Photo-Fenton reaction at mildly acidic conditions: assessing the effect of bio-organic substances of different origin and characteristics through experimental design

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ABSTRACT

Urban-waste bio-organic substances (UW-BOS) have been shown to be capable of extending the photo-Fenton reaction to mildly acidic conditions. In this study, the effects of pH (3-7), UW-BOS, H_2O_2 and iron concentrations on the photo-Fenton process were systematically assessed using a Doehlert experimental design and response surface methodology for two UW-BOS (CVT230 and FORSUD). Solutions of the model antibiotic sulfadiazine (SDZ) were irradiated in a solar simulator equipped with a 550 W Xenon lamp. The results showed that for UW-BOS contents below 30 mg L^{-1}, SDZ removal proceeds at pH 5 with similar rates for both CVT230 and FORSUD, regardless of Fe(III) concentration. For 50 mg L^{-1} of UW-BOS or higher, CVT230 performs better than FORSUD, even for low Fe(III) content (1-3 mg L^{-1}). In contrast, half-life times of 35-40 min can only be achieved under mildly acidic conditions with FORSUD for iron concentrations higher than 10 mg L^{-1}. The better performance of CVT230 can be associated with its high hydrophilic/hydrophobic ratio, low E2:E3, higher iron content, and possibly higher yields of triplet reactive species generation upon solar irradiation. The most appropriate conditions for each UW-BOS studied are discussed for the first time, which are advantageous for possible engineered applications.

KEYWORDS: Urban-waste bio-organic substances (UW-BOS), sulfadiazine, advanced oxidation processes, photo-Fenton, Doehlert uniform array, response surface.

INTRODUCTION

Advanced oxidation processes (AOP), based on the generation of highly reactive species, such as hydroxyl radicals (•OH), [1, 2] have been considered an important treatment alternative to remove pharmaceuticals from water matrices. Among AOPs, the photo-Fenton process has been widely used. [3] It is based on the decomposition of H_2O_2 into •OH radicals by iron species, which is accelerated by irradiation. [4] The pH has a significant effect on the photo-Fenton reaction, which depends on the speciation of Fe(III). [4] In aqueous solution at very low pH, Fe(III) exists as the aquacomplex $[Fe(H_2O)_6]^{3+}$. At a pH slightly below 3, this complex hydrolyzes leading to hydroxylated species such as $[Fe(OH)(H_2O)_5]^{2+}$ and $[Fe(OH)_2(H_2O)_4]^{+}$; once irradiated, these species regenerate Fe(II). However, at higher pH, Fe(III) precipitates to non-active amorphous ferric oxyhydroxides, hindering the Fenton degradation. Therefore, in the absence of other complexing agents, the optimum pH for the photo-Fenton process is about 3. [4] The pH issue has therefore been regarded as a serious operational and economical constraint for employing the photo-Fenton process in full-scale water decontamination. [3] Nevertheless, iron complexation in the presence of organic compounds, giving photoactive complexes at mild pH, seem promising for extending the optimum pH range and enabling light absorption in the UV-visible region. Different substances have been employed for this purpose, such as EDDS, [5] EDTA [6] or humic-like substances. [7]

Recent papers have demonstrated that urban-waste bio-organic substances (UW-BOS) derived from solid urban residues, are able to extend the photo-Fenton reaction to pH 5 with an acceptable loss of efficiency. [8-10] UW-BOS are solid materials containing a mixture of macromolecules with average molecular weights in the range 67-463 kg mol^{-1}; they are characterized by long aliphatic carbon chains, aromatic rings, and numerous functional groups such as carboxylic, amide, carbonyl, phenolic, alkoxy or amine. [11] Therefore, they compare with macromolecules present in dissolved natural organic matter (NOM) in terms of similar chemical nature and good properties as complexing agents and surfactants. [8] Additionally, these materials contain a significant mineral portion, particularly iron (about 0.16-0.77% w/w, according to Gomis et al. [8]). Owing to their characteristics, the use of UW-BOS in the field of AOPs has been considered a green technology for water detoxification. [12]

Thus far, the photosensitizing properties of UW-BOS have been demonstrated for the photodegradation of azo dyes, [13] phenols, [14] and some pharmaceuticals. [8] However, owing to light absorption by UW-BOS in a wide wavelength range, the decrease in pollutants removal by the sunlight screening effect should be considered. [15] As a result, the search for optimal pH, UW-BOS, H_2O_2 and iron concentrations is needed for each type of bio-organic substance. Nevertheless, a systematic investigation had not yet been carried out to compare UW-BOS of different origins and characteristics. In fact, the performance of UW-BOS of different structures and compositions (CVT230, CVDFT110 and FORSUD) has been only compared for a single set of very particular values of $[\text{UW-BOS}]_0$, $[\text{Fe(II)}]_0$, and $[H_2O_2]_0$, [8] which is not necessarily the most appropriate for different UW-BOS; indeed, these substances might exhibit contrasting performances depending on the experimental conditions. On the other hand, in the only study reported in the literature in which the UW-BOS-driven photo-Fenton process was investigated through an experimental design approach, [9] only CVT230 was used, therefore limiting the comprehensiveness of the conclusions regarding the origin and characteristics of the organic matter additive. In addition, none of these studies were devoted to sulfadiazine degradation, a sulfonamide antibiotic of emerging concern, not readily biodegradable and found in water matrices.

In this study, the effects of pH, UW-BOS, H_2O_2 and iron concentrations on the photo-Fenton degradation of sulfadiazine (SDZ) were systematically assessed using the Doehlert experimental design and the response surface methodology for two UW-BOS of different origin, structure, and composition (CVT230 and FORSUD). Finally, an additional experiment was performed in a CPC reactor under natural sunlight in view of future practical applications.

EXPERIMENTAL

Reagents

SDZ (99%) provided by Sigma-Aldrich was employed to prepare the solutions in Milli-Q water (water solubility of 77 mg L^{-1} at 25 °C, according to Mohajerani et al. [16] and Conde-Cid et al. [17]). $Fe_2(SO_4)_3.5H_2O$, used as the primary source of iron (Fe(III)), and H_2O_2 (30% v/v), were acquired from Panreac. To prepare the mobile phase for the HPLC system, methanol (HPLC quality) and acetic acid (80% v/v) were acquired from Panreac and Scharlau, respectively.

Two different UW-BOS, identified by the acronyms CVT230 and FORSUD, were employed in this study. They were obtained from urban bio-wastes sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo (Italy). [11] Briefly, these UW-BOS were collected from different biowastes, aged for different times under non-aerobic or aerobic digestion. The main characteristics of the UW-BOS materials used in this study (see SUPPORTING MATERIALS, Table 1S), including their surfactant activity, biodegradability and toxicity, was characterized by Gomis et al. [8] The authors concluded that CVT230 and FORSUD are poorly-biodegradable, although non-toxic materials.

Experiments

Solutions were irradiated in a solar simulator (SUN 2000, model 11014, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp (maximum irradiance AM 1.5G of 7000 W m^{-2})

and a Pyrex glass filter, used to cut off radiation in the range 280-295 nm. The reactions were conducted in a 250-mL beaker under continuous stirring at 30-35 °C, positioned at a working distance of about 125 mm from the lamp. The initial SDZ concentration was 25 mg L^{-1} (TOC = 12 mg L^{-1}), which was selected to allow HPLC quantification without using pre-concentration steps, thus preventing the introduction of variability in the experimental data. Solid UW-BOS (5-50 mg L^{-1}) was dissolved and reactions were run at pH 3, 5 and 7 to check the effect of pH on SDZ degradation. In the case of the photo-Fenton reaction, the initial H_2O_2 concentration was varied between half the stoichiometric amount to mineralize SDZ (61 mg L^{-1}) and twice the amount required for this purpose (244 mg L^{-1}); $Fe_2(SO_4)_3.5H_2O$ was added to achieve a concentration of iron between 1 and 15 mg L^{-1}. Aqueous solutions containing 0.1 mol H_2SO_4 L^{-1} or 0.1 mol NaOH L^{-1} were used for pH correction. The samples were withdrawn from the solution, filtered through a polypropylene membrane (0.45 µm) and diluted 1:1 with methanol to quench the reaction in the samples when iron and residual H_2O_2 were present.

