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Unveiling the Dependence between Hydroxyl Radical Generation and Performance of Fenton Systems with Complexed Iron

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ABSTRACT: Humiclike substances (HLS) have been demonstrated to be useful auxiliaries to drive the (photo)-Fenton process at mild pH, by avoiding iron inactivation via formation of active complexes. However, the actual performance of the process is affected by a manifold of opposite processes. In this work, the generation of hydroxyl radical-like reactive species in the Fentonlike process has been investigated using electron paramagnetic resonance, employing 5,5-dimethyl-1-pyrroline-N-oxide as a probe molecule. The signal obtained with the Fe(II)−HLS−H_2O_2 system at pH = 5 was very intense but decreased with time, in line with the difficult reduction of the formed Fe(III) to Fe(II). On the contrary, the signal of the Fe(III)−HLS−H_2O_2 system was weak but stable. The most intense signal was observed at HLS concentration of ca. 30 mg/L. Interestingly, the performance of the Fenton system at pH = 5 to degrade caffeine followed the same trends, although caffeine removal was very low after 1 h of irradiation. The results were more evident in a solar simulated photo-Fenton process, where an increase in the abatement of caffeine was observed until an HLS concentration of 30 mg/L, where 98% removal was reached after 1 h.
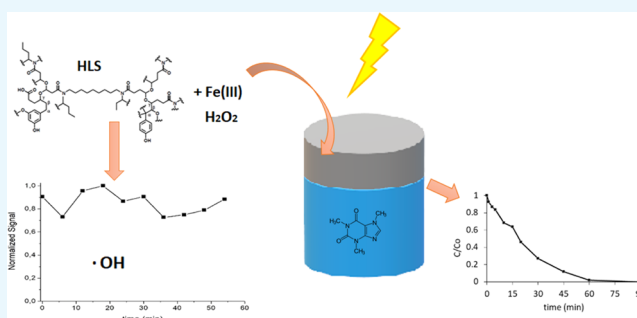
INTRODUCTION

The Fenton reagent, which consists of a combination of iron salts and hydrogen peroxide, has been widely used in wastewater treatment processes because of its ability to oxidize organic matter.[1] Although the mechanism is complex, hydroxyl radicals are described to play a major role in the process. One among the factors that enhance the effect of Fenton reagent is irradiation in the UV−vis range (540 nm < λ, and hence sunlight can be used for this purpose).[2] On the contrary, mild pH is detrimental for pollutant oxidation, as the optimum value is 2.8 and iron inactivation occurs at higher values, attributable to the formation of iron hydroxides.[1,3]

To overcome the environmental and economic barrier that involves the sequence acidification- (photo)-Fenton-neutralization,[4] different strategies have been proposed to drive the (photo)-Fenton process at mild pH.[3,5] In particular, the use of chemical auxiliaries able to complex iron has been studied as a way to modify the coordination sphere of this cation and to prevent its inactivation.[6] It is important to highlight that these iron(III) complexes must be photoactive to allow carrying out the iron photoreduction. For this purpose, different substances have been studied, such as carboxylates,[7] EDTA, EDDS, or NTA.[8−11] Alternatively, macromolecules with chemical structures related to humic substances have been investigated.[12,13] These compounds contain functional groups

(e.g., carboxylic acids, amines, hydroxyls, or amides) able to complex iron efficiently.[14,15]

Humiclike substances (HLS) can be isolated from different sources, such as solid urban wastes or olive oil mill residues.[16,17] They have been demonstrated to be nontoxic and able to drive the photo-Fenton process at mild pH conditions.[18] However, the real efficiency of the treatment based on the Fe−HLS system is difficult to predict because of the combination of a complex and not-well-established mechanism with the existence of opposite effects.[19]

