutically active compounds during 1-year period in wastewaters from four wastewater treatment plants in Seville (Spain)", *J. Hazard. Mater.*, vol. 164, pp.1509-1516, 2009.
- [6] M. Huerta-Fontela, M.T. Galceran, and F. Ventura, "Occurrence and removal of pharmaceuticals and hormones through drinking water treatment", *Water Res.*, vol. 45, pp. 1432-1442, 2011.
- [7] M.D. Camacho-Muñoz, J. Martín, J.L. Santos, I. Aparicio, and E. Alonso, "Occurrence, temporal evolution and risk assessment of pharmaceutically active compounds in Doñana Park (Spain)", *J. Hazard. Mater.*, vol. 183, pp.602-608, 2010.
- [8] C. Fernández, M. González-Doncel, J. Pro, G. Carbonell, and J.V. Tarazona, "Occurrence of pharmaceutically active compounds in surface waters of the Henares-Jarama-Tajo river system (Madrid, Spain) and a potential risk characterization", *Sci. Total Environ.*, vol.408, pp. 543-551, 2010.
- [9] C. Adams, Y. Wang, K. Loftin, and M. Meyer, "Removal of antibiotics from surface and distilled water in conventional water treatment processes", *J. Environ. Eng.-ASCE*, vol. 128, pp. 253-260, 2002.
- [10] T. A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.J. Brauch, B.H. Gulde, G. Preuss, U. Wilme, and N.Z. Seibert, "Removal of pharmaceuticals during drinking water treatment", *Environ. Sci. Technol.*, vol. 36, pp. 3855-3863, 2002.
- [11] M. Klavarioti, D. Mantzavinos, and D. Kassinos, "Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes", *Environ. Int.*, vol. 35, pp. 402-417, 2009.
- [12] F.J. Beltrán, A. Aguinaco, J.F. García-Araya, and A. Oropesa, "Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water", *Water Res.*, vol. 42, pp. 3799-3808, 2008.
- [13] A. Aguinaco, F.J. Beltrán, J.F. García-Araya, and A. Oropesa, "Photocatalytic ozonation to remove the pharmaceutical diclofenac from water: Influence of variables", *Chem. Eng. J.*, vol. 189-190, pp. 275-282, 2012.
- [14] Merck & Co. The Merck Manual of Diagnosis and Therapy, 17<sup>th</sup> edition. Editors: Mark H. Beers and Robert Berkow, John Wiley and Sons, Indianapolis, 1999.
- [15] P. Xiong, and J. Hu, "Degradation of acetaminophen by UVA/LED/TiO<sub>2</sub> process", *Sep. Purif. Technol.*, vol. 91, pp. 89-95, 2012.
- [16] C.G. Hatchard, and C.A. Parker, "A New Sensitive Chemical Actinometer. 2. Potassium Ferrioxalate as a Standard Chemical Actinometer", *Proceed. of the Royal Society of London Series A. Mathematical and Physical Sciences*, vol. 235, pp. 518-536, 1956.
- [17] H. Bader, and J. Hoigné, "Determination of ozone in water by indigo method", *Water Res.*, vol. 15, pp. 449-456, 1981.
- [18] W. Masschelein, M. Denis, R. Ledent, "Spectrophotometric determination of residual hydrogen peroxide", *Water Sew. Works*, vol. 8, pp. 69-72, 1977.
- [19] L.L. Stookey, "Ferrozine- a new spectrophotometric reagent for iron", *Anal. Chem.*, vol. 42, pp. 779-781, 1970.
- [20] Y. Zuo, "Kinetics of photochemical/chemical cycling of iron coupled with organic substances in cloud and fog droplets", *J. Hazard. Mater.*, vol. 59, pp. 3123-3130, 1995.
- [21] W. A. Moore, R.C. Kroner, and C.C. Ruchhof, "Dichromate reflux method for the determination of oxygen demand", *Anal. Chem.*, vol. 21, pp. 953-957, 1949.

- [22] J.L. Means, and S.J. Anderson, "Comparison of five different methods for measuring biodegradability in aqueous environments", *Water Air Soil Poll.*, vol.16, pp. 301-315, 1981.
- [23] R.E. Bühler, J. Staehelin, and J. Hoigne, "The ozone decomposition in water by use radiolysis I.  $\text{HO}_2/\text{O}_2^-$  and  $\text{HO}_3/\text{O}_3^-$  as intermediates", *J. Phys. Chem.*, vol. 88, pp. 2560-2564, 1984.
- [24] J. Staehelin, R.E. Bühler, and J. Hoigne, "The ozone decomposition in water by use radiolysis II.  $\text{HO}_4$  as chain intermediates." *J. Phys. Chem.*, vol. 88, pp. 5999-6004, 1984.
- [25] R. Criegee, *Justus Liebigs Annalen Chemistry*, vol.564, pp. 9-20, 1953.
- [26] R. Criegee, "The course of ozonation of unsaturated compounds." *Record of Chemical Progress*, vol. 18, pp. 110-120, 1957.
- [27] J. Hoigne, and H. Bader, "Rate constants of the reactions of ozone with organic and inorganic compounds. II. Dissociating organic compounds", *Water Res.*, vol. 17, pp. 185-194, 1983.
- [28] B. Utset, J. Garcia, J. Casado, X. Doménech, and J. Peral, "Replacement of  $\text{H}_2\text{O}_2$  by  $\text{O}_2$  in Fenton and photo-Fenton reactions", *Chemosphere*, vol. 41, pp. 1187-1192, 2000.