CPC reactor

An experiment was performed in a CPC reactor (Solardetox Acadus-2001, Ecosystem) under natural sunlight, in Alcoy (Eastern Spain, 38°42' N–0°28' W), in order to evaluate the photo-Fenton-driven SDZ removal for a set of adequate conditions; the experimental set-up has been described elsewhere. [18] Briefly, the CPC consists of four borosilicate glass tubes, with an irradiated volume of 1.83 L and an irradiated CPC surface of 0.26 m^2, tilted 30° with the horizon. The liquid flows through the system with the aid of a centrifugal pump at a flow rate that guarantees a turbulent regime. Solar irradiance was measured using a spectroradiometer (Acadus 85). The reservoir tank was fed with 4 L of SDZ solution (25 mg L^{-1}), UW-BOS (20 mg L^{-1}), Fe(III) (5 mg L^{-1}), H_2O_2 (244 mg L^{-1}) at pH 5, prepared with Milli-Q water. In this experiment, 1.68-mL aliquots of hydrogen peroxide solution (30% v/v) were added at variable time intervals in order to keep the H_2O_2 concentration around 100-1000 mg L^{-1} (measured with MQuant™ H_2O_2 test strips).

Analysis

The extent of SDZ photodegradation was monitored by an HPLC system (Perkin Elmer Hitachi XL Autosystem D-7000 model) equipped with a RP18 column (Superspher 100 model, 250 mm × 4.6 mm; 5 µm). Liquid samples were analyzed at room temperature using the following gradient (A: acetic acid 1% v/v; B: methanol): 0-2 min 100% A, 2-12 min 90% A, 12-15 min 30% A, 15-20 min 100% A; the flow rate was 1 mL min^{-1}. The injection volume and the detection wavelength were 30 µL and 266 nm, respectively. Under these conditions, the SDZ retention time was about 10 minutes and the detection limit was 0.044 mg L^{-1}.

Antibiotic mineralization was followed by the decay of TOC concentration using a carbon analyzer (TOC-L from Shimadzu).

Experimental designs and response surface methodology

For the photo-Fenton reaction in the presence of CVT230, an experimental Doehlert uniform array design [19] for $k = 3$ variables (pH: 3, 5 and 7; iron: 1-15 mg L^{-1}; and UW-BOS: 5-50 mg L^{-1}) concentrations) at two different initial H_2O_2 concentrations (61 and 244 mg L^{-1}) was used; the conditions are shown in Table 1. Another experimental design was carried out with FORSUD at pH 5 to study the effect of $[\text{FORSUD}]_0$ (in the range 5-50 mg L^{-1}) and $[\text{Fe(III)}]_0$ (1-15 mg L^{-1}) at high initial H_2O_2 concentration (244 mg L^{-1}) (Table 2). These designs comprised 15 and 9 experiments for CVT230 and FORSUD, respectively (k^2+k plus three replicates of the central point). Based on the triplicates of the central levels, the average standard-deviation of the [SDZ] time-data was 0.53 mg L^{-1}. For both UW-BOS, the response was the irradiation time required to achieve 50% SDZ degradation ($t_{50\%}$). Fitting of the response surface model to experimental data was carried out using the software Statgraphics Centurion XVI.

RESULTS AND DISCUSSION

Irradiation of SDZ in the presence of UW-BOS

SDZ photolysis was studied at pH 3 and 5 under simulated sunlight. Figure 1A shows that although some direct photolysis occurred, explained by a certain overlap between the emission spectrum of the lamp and the absorption spectrum of SDZ (see SUPPORTING MATERIALS, Figure 1S), it was low, as only ca. 20% decrease in SDZ concentration was observed at pH 3, and 25% at pH 5 after 180 min of irradiation.

The presence of CVT230 (20 mg L^{-1}) had a negligible effect on the process, as described in a previous publication. [20] In fact, CVT230 showed very low photochemical activity, compensated by the screen effect of the UW-BOS that decreased direct photolysis. On the other hand, FORSUD seemed to slightly enhance the pollutant photolysis, although SDZ percent removals were still very low. This can be due to the lower absorption of FORSUD in the UV-vis region, which resulted in a lower screen effect.

The addition of hydrogen peroxide (244 mg L^{-1}) resulted in the acceleration of SDZ removal as shown in Figure 1B. However, in the absence of UW-BOS, more than 60% of the initial amount of the antibiotic remained in the solution after 3 hours of irradiation. Therefore, the presence of UW-BOS resulted in the enhancement of the process. As SDZ decreased faster at pH 3, this effect can be attributed to the photo-Fenton process driven by the iron found in the UW-BOS, as at this pH the performance of the photo-Fenton reaction is better than at pH 5. However, even at pH 5, UW-BOS played a positive role in SDZ photodegradation, indicating that the photo-Fenton reaction also occurs at mild acidic conditions, as already observed for other pollutants. [8, 10, 20] Under these conditions, CVT230 was more efficient than FORSUD: besides the higher hydrophilic/hydrophobic ratio of CVT230, this could also be due to the presence of higher amounts of iron in its composition (ca. 0.8% w/w) when compared with FORSUD (0.15% w/w) (see SUPPORTING MATERIALS, Table 1S). In fact, the addition of 20 mg L^{-1} of CVT230 represents about 3% more iron in the system, which is significantly higher in comparison with the amount resulting from FORSUD (only 0.64%).

When iron(III) and hydrogen peroxide were present in the reaction medium, a very fast SDZ removal was observed at pH 3, in the presence or absence of UW-BOS, as less than 1% of the initial antibiotic amount remained in the solution after 30 min of irradiation (Fig. 1C). Moreover, the addition of both CVT230 or FORSUD enhanced the photo-Fenton degradation of SDZ at pH 3 in comparison with the system in the absence of UW-BOS.

It is worth observing that the ratio $k_{\text{UW-BOS}}/k_0$ between the pseudo-first order rate constants obtained for SDZ photodegradation at pH 3 and 5, in the presence ($k_{\text{UW-BOS}}$) and absence (k_0) of UW-BOS, was systematically above 1.0 in most cases (see SUPPORTING MATERIALS, Table 2S), showing that the UW-BOS was able to significantly hasten the photo-Fenton process, most probably due to its ability to increase the availability of photochemically active iron species by preventing the formation of iron oxides or hydroxides. However, for FORSUD at pH 5, a value of $k_{\text{UW-BOS}}/k_0 = 0.71$ was observed, probably due to stronger inner filter effect and/or •OH radicals scavenging, as well as limited ability to complex iron owing to its lower amount of hydrophilic (carboxylic, phenolic, carbonilic) moieties, *i.e.*, its high lipophilic/hydrophilic ratio (see SUPPORTING MATERIALS, Table 1S).

In addition, Silva et al. [21] studied the photochemical generation of reactive intermediates from UW-BOS and Suwanee River natural organic matter (SRNOM), under simulated sunlight. The authors quantified the formation quantum yields of singlet oxygen [$\Phi(+^1O_2)$] and hydroxyl radicals [$\Phi(+\bullet OH)$], and also the quantum yield coefficient of TMP degradation (f_{TMP}) (indicative of the formation of excited triplet states of organic matter, $^3OM^*$). Although CVT230 showed lower $\Phi(+^1O_2)$ and $\Phi(+\bullet OH)$ in comparison with SRNOM, it exhibited a f_{TMP} value 2.2 times higher than that obtained for SRNOM, meaning that CVT230 contributes more to the formation of $^3OM^*$ upon sunlight irradiation, which exhibits large second-order rate constants with antibiotics. [22]

The ratio of the absorbances at 250 and 365 nm (E2:E3), commonly used to characterize dissolved organic matter, decreases with increasing molecular weight and aromaticity of the macromolecules. [23] It is worth observing that SRNOM presents a high E2:E3 ratio (3.57), which is close to that exhibited by FORSUD (3.83), suggesting that both species have lower molecular weight and aromaticity in comparison with CVT230 (E2:E3 = 2.38). Based on the information in the immediately preceding paragraph, we could thus argue that the formation of $^3OM^*$ upon solar irradiation would be higher for CVT230 in comparison with FORSUD, which can also help explain the enhanced SDZ removal at mildly acidic conditions observed for CVT230, besides its increased ability to complex iron and higher intrinsic iron content.