The HLS have been demonstrated to be photoactive and able to generate reactive species, such as singlet oxygen and hydroxyl radicals, to a minor extent;[20] however, this process is not very efficient and only high amounts of HLS are able to reach a noticeable pollutant degradation.[21] On the other hand, the Fe−HLS complex has been demonstrated to increase the efficiency of photo-Fenton at mild pH, most probably due to enhanced production of highly oxidizing species, such as hydroxyl radicals.[17]

Alternatively, HLS are colored molecules, whose absorbance is not negligible in the UVA−vis region. Hence, they can act as inner filters, decreasing the number of photons reaching the

deeper parts of the solution. This effect is expected to decrease the direct photolysis of the pollutants, as observed with humic acids,[22] and to limit the efficiency of the HLS−Fe system.

Being the HLS organic macromolecules, they are expected to interact with the reactive species generated by the photo-Fentonlike process. As a matter of fact, HLS have been reported to suffer significant oxidation under mild photo-Fenton conditions, changing the structural characteristics of these macromolecules.[18] Taking this into account, a competitive process between the humiclike substances and the pollutant is expected, which involves a decrease of the rate of pollutant removal upon increasing the HLS concentration. Furthermore, higher amounts of hydrogen peroxide will be required.

Finally, HLS are able to improve the photo-Fenton-based degradation of pollutants at amounts that are above the limit of solubility.[23] This might be attributed to the surface active properties of these substances that are able to confine the pollutants inside the micelles and, at the same time, to approach the substrates and the photo-Fenton system.

To gain further insight into the ability of the HLS−Fenton system to generate reactive species, in particular, hydroxyl radicals, indirect methods based on the detection of species that are formed upon reaction with •OH have to be used.[24] One of these analytical techniques is based on the use of electron paramagnetic resonance (EPR). The adduct formed by •OH and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) gives a typical signal, as described in detail elsewhere.[25] This procedure has already been employed to estimate the ability of different substances to form hydroxyl radicals, including phenols in wine[26] or biological systems.[27] Also in the field of wastewater treatment processes, EPR has been employed to detect the generation of reaction species,[28,29] and in particular, some studies deal with the Fenton system.[17,30,31] With this background, the aim of this paper is to estimate the relative amount of hydroxyl radicals that can react with a pollutant under different conditions. To avoid the effect of photolysis and the inner filter, the experiments have been carried out in the dark. Finally, those mechanistic results have been correlated with the performance of the (photo)-Fentonlike system with HLS using caffeine as a probe molecule. This molecule has been chosen because it is a substance commonly found in effluents,[32] and its removal via the (photo)-Fenton process has been widely studied and suffers negligible photolysis under solar conditions.

■ RESULTS AND DISCUSSION

Generation of Reactive Species by Fe(II)−HLS and Fe(III)−HLS Systems. A first series of experiments were devoted to the study of the ability of Fe(II) in combination with hydrogen peroxide to form a DMPO-OH adduct, as well as the variation of the signal attributed to this adduct vs time. The pH value was selected to be five, since it is the highest pH value which can be employed to drive the photo-Fenton process in the presence of HLS with an acceptable efficiency.[5] Figure 1a shows the signal obtained at pH = 5 in the presence of the HLS (20 mg/L) and Fe(II) (5 mg/L), immediately after the addition of hydrogen peroxide (34 mg/L); this corresponds to a molar ratio Fe/H_2O_2 of 1:10 that has been reported to optimize the generation of hydroxyl radicals.[33] The high signal/noise ratio shows that there was an efficient generation of •OH under these experimental conditions. To see if the ability of the Fe(II)−HLS is constant or varies with
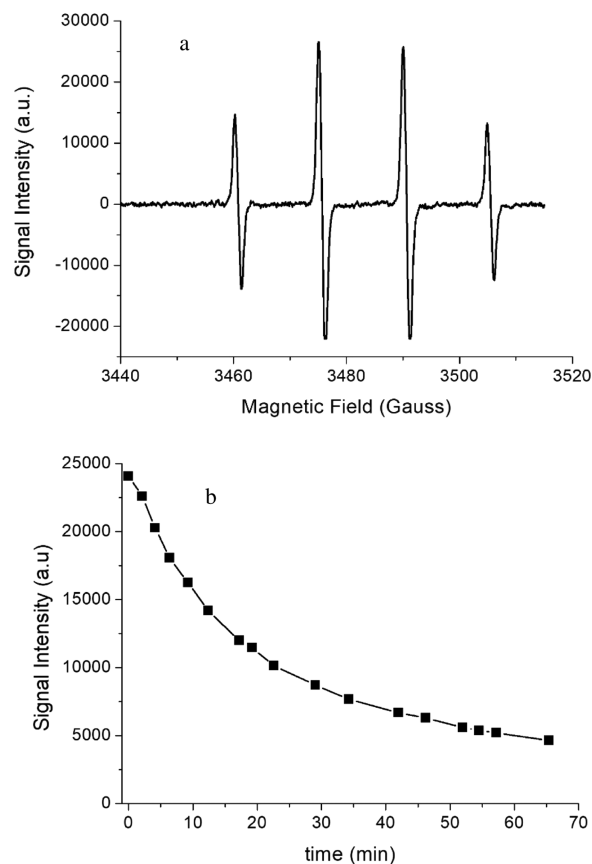

Figure 1. (a) EPR spectrum of the DMPO-OH adduct recorded at pH = 5 in the presence of HLS (20 mg/L) and Fe(II) (5 mg/L), immediately after the addition of hydrogen peroxide (34 mg/L). (b) Variation of the signal (calculated as the average intensity of the two central lines) vs time.

time, the spectra were recorded again at different times after the addition of hydrogen peroxide. The intensity of the signal was calculated as an average of the height of the four characteristic peaks of the spectrum and given in relative values. The obtained relative intensities were plotted vs the delay time between addition of H_2O_2 and recording the spectrum. Figure 1b shows that there is a fast decrease in the signal, what is compatible with an inactivation of the Fenton system. This is a well-known phenomenon, which is attributable to the existence of two main reactions in the Fenton process (eqs 1 and 2). The first equation is very fast and generates efficiently •OH; however, Fe(II) is oxidized to Fe(III) and the reduction of Fe(III) is slow.[34] Hence, as the initial Fe(II) is oxidized, its concentration decreases and there is a noticeable loss of efficiency in the generation of •OH.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \qquad (2)$$

Taking into account those results, it seems interesting to test the behavior of the system when iron is added as Fe(III). Figure 2a shows that the signal to noise ratio is clearly lower in this case, showing that the generation of hydroxyl radicals under these conditions is less efficient. However, Figure 2b indicates that the signal of the adduct is nearly constant vs time; hence, the Fe(III) does not suffer a remarkable loss of efficiency in generating •OH. This is in agreement with the
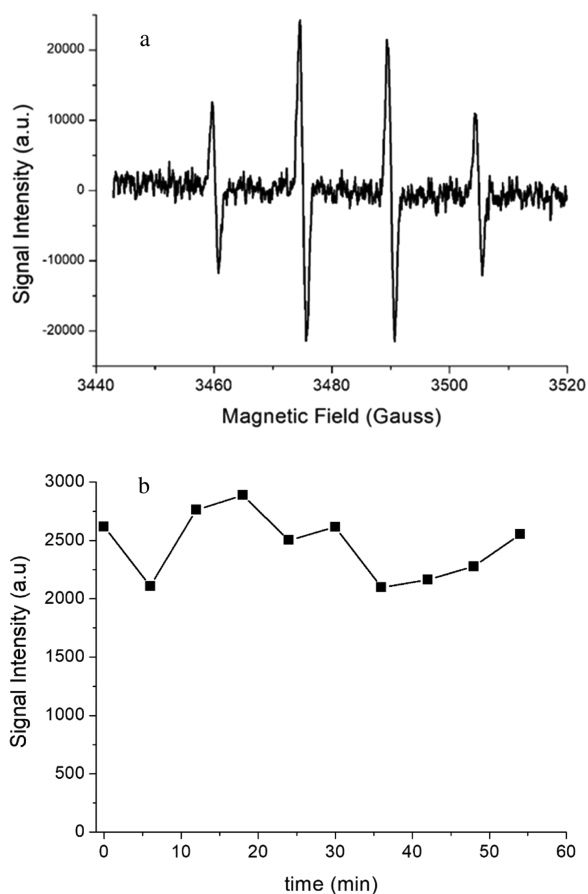
Figure 2. (a) EPR spectrum of the DMPO-OH adduct recorded at pH = 5 in the presence of HLS (20 mg/L) and Fe(III) (5 mg/L), immediately after the addition of hydrogen peroxide (34 mg/L). (b) Variation of the signal vs time.