Effect of operational variables on the photo-Fenton process in the presence of UW-BOS

CVT230

Two experimental designs, based on the Doehlert matrix were employed to check the effect of Fe(III) concentration (in the range 1-15 mg L^{-1}), CVT230 concentration (5-50 mg L^{-1}), and pH

(3, 5 and 7) as indicated in Table 1. The experimental designs only differed in the initial amount of hydrogen peroxide, which was twice the stoichiometric amount required to completely oxidize SDZ in one case (244 mg L^{-1}), and half the stoichiometric amount in the other case (61 mg L^{-1}). The average values of the response variable ($t_{50\%}$) at the central point of the experimental designs were (48.9 ± 2.3) min and (153.0 ± 23.9) min for the high and low initial H_2O_2 concentrations, respectively.

Quadratic response surface models (Equations 1 and 2) were obtained to predict the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$), which are presented in terms of the coded variables X_1 ([Fe(III)]$_0$), X_2 ([CVT230]$_0$) and X_3 (Table 1). In the case of high initial H_2O_2 concentration, a good correlation was obtained (Equation 1, R^2 = 0.99). The corresponding ANOVA (see SUPPORTING MATERIALS, Table 3S) and the Pareto chart (Fig. 2A) showed that all the parameters studied were significant at 95% confidence level, except for the quadratic terms of iron and CVT230 concentrations.

Conversely, for the lower initial hydrogen peroxide concentration (61 mg L^{-1}) the determination coefficient was R^2 = 0.95 (Equation 2), and only pH and iron concentrations showed significant effects, as indicated by the corresponding ANOVA (see SUPPORTING MATERIALS, Table 4S) and the Pareto chart (Fig. 2B), resulting from the lack of hydrogen peroxide. In fact, $t_{50\%}$values were systematically higher for low than for high initial hydrogen peroxide concentration.

$$t_{50\%}(\mathrm{min}) = 48.87 - 8.08 \times X_1 - 10.45 \times X_2 + 77.26 \times X_3 - 5.02 \times X_1^2 - 5.32 \times X_2^2 + 31.83 \times {X_3}^2 + 16.22 \times X_1 \times X_2 - 19.26 \times X_1 \times X_3 - 21.55 \times X_2 \times X_3 \qquad (1)$$

$$t_{50\%}(\mathrm{min}) = 153.0 - 43.16 \times X_1 + 33.47 \times X_2 + 146.36 \times X_3 - 13.55 \times X_1^2 - 69.85 \times X_2^2 - 17.87 \times {X_3}^2 - 71.88 \times X_1 \times X_2 + 36.20 \times X_1 \times X_3 + 40.66 \times X_2 \times X_3 \qquad (2)$$

Taking into account that the best results were achieved for the higher initial hydrogen peroxide concentration, all the discussion will be focused on this case ($[H_2O_2]_0$ = 244 mg L^{-1}). Bi-dimensional plots were obtained by fixing a parameter at the desired value. Figure 3 shows the plots of $t_{50\%}$ as a function of $[CVT230]_0$ vs. pH at the fixed lowest (1 mg L^{-1}), central (8 mg L^{-1}) and highest (15 mg L^{-1}) iron concentrations. As expected, the performance of the degradation process increases with decreasing pH; however, for pH values up to about 5, the loss of efficiency would be acceptable since the increase in the irradiation time can be compensated by the decrease in the amount of acid solution required to lower the pH. Similar plots can be observed for $[Fe(III)]_0$ vs. pH at fixed $[CVT230]_0$ values.

Figure 4 shows the plots of $t_{50\%}$ as a function of $[Fe(III)]_0$ and $[CVT230]_0$ at pH of 3, 5 and 7 for $[H_2O_2]_0$ = 244 mg L^{-1}. At pH 3, the reaction is very fast in the entire domain studied, with a certain loss of efficiency for high iron and CVT230 concentrations. This effect can be associated to the scavenging of hydroxyl radicals by organic matter and iron at higher concentrations, [8] limiting SDZ degradation rate. At pH 5, the reaction rate increases with iron and CVT230 concentrations, achieving the best performance for $[Fe(III)]_0 > 12$ mg L^{-1} and $[CVT230]_0 > 35$ mg L^{-1}. In this case, the process is ruled by iron availability, as this species is known to form non-active oxides or hydroxides at pH > 3-4. Hence, the presence of UW-BOS is beneficial towards iron complexation to form photochemically active chelates. Finally, at pH 7, the process is very inefficient ($t_{50\%}$ values systematically above 100 minutes) as even UW-BOS is not able to prevent iron removal.

It is worth comparing the surface obtained at pH 5 with that calculated for the low concentration of hydrogen peroxide (Fig. 5). When the initial amount of hydrogen peroxide was low, the UW-BOS concentration was observed to be detrimental in the whole range of concentrations, and this effect is more remarkable at low iron concentrations.

This different behaviour can be explained by assuming that iron is no longer the limiting factor in the process, but hydrogen peroxide. Hence, the presence of UW-BOS results in an extra amount of organic matter that competes for the reactive species. However, $t_{50\%}$ values were always higher for low initial H_2O_2 concentration, indicating that the presence of UW-BOS is only beneficial for the photo-Fenton reaction when there is a sufficient amount of H_2O_2, therefore preventing competition for the oxidizing species.

FORSUD

The results of the second experimental design performed with FORSUD at pH 5 are shown in Table 2. With these data, a second order response surface model (Equation 3) describing the behaviour of $t_{50\%}$ was obtained, which is presented in terms of the coded variables X_1 ($[Fe(III)]_0$) and X_2 ($[FORSUD]_0$) (Table 2). The determination coefficient R^2 was 0.94 and the Pareto chart shows that only the initial FORSUD concentration was significant at 95% confidence level (see SUPPORTING MATERIALS, Figure 2S and Table 5S). The average value of the response variable ($t_{50\%}$) at the central point of the experimental design was (38.3 ± 3.4) min.

$$t_{50\%}(\mathrm{min}) = 38.33 - 4.68 \times X_1 + 8.98 \times X_2 + 4.12 \times X_1^2 + 19.82 \times X_2^2 + 14.95 \times X_1 \times X_2 \qquad (3)$$

The contour plots corresponding to Equation 1 (CVT230) and Equation 3 (FORSUD) for $[H_2O_2]_0 = 244$ mg L^{-1} are shown in Figure 6, and clearly reveal distinct behaviours depending on the type of UW-BOS. Accordingly, an increase in CVT230 concentration always results in lower $t_{50\%}$ values, for iron concentrations up to about 10 mg L^{-1}; in fact, faster SDZ removals can be achieved for $[Fe(III)]_0$ as low as 1-3 mg L^{-1} by increasing the CVT230 dose in the range

5-50 mg L^{-1}. In contrast, a significant difference is observed for FORSUD: regardless of $[Fe(III)]_0$, an increase in FORSUD dose in the range 5-30 mg L^{-1} results in faster SDZ removals; nevertheless, beyond this point, extra addition of FORSUD results in higher $t_{50\%}$ values. Moreover, for FORSUD, half-life times of 35-40 min can only be obtained by using iron doses higher than 10 mg L^{-1}, which is quite disadvantageous in comparison with CVT230. This behaviour can be attributed to a competitive effect with the pollutant for the reactive species when the FORSUD concentration is high. The presence of higher amounts of iron accelerates the process, in agreement with iron availability limiting the photo-Fenton reaction.

These results indicate that SDZ removal can be efficient if iron availability is increased (if necessary, by complexing with UW-BOS) and the UW-BOS concentration is not detrimental, be it by reducing the availability of the oxidizing agent or by decreasing the number of photons reaching the catalyst by the inner-screen effect. However, the systematic experimental design of the present study clearly shows that the type of UW-BOS (origin, composition and characteristics) and its concentration should be carefully considered. Actually, our results show that SDZ removal occurs with similar rates for both CVT230 and FORSUD, for $[UW\text{-}BOS]_0 <$ 30 mg L^{-1}, regardless of Fe(III) concentration; for $[UW\text{-}BOS]_0$ of 50 mg L^{-1} or higher, however, CVT230 clearly performs better than FORSUD (see Figure 6). Despite of being less coloured, the results obtained in this work suggest that FORSUD shows lower ability to complex iron and form triplet active organic species. In contrast, CVT230 shows a higher hydrophilic/hydrophobic ratio (leading to increased iron complexation), higher amounts of iron in its composition, and possibly higher ability to originate triplet reactive species upon solar irradiation.

TOC removal

In contrast to the aforementioned SDZ removal results, TOC analysis showed that less than 35% mineralization was achieved after 90 min of irradiation for both UW-BOS (Fig. 7); in the absence of UW-BOS, ca. 50% of mineralization was achieved. Additionally, less than 5% mineralization was obtained after 90 min of irradiation for the solutions containing only UW-BOS (results not shown). These results are associated with the formation of more recalcitrant compounds during the photo-Fenton process in all the systems studied. Probably, the remaining amount of oxidant did not limit the TOC abatement in the presence of UW-BOS, since the initial H_2O_2 concentration was the same in these experiments (244 mg L^{-1}) and the increase in the organic matter content with the addition of UW-BOS was small – from 14.9 mg L^{-1} to 18.8 mg L^{-1} (CVT230) and 17.9 mg L^{-1} (FORSUD). The formation of distinct degradation products and the screening effect caused by UW-BOS may be hypothesized as possible reasons to explain the TOC-time patterns obtained, and should investigated. Finally, Figure 7 shows that the time variation of TOC for both CVT230 and FORSUD is quite similar, in such a way that no conclusions can be drawn regarding the effect of UW-BOS on TOC removal.

Photo-Fenton process under natural sunlight

Figure 8 shows that more than 80% SDZ removal was achieved after about t_{30W} = 75 min (which corresponds to 180 minutes of sunlight exposure); the corresponding TOC removed was about 70%. This experiment suggests that the UW-BOS-assisted photo-Fenton treatment of antibiotic-containing wastewater, without previous acidification to pH 3 would be a feasible alternative for practical applications.

CONCLUSIONS

The use of soluble bio-organic substances (UW-BOS) as photosensitizers and/or for implementing circumneutral photo-Fenton processes may be considered in photochemical wastewater treatment processes. The effects of UW-BOS, H_2O_2 and iron concentrations upon the photo-Fenton degradation of sulfadiazine (SDZ) were assessed in this work using the Doehlert design and the response surface methodology for two different types of UW-BOS (namely, CVT230 and FORSUD). For CVT230, two experimental designs were performed for evaluating the effects of the initial amount of hydrogen peroxide, which was twice the stoichiometric amount required to completely oxidize SDZ in one case (244 mg L^{-1}), and half the stoichiometric amount in the other case (61 mg L^{-1}), besides the effects of $[\text{UW-BOS}]_0$, $[\text{Fe(III)}]_0$, and pH. For FORSUD, the Doehlert design was again used to assess the effects of $[\text{UW-BOS}]_0$ and $[\text{Fe(III)}]_0$, at constant $[H_2O_2]_0$ and pH. From these designs it was therefore possible for the first time to draw and systematize conclusions regarding the most appropriate photo-Fenton conditions for each UW-BOS studied.

To sum up, we found that for UW-BOS contents below 30 mg L^{-1}, SDZ removal proceeds with similar rates at pH 5 for both CVT230 and FORSUD, regardless of Fe(III) concentration. For 50 mg L^{-1} of UW-BOS or higher, CVT230 performs better than FORSUD, even for low Fe(III) concentrations (1-3 mg L^{-1}). In contrast, half-life times of 35-40 min can only be achieved under mildly acidic conditions with FORSUD for iron doses higher than 10 mg L^{-1}, which is quite disadvantageous in comparison with CVT230. The high hydrophilic/hydrophobic ratio (leading to increased iron complexation), low E2:E3, higher amounts of iron in its composition, and possibly higher ability to originate triplet reactive species upon solar irradiation, make CVT230 a better additive in the photo-Fenton system.

These findings are advantageous for possible engineered applications, including solar-driven processes, such as the treatment of sulfonamides-containing wastewater without previous pH correction and/or hybrid (chemical-biological) remediation systems. Finally, further studies concerning the optimization of the operating conditions in the case of real water matrices, contaminant concentration levels and by-products identification are needed.

ACKNOWLEDGEMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors express their gratitude to CNPq (National Council for Scientific and Technological Development) and to the European Union (PIRSES-GA-2010-269128, EnvironBOS).

REFERENCES

[1] Ikehata, K.; Naghashkar, N. J.; Ei-Din, M. G., Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. *Ozone-Science & Engineering* **2006,** *28* (6), 353-414.

[2] Klavarioti, M.; Mantzavinos, D.; Kassinos, D., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environment International* **2009,** *35* (2), 402-417.

[3] Malato, S.; Fernandez-Ibanez, P.; Maldonado, M. I.; Blanco, J.; Gernjak, W., Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today* **2009,** *147* (1), 1-59.

[4] Pignatello, J. J.; Oliveros, E.; MacKay, A., Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology* **2006,** *36* (1), 1-84.

[5] Wu, Y.; Passananti, M.; Brigante, M.; Dong, W.; Mailhot, G., Fe(III)-EDDS complex in Fenton and photo-Fenton processes: From the radical formation to the degradation of a target compound. *Environmental Science and Pollution Research* **2014,** *21* (21), 12154-12162.

[6] Klamerth, N.; Malato, S.; Aguera, A.; Fernandez-Alba, A., Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Research* **2013,** *47* (2), 833-840.

[7] Bernabeu, A.; Palacios, S.; Vicente, R.; Vercher, R. F.; Malato, S.; Arques, A.; Amat, A. M., Solar photo-Fenton at mild conditions to treat a mixture of six emerging pollutants. *Chemical Engineering Journal* **2012,** *198*, 65-72.

[8] Gomis, J.; Goncalves, M. G.; Vercher, R. F.; Sabater, C.; Castillo, M.-A.; Prevot, A. B.; Amat, A. M.; Arques, A., Determination of photostability, biocompatibility and efficiency as photo-Fenton auxiliaries of three different types of soluble bio-based substances (SBO). *Catalysis Today* **2015,** *252*, 177-183.

[9] Gomis, J.; Carlos, L.; Prevot, A. B.; Teixeira, A. C. S. C.; Mora, M.; Amat, A. M.; Vicente, R.; Argues, A., Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: Optimization of operational variables. *Catalysis Today* **2015,** *240*, 39-45.

[10] Gomis, J.; Vercher, R. F.; Amat, A. M.; Martire, D. O.; Gonzalez, M. C.; Prevot, A. B.; Montoneri, E.; Arques, A.; Carlos, L., Application of soluble bio-organic substances (SBO) as photocatalysts for wastewater treatment: Sensitizing effect and photo-Fenton-like process. *Catalysis Today* **2013,** *209*, 176-180.

[11] Montoneri, E.; Boffa, V.; Savarino, P.; Perrone, D.; Ghezzo, M.; Montoneri, C.; Mendichi, R., Acid soluble bio-organic substances isolated from urban bio-waste. Chemical composition and properties of products. *Waste Management* **2011,** *31* (1), 10-17.

[12] *Soluble Bio-based Substances Isolated From Urban Wastes: Environmental Applications*. 1 ed.; Springer International Publishing: 2015; p 71.

[13] Prevot, A. B.; Fabbri, D.; Pramauro, E.; Baiocchi, C.; Medana, C.; Montoneri, E.; Boffa, V., Sensitizing effect of bio-based chemicals from urban wastes on the photodegradation of azo-dyes. *Journal of Photochemistry and Photobiology a-Chemistry* **2010,** *209* (2-3), 224-231.

[14] Prevot, A. B.; Avetta, P.; Fabbri, D.; Laurenti, E.; Marchis, T.; Perrone, D. G.; Montoneri, E.; Boffa, V., Waste-derived bioorganic substances for light-induced generation of reactive oxygenated species. *Chemsuschem* **2011,** *4* (1), 85-90.

[15] Carlos, L.; Martire, D. O.; Gonzalez, M. C.; Gomis, J.; Bernabeu, A.; Amat, A. M.; Arques, A., Photochemical fate of a mixture of emerging pollutants in the presence of humic substances. *Water Research* **2012,** *46* (15), 4732-4740.

[16] Mohajerani, M.; Mehrvar, M.; Ein-Mozaffari, F., Using an external-loop airlift sonophotoreactor to enhance the biodegradability of aqueous sulfadiazine solution. *Separation and Purification Technology* **2012,** *90*, 173-181.

[17] Conde-Cid, M.; Alvarez-Esmoris, C.; Paradelo-Nunez, R.; Novoa-Munoz, J. C.; Arias-Estevez, M.; Alvarez-Rodriguez, E.; Fernandez-Sanjurjo, M. J.; Nunez-Delgado, A., Occurrence of tetracyclines and sulfonamides in manures, agricultural soils and crops from different areas in Galicia (NW Spain). *Journal of Cleaner Production* **2018,** *197*, 491-500.