Figure 3. Plot of the relative concentration of caffeine (C/C_o, where C_o is the initial concentration, namely 5 mg/L, and C is the concentration at the sampling time) vs time: (●) with Fe(II) and (■) with Fe(III). The reaction was performed at pH = 5, with 5 mg/L of iron and 60 mg/L of hydrogen peroxide.

Figure 4. Plot of the relative signal of the DMPO-OH adduct vs the concentration of HLS at pH = 5, 5 mg/L of Fe(III) and 34 mg/L of hydrogen peroxide.

above given explanation: eq 2 is the limiting step of the process, and as Fe(III) is reduced to form Fe(II), •OH is quickly formed by eq 1, and iron oxidized again to Fe(III) closing the cycle; in other words, when starting with Fe(III) instead of Fe(II), a steady state for Fe(II)/Fe(III) speciation is quickly reached and hence a stable signal is obtained. Hence, for practical reasons, the use of Fe(III) seems more advisable for the rest of EPR-based experiments.

It is interesting to compare the mechanistic experiments with the real behavior of the system. For this purpose, the Fenton degradation of caffeine was studied. Figure 3 shows that there was a very fast initial pollutant removal when the reaction was carried out with Fe(II) but then the reaction was clearly slower. On the other hand, when Fe(III) was used, the reaction was very slow but the reaction rate was kept constant all along the process. This is completely in line with the signal measured in the EPR experiments.

Determination of the Effect of HLS Concentration. The EPR signal of the DMPO-OH adduct was measured in the presence of different amounts of HLS. The plot of the signal vs concentration of HLS can be seen in Figure 4. It can be observed that even in the absence of a complexing agent, generation of some •OH radicals occurs, more probably due to the small fraction of iron that is not deactivated. As a matter of fact, using an iron concentration below 1 mg/L is a strategy that has been reported to implement the photo-Fenton process at mild pH, when low efficiencies can be assumed.
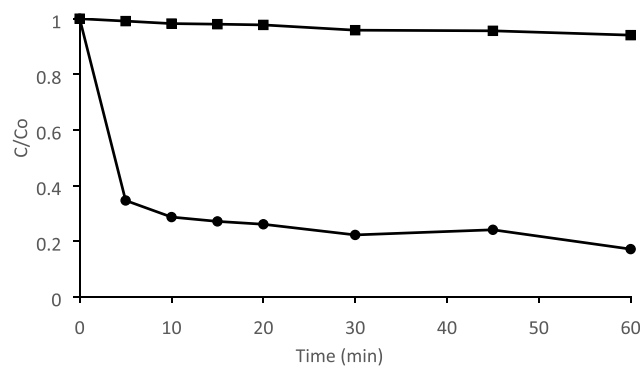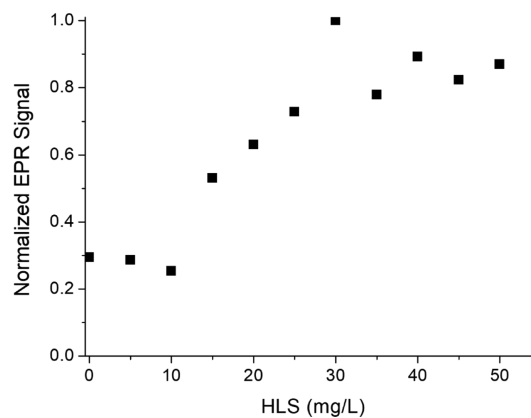
Interestingly, the natural amounts of iron present in water have been used to remove pollutants at low concentration.[35]

Addition of low amounts of HLS (below 10 mg/L) does not seem to increase significantly the production of •OH; this can be attributable to the fact that there is not enough amount of ligands to complex efficiently the iron present in the solution. However, beyond this point, there is a clear enhancement in the generation of reactive species, in line with the improved complexation of iron. Beyond 30 mg/L, further addition of HLS did not result in a noticeable increase in the EPR signal, which can be attributed to two different causes: (a) most of the iron is already in the form Fe—HLS and (b) the excess of HLS acts as a scavenger of the formed radicals, thus producing a detrimental effect.

However, it is necessary to relate the mechanistic results with the real removal of the pollutants. For this purpose, a series of experiments was carried out using caffeine as a model pollutant. The Fenton process was carried out with 5 mg/L of caffeine, 5 mg/L of Fe(III), and the stoichiometric amount of hydrogen peroxide. The efficiency of the process was very low, as percentages of removal after 60 min of treatment were systematically below 20%, in agreement with the bad performance of the Fenton system at pH = 5 (see Figure 5). However, significant differences could be observed: the caffeine removal was lower with 10 mg/L of HLS than in the absence of this compound, while HLS amounts in the
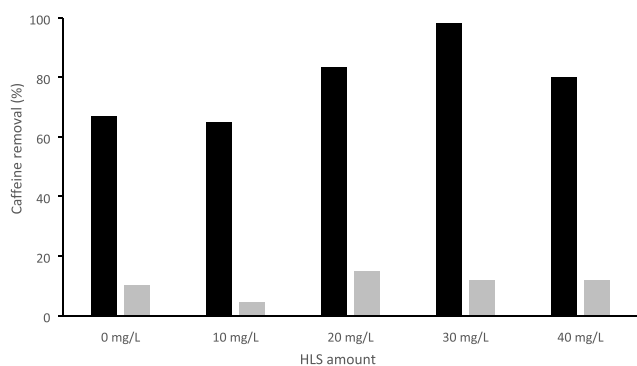
Figure 5. Caffeine removal calculated after 60 min of Fenton (gray bars) and photo-Fenton treatment at pH = 5 of a 5 mg/L solution of caffeine in the presence of 60 mg/L of H_2O_2 and different amounts of HLS.

Figure 6. Concentration of total iron according to the *o*-phenantro-line standard method after 5 min (white bars) and 60 min (gray bars) at pH = 5 when 5 mg/L of Fe(III) were added in the presence of different concentrations of HLS. A control experiment, involving the addition of 5 mg/L of Fe(II) without HLS, is also given.

range 20−40 mg/L were able to enhance caffeine degradation. These trends are coincident with the generation of $^\bullet$OH radicals detected by the EPR experiments.

To obtain more reliable data, stronger experimental conditions have to be employed, to enhance caffeine degradation. For this purpose, the photo-Fenton removal of caffeine was studied under the same conditions described above, but using simulated sunlight as the irradiation source. Figure 5 shows the percentages of caffeine removal after 60 min of irradiation. These values were always above 65%, in line with the higher efficiency of photo-Fenton when compared with Fenton. Under those circumstances, trends became more evident and coincident with the EPR data: the results were very similar without HLS and with 10 mg/L of this substance; beyond this point (20−40 mg/L), there was a clear enhancement of the process, in line with the improved generation of reactive species. The best results were achieved for 30 mg/L, as further addition of HLS did not result in an improved formation of reactive species, according to EPR experiments and the shadowing effect of the HLS might also be detrimental.