[18] Amat, A. M.; Arques, A.; Garcia-Ripoll, A.; Santos-Juanes, L.; Vicente, R.; Oller, I.; Maldonado, M. I.; Malato, S., A reliable monitoring of the biocompatibility of an effluent along an oxidative pre-treatment by sequential bicassays and chemical analyses. *Water Research* **2009,** *43* (3), 784-792.

[19] Ferreira, S. L. C.; dos Santos, W. N. L.; Quintella, C. M.; Neto, B. B.; Bosque-Sendra, J. A., Doehlert matrix: a chemometric tool for analytical chemistry - review. *Talanta* **2004,** *63* (4), 1061-1067.

[20] Gomis, J.; Prevot, A. B.; Montoneri, E.; Gonzalez, M. C.; Amat, A. M.; Martire, D. O.; Arques, A.; Carlos, L., Waste sourced bio-based substances for solar-driven wastewater remediation: Photodegradation of emerging pollutants. *Chemical Engineering Journal* **2014,** *235*, 236-243.

[21] Silva, M. P.; Lastre-Acosta, A. M.; Mostafa, S.; McKay, G.; Linden, K. G.; Rosario-Ortiz, F. L.; Teixeira, A.C.S.C., Photochemical generation of reactive intermediates from urban-waste bio-organic substances under UV and solar irradiation. *Environmental Science and Pollution Research* **2017,** *24* (22), 18470-18478.

[22] Lastre-Acosta, A. M.; Barberato, B.; Parizi, M. P. S.; Teixeira, A. C. S. C., Direct and indirect photolysis of the antibiotic enoxacin: kinetics of oxidation by reactive photo-induced species and simulations. *Environmental Science and Pollution Research* **2018**. DOI 10.1007/s11356-018-2555-4.

[23] Helms, J. R.; Stubbins, A.; Ritchie, J. D.; Minor, E. C.; Kieber, D. J.; Mopper, K., Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography* **2008,** *53* (3), 955-969.

FIGURE CAPTIONS

Figure 1. SDZ removal by different processes. (A) Photolysis ($[SDZ]_0$ = (26.2 ± 0.3) mg L^{-1}). (B) H_2O_2/UV ($[SDZ]_0$ = (25.8 ± 1.3) mg L^{-1}; $[H_2O_2]_0$ = 244 mg L^{-1}). (C) Photo-Fenton ($[SDZ]_0$ = (26.3 ± 1.1) mg L^{-1}; $[H_2O_2]_0$ = 244 mg L^{-1}; $[Fe(III)]_0$ = 5 mg L^{-1}). Experimental conditions: (△) without UW-BOS at pH 3; (▲) without UW-BOS at pH 5; (☐) with CVT230 (20 mg L^{-1}) at pH 3; (■) with CVT230 (20 mg L^{-1}) at pH 5; (○) with FORSUD (20 mg L^{-1}) at pH 3; (●) with FORSUD (20 mg L^{-1}) at pH 5.

Figure 2. Pareto chart for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$, min) obtained for the photo-Fenton degradation of SDZ in the presence of CVT230, where $[Fe(III)]_0$ and $[CVT230]_0$ represent the uncoded factors. (A) $[H_2O_2]_0$ = 244 mg L^{-1}. (B) $[H_2O_2]_0$ = 61 mg L^{-1}. Experimental conditions: $[SDZ]_0$ = (25.4 ± 1.1) mg L^{-1}, $[CVT230]_0$ = 5-50 mg L^{-1}, $[Fe(III)]_0$ =1-15 mg L^{-1}, pH 3, 5 and 7.

Figure 3. Contour plots of $t_{50\%}$ (min) as a function of $[CVT230]_0$ and pH for the photo-Fenton degradation of SDZ for $[Fe(III)]_0$ = 1, 8 and 15 mg L^{-1} and $[H_2O_2]_0$ = 244 mg L^{-1}.

Figure 4. Contour plots of $t_{50\%}$(min) as a function of $[Fe(III)]_0$ and $[CVT230]_0$ for the photo-Fenton degradation of SDZ at pH 3, 5 and 7 and $[H_2O_2]_0$ = 244 mg L^{-1}.

Figure 5. Contour plots of $t_{50\%}$ (min) as a function of $[Fe(III)]_0$ and $[CVT230]_0$ for the photo-Fenton degradation of SDZ at pH 5 for low and high initial H_2O_2 concentrations.

Figure 6. Contour plots of $t_{50\%}$ (min) as a function of $[\text{UW-BOS}]_0$ and $[\text{Fe(III)}]_0$ for CVT230 and FORSUD for $[H_2O_2]_0 = 244$ mg L^{-1} and pH 5.

Figure 7. TOC removal by the photo-Fenton process in the absence of UW-BOS (○, $[\text{TOC}]_0 = 14.9$ mg L^{-1}) and in the presence of CVT230 (△, $[\text{TOC}]_0 = 18.8$ mg L^{-1}) and FORSUD (□, $[\text{TOC}]_0 = 17.9$ mg L^{-1}). Experimental conditions: $[\text{SDZ}]_0 = (25.7 \pm 1.76)$ mg L^{-1}, $[\text{UW-BOS}]_0 = 20$ mg L^{-1}, $[H_2O_2]_0 = 244$ mg L^{-1}, $[\text{Fe(III)}]_0 = 5$ mg L^{-1}, pH 5.

Figure 8. SDZ degradation (●, $[\text{SDZ}]_0 = 24.4$ mg L^{-1}) and TOC removal (○, $[\text{TOC}]_0 = 15.1$ mg L^{-1}) by the photo-Fenton process in the presence of CVT230 in a CPC reactor under natural sunlight. Experimental conditions: $[\text{CVT230}]_0 = 20$ mg L^{-1}, $[H_2O_2]_0 = 244$ mg L^{-1}, $[\text{Fe(III)}]_0 = 5$ mg L^{-1}, pH 5. Accumulated UV radiation is expressed as t_{30W} to normalize the intrinsically changing irradiation conditions [20].

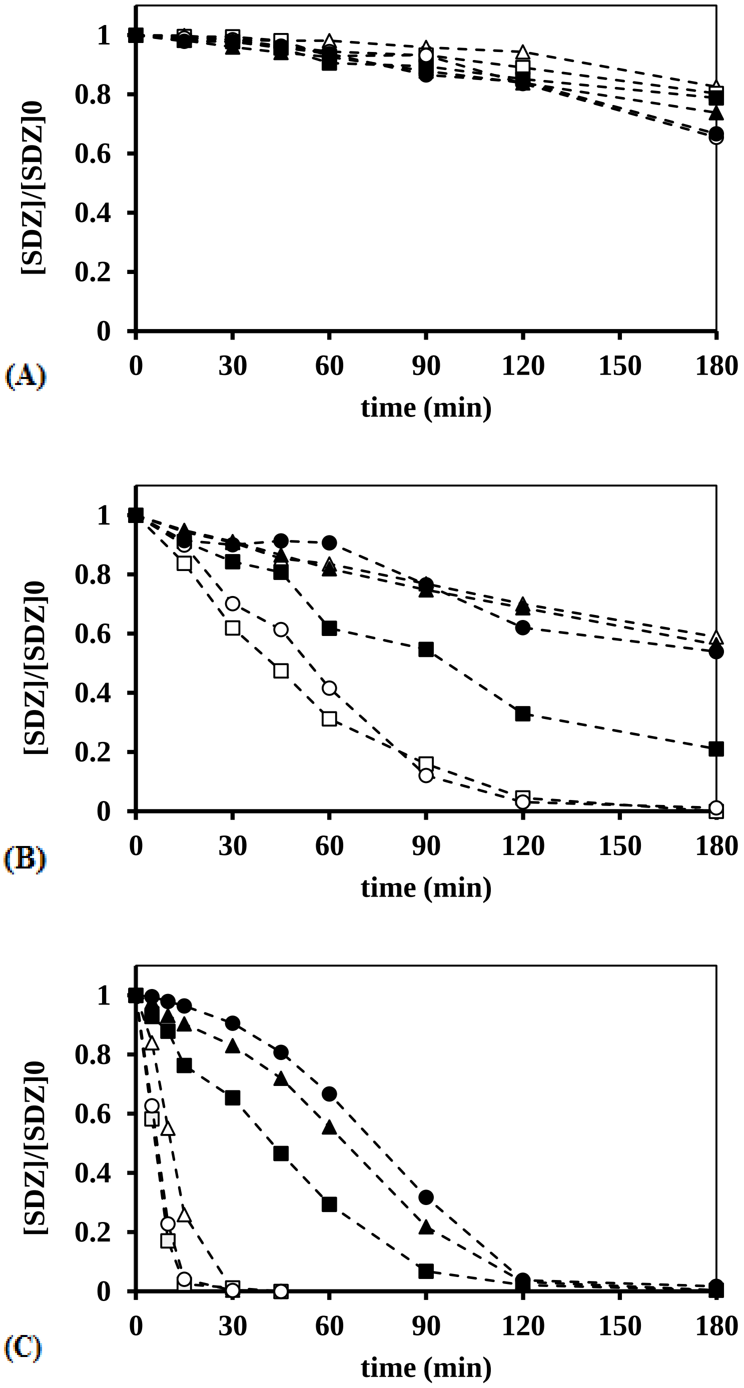
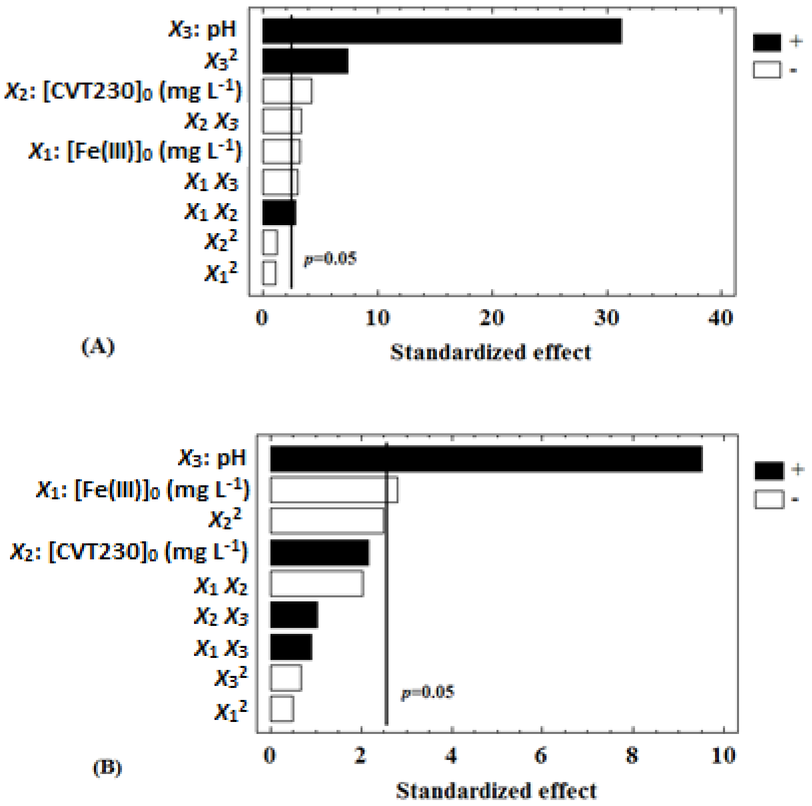


Fig. 1



X3: pH
X3²
X2: [CVT230]0 (mg L-1)
X2 X3
X1: [Fe(III)]0 (mg L-1)
X1 X3
X1 X2
X2²
X1²
p=0.05
+
-
0
10
20
30
40
Standardized effect
(A)
X3: pH
X1: [Fe(III)]0 (mg L-1)
X2²
X2: [CVT230]0 (mg L-1)
X1 X2
X2 X3
X1 X3
X3²
X1²
p=0.05
+
-
0
2
4
6
8
10
Standardized effect
(B)

Fig. 2

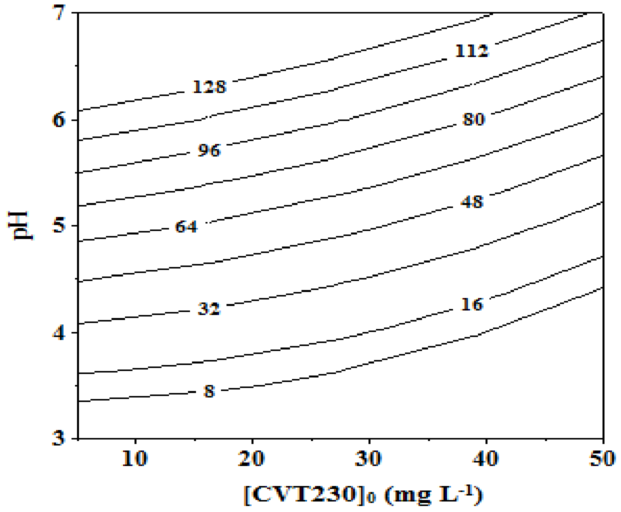
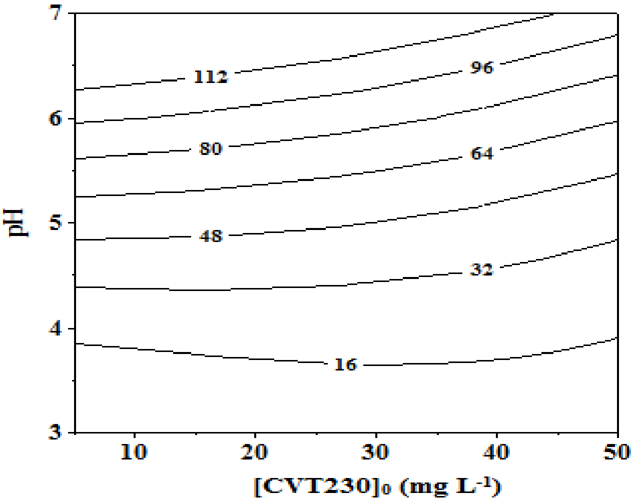
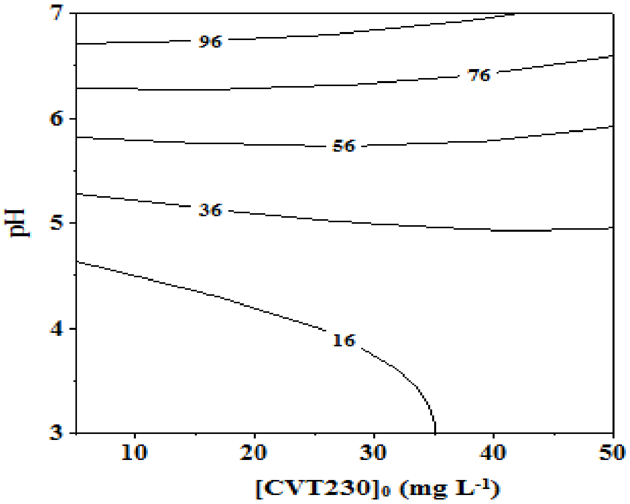
[Fe(III)]$_0$ (mgL^{-1})	**Contour Plots of $t_{50\%}$ (min)**
1	
8	
15	