To obtain additional evidence on this explanation, the concentration of iron was determined after 15 min and 60 min in the presence of HLS in the range 0−40 mg/L. Figure 6 shows that the results are in agreement with expectations, as the concentration of Fe(III) in solution increased with increasing amounts of HLS. However, when HLS was above 30 mg/L of HLS, the iron concentration was higher than 4 mg/L even after 1 h. The same experiment was carried out employing Fe(II) as a control and, in agreement with its higher solubility, the initial 5 mg/L were maintained for 1 h.

Finally, Figure 7 shows the plot of the relative concentration of caffeine in two selected experiments: without HLS and with 30 mg/L of HLS (which was the optimal HLS concentration). It can be observed that initial reaction rates were similar, but when HLS was not present, the decrease in caffeine concentration was slower after 15 min of irradiation, and the process nearly stopped after 45 min of treatment. This is explained by deactivation of iron(III) at mild pH, which can be avoided by the complexing effect of HLS.

■ CONCLUSIONS

EPR has been demonstrated as a good method to gain further insight into one of the aspects limiting the applicability of HLS to drive the (photo)-Fenton process at pH = 5, namely the
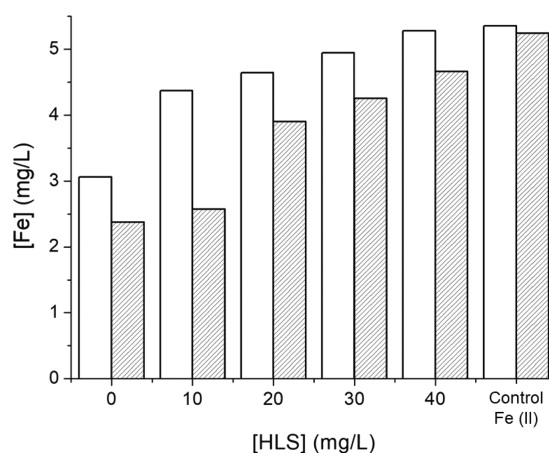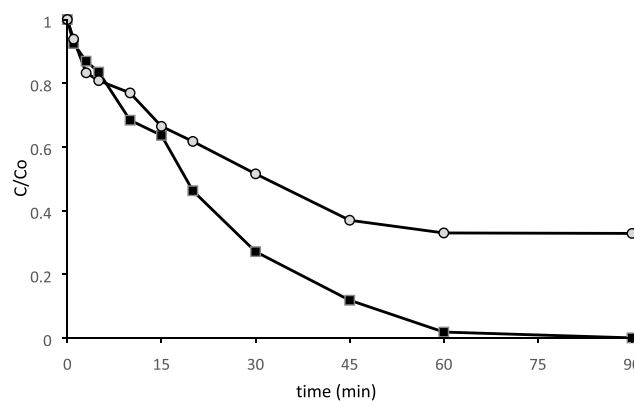

Figure 7. Plot of the relative concentration of caffeine (C/C_o, where C_o is the initial concentration, namely 5 mg/L, and C is the concentration at the sampling time) vs time in a photo-Fenton process with 5 mg/L of iron(III) and 60 mg/L of hydrogen peroxide at pH = 5: (○) without HLS and (■) with 30 mg/L of HLS.

ability of generating extra amounts of reactive species vs the scavenging role of those substances in the generation of reactive species.

A very good correlation has been observed between the trends found with these mechanistic experiments and caffeine removal by a (photo)-Fentonlike process. Too low amounts of HLS have no effect on $^\bullet$OH generation, since they are not able to complex efficiently the iron present in the system, and too high concentrations are detrimental because of the scavenging role of those organic substances for the reactive species, thus decreasing their concentration. According to EPR experiments and caffeine removal by photo-Fenton, the best results were achieved with 30 mg/L of HLS.