Fig. 3

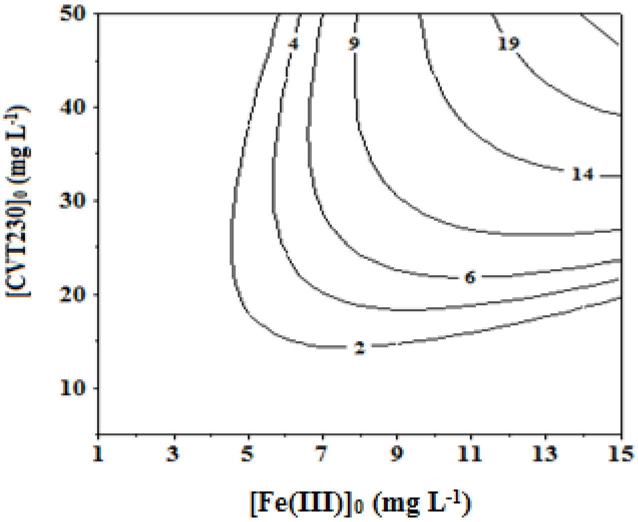
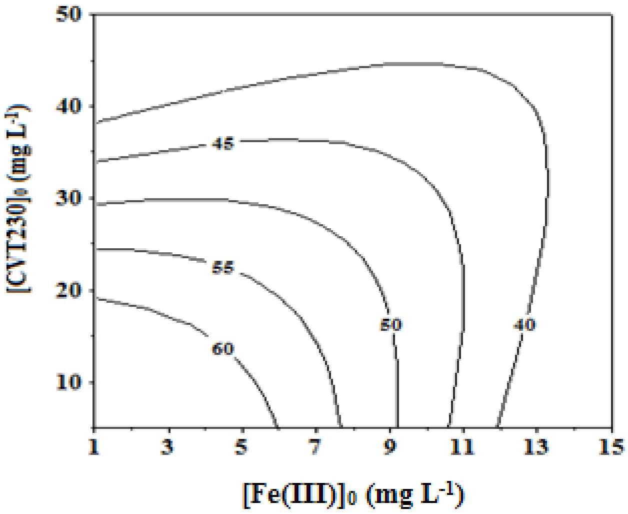
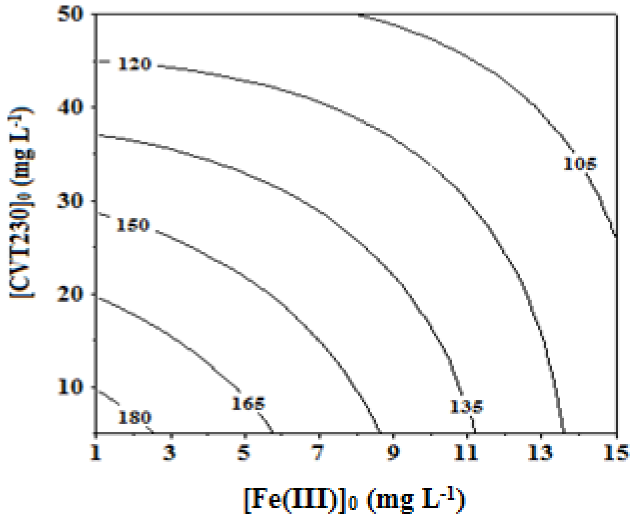
pH	Contour Plots of $t_{50\%}$ (min)
3	
5	
7	

Fig. 4

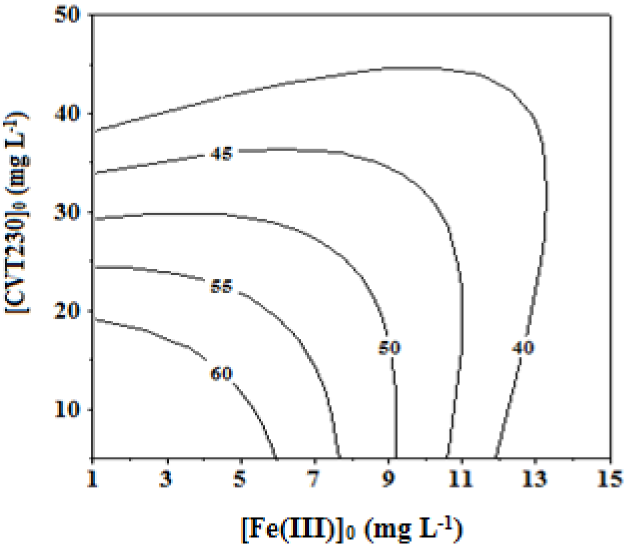
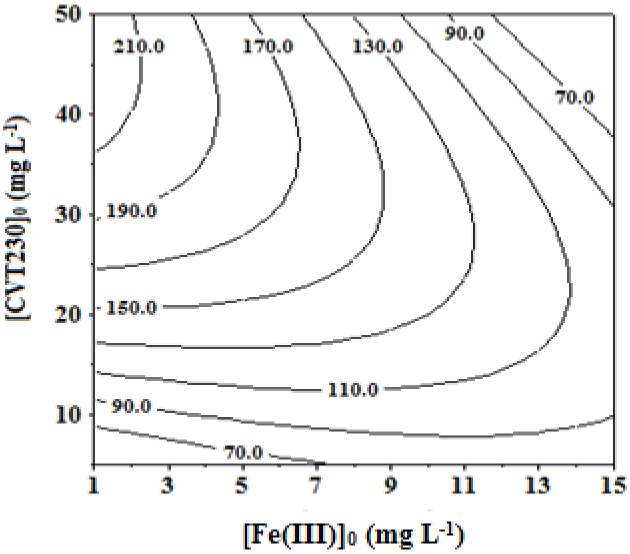
$[H_2O_2]_0$	Contour Plots of $t_{50\%}$ (min)
High $[H_2O_2]_0$ **(244 mg L^{-1})**	
Low $[H_2O_2]_0$ **(61 mg L^{-1})**	

Fig. 5

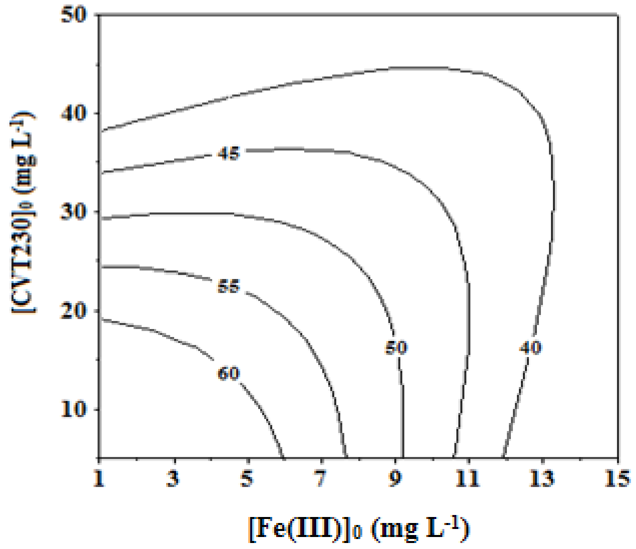
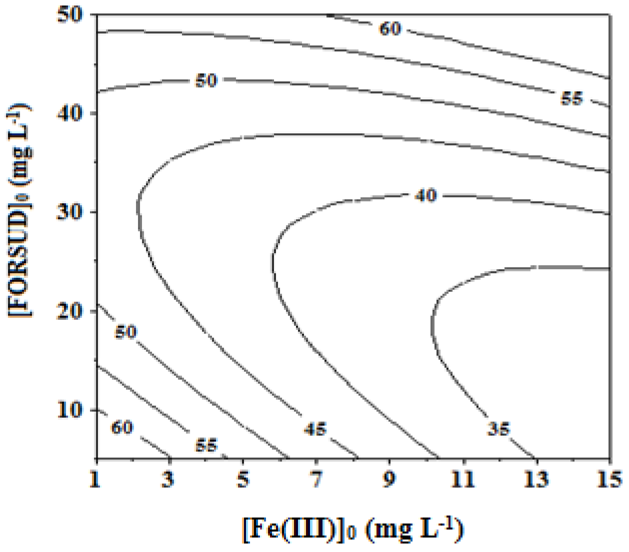
UW-BOS	Contour Plots of $t_{50\%}$(min)
CVT230	
FORSUD	

Fig. 6

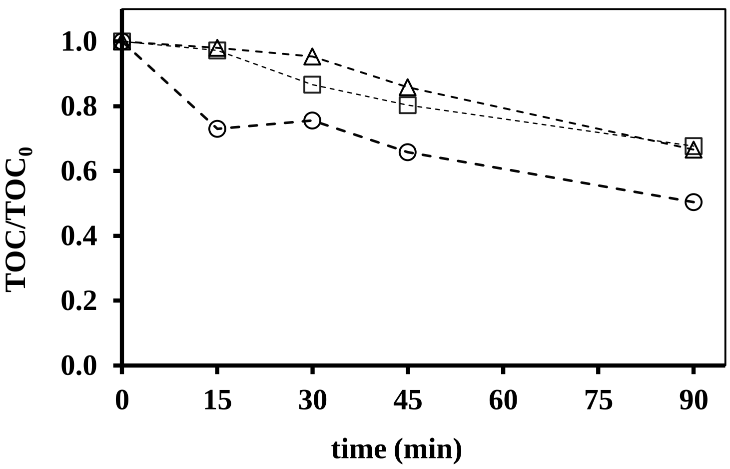


Fig. 7

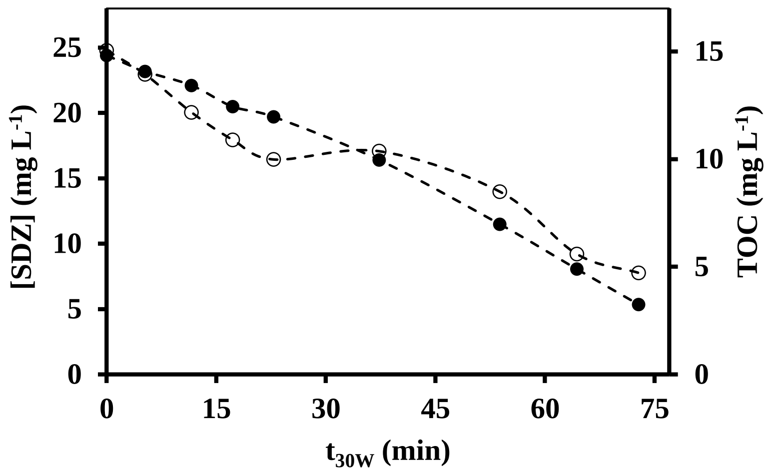


Fig. 8

Table 1. Doehlert design matrix for three factors and two different initial H_2O_2 concentrations. Variables X_1, X_2, and X_3 represent the coded values of $[Fe(III)]_0$, $[CVT230]_0$ and pH, respectively. $[SDZ]_0$ = (25.4 ± 1.1) mg L^{-1}.