Finally, Fe(III) has been demonstrated to be more useful for the DMPO-OH measurement; although the signal is lower than that obtained with Fe(II), it is more stable vs time because of the mechanism of the Fenton process.

■ EXPERIMENTAL SECTION

Reagents. Iron(II) sulfate, iron(III) chloride, hydrogen peroxide (30% w/w), sodium hydroxide, and sulfuric acid (96%) were supplied by Panreac. 5,5-Dimethyl-1-pyrroline *N*-

oxide (DMPO) and caffeine were purchased from Sigma-Aldrich. Water employed in all solutions was of Milli-Q grade. Humiclike substances were isolated from urban wastes following a procedure previously described in detail.[16] Briefly, it involves basic digestion of the wastes, followed by filtration to remove the nonsoluble phase. Then, ultrafiltration was employed, and HLS were concentrated in the retantate. Finally, the solid HLS were obtained upon evaporation of water in an oven. The composition of the HLS can also be found elsewhere.[14]

EPR Analyses. The amount of HLS required for each experimental condition was dissolved in Milli-Q water, and the pH was adjusted to 4.5. Then, the iron salt was dissolved to reach a concentration of 5 mg/L of Fe(II) or Fe(III). The pH was carefully adjusted to 5 by dropwise addition of hydrochloric acid or sodium hydroxide; then, DMPO (17 mM) was added to the sample and finally hydrogen peroxide (1 mM) was also added. Once hydrogen peroxide is present in the solution, the reaction starts, and therefore it was the last reactive species added to minimize the time between the addition of all reagents and the EPR measurements.

EPR spectra were acquired at room temperature with a Bruker ESP300E spectrometer. Measurements were carried out in quartz capillary tubes. The following parameters were set: the microwave frequency was 9.78 GHz, and the power was 5 mW; the modulation frequency was 100 kHz with an amplitude of 0.4 Gauss; and the time constant was 40 ms. For the Fe(III) experiments, 10 scans were accumulated (this was not necessary in Fe(II) measurements because of the high intensity of the signal). The intensity was determined by an average of the height of the two central lines of the DMPO-OH spectrum, and then the value was normalized.

(Photo)-Fenton Reactions. Reactions were performed in open glass cylindrical reactors (55 mm i.d.), which were loaded for each experiment with 250 mL of solution containing caffeine (5 mg/L), iron (5 mg/L) added as iron(III) chloride, and HLS (0−40 mg/L). The pH was adjusted to 5 by adding diluted sulfuric acid and then hydrogen peroxide (60 mg/L), which accounts for the stoichiometric amount required to mineralize the caffeine. In the photo-Fenton experiments, a solar simulator (Sun 2000, Abet Technologies) equipped with a 300 W Xenon Short Arc Lamp was employed as the irradiation source; a glass filter was employed to cut off the residual radiation below 300 nm. Throughout the experiment, samples were periodically taken to be analyzed; they were diluted 1:6 with methanol to avoid further reaction because of the excess of H_2O_2. Before analysis, samples were filtered through polypropylene (0.45 μm; VWR int.).

Chemical Analyses. The concentration of caffeine was determined by liquid chromatography, using a Flexar UHPLC FX-10 chromatograph (PerkinElmer). The stationary phase was a Brownlee Analytical DV C18 column. The mobile phase consisted of a gradient of acetonitrile (A) and formic acid, 0.01 M (B), which was changed from 5% of A to 50% of A in 4 min. The flow was 0.3 mL/min. The apparatus is also equipped with an autosampler, (S200 Autosampler Comm KIT-1022 PUS), a pump (Flexar FX-10 UHO PUMP), a thermostatic oven, and a UV detector (UV/VIS KIT-UHPLC Detector Tubing). Detection was based on absorption at 275 nm. The amount of iron present in solution was determined according to the *o*-phenantroline standard method.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
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