Exp. number	X_1	X_2	X_3	$[Fe(III)]_0$ (mg L^{-1})	$[CVT230]_0$ (mg L^{-1})	pH –	$t_{50\%}$(min) $[H_2O_2]_0$=244 mg L^{-1}	$t_{50\%}$(min) $[H_2O_2]_0$=61 mg L^{-1}
1	0	0	0	8	27.5	5	46.6	179.2
1'	0	0	0	8	27.5	5	51.2	132.5
1"	0	0	0	8	27.5	5	48.8	147.3
2	1	0	0	15	27.5	5	36.7	77.6
3	0.5	0.866	0	11.5	50.0	5	40.7	62.9
4	0.5	0.289	0.817	11.5	35.0	7	109.8	282.8
5	−1	0	0	1	27.5	5	51.0	201.3
6	−0.5	−0.866	0	4.5	5.0	5	60.6	69.3
7	−0.5	−0.289	−0.817	4.5	20.0	3	5.8	8.9
8	0.5	−0.866	0	11.5	5.0	5	39.8	76.5
9	0.5	−0.289	−0.817	11.5	20.0	3	5.6	6.2
10	0	0.577	−0.817	8	42.5	3	4.4	7.7
11	−0.5	0.866	0	4.5	50.0	5	33.4	180.2
12	−0.5	0.289	0.817	4.5	35.0	7	132.1	267.9
13	0	−0.577	0.817	8	12.5	7	152.6	189.6

Table 2. Doehlert design matrix for two factors at pH 5 and $[H_2O_2]_0$ = 244 mg L^{-1}. Variables X_1 and X_2 represent the coded values of $[Fe(III)]_0$ and $[FORSUD]_0$, respectively. $[SDZ]_0$ = (24.6 ± 1.0) mg L^{-1}.

Exp. number	X_1	X_2	**$[Fe(III)]_0$ (mg L^{-1})**	**$[FORSUD]_0$ (mg L^{-1})**	$t_{50\%}$ **(min)**
1	0	0	8	27.5	34.5
1'	0	0	8	27.5	39.4
1"	0	0	8	27.5	41.1
2	1	0	15	27.5	39.9
3	0.5	0.866	11.5	50.0	64.0
4	–1	0	1	27.5	45.0
5	–0.5	–0.866	4.5	5.0	57.4
6	0.5	–0.866	11.5	5.0	35.5
7	–0.5	0.866	4.5	50.0	60.0

SUPPORTING MATERIALS

Figure 1S. Emission spectrum of the Xenon lamp and UV-vis absorption spectra of (A) SDZ (25 mg L^{-1}) and (B) CVT230 (20 mg L^{-1}) at pH 3, 5 and 7.

Figure 2S. Pareto chart for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$, min) obtained for the photo-Fenton degradation of SDZ in the presence of FORSUD for $[H_2O_2]_0$ = 244 mg L^{-1} and pH 5; where $[Fe(III)]_0$ and $[FORSUD]_0$ represent the uncoded factors.

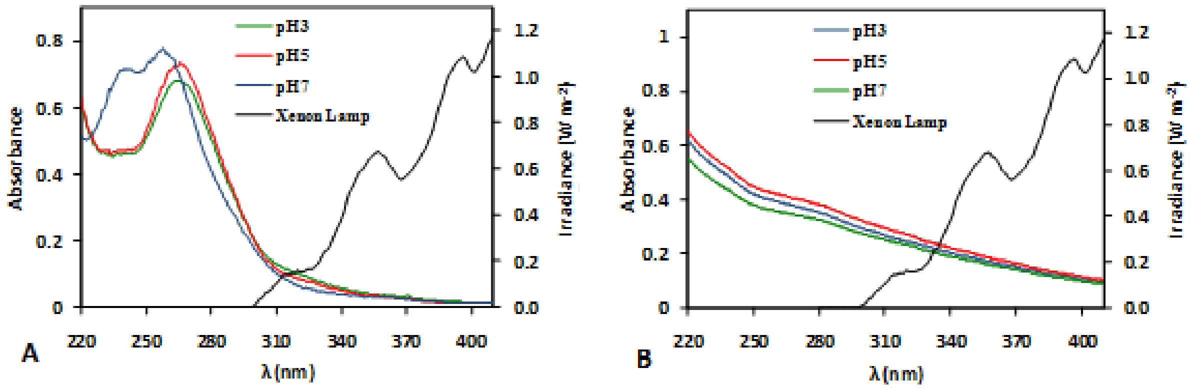

A
Absorbance
0.8
0.6
0.4
0.2
0
220
250
280
310
340
370
400
λ (nm)
Irradiance (W m-2)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
pH3
pH5
pH7
Xenon Lamp
B
Absorbance
1
0.8
0.6
0.4
0.2
0
220
250
280
310
340
370
400
λ (nm)
Irradiance (W m-2)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
pH3
pH5
pH7
Xenon Lamp

Fig. 1S

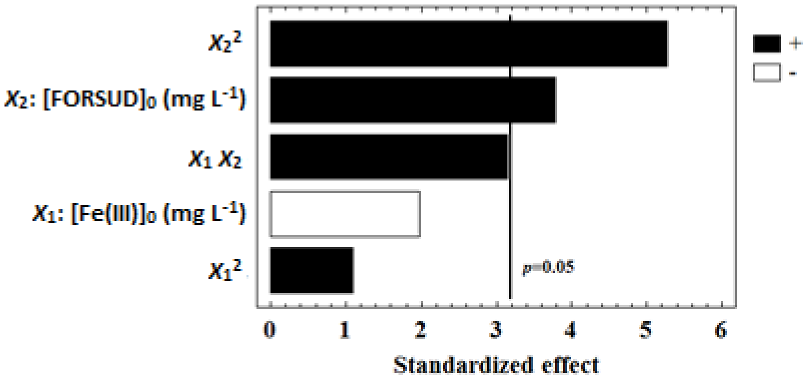

X_2^2
X_2: [FORSUD]$_0$ (mg L^{-1})
X_1 X_2
X_1: [Fe(III)]$_0$ (mg L^{-1})
X_1^2
p=0.05
0
1
2
3
4
5
6
Standardized effect
+
-

Fig. 2S

Table 1S. Characterization of UW-BOS: aging days, sources description, elemental composition and main functional groups [8].

Characterization of UW-BOS	CVT230	FORSUD
Aging days	230	15
Source materials	Gardening and park trimming residues	Digestate of urban waste organic humid fraction obtained by anaerobic treatment
Volatile solids (%, w/w)	72.1	84.6
Carbon (%, w/w)	38.2	45.1
Total Fe (% w/w)	0.77	0.16
Aliphatic carbon (%)	37	43
Aromatic (%)	13	10
Carboxylic (%)	12	7
Carbonilic (%)	5	1
Lipophilic/hydrophilic ratio	3.6	9.3
Aliphatic/aromatic ratio	1.8	3.3

Table 2S. Ratio between the pseudo-first order rate constants obtained for SDZ photodegradation at pH 3 and 5, in the presence ($k_{\text{UW-BOS}}$) and absence (k_0) of UW-BOS.

	$k_{\text{UW-BOS}}/k_0$	
UW-BOS	**pH 3**	**pH 5**
CVT230	2.11	1.22
FORSUD	1.77	0.71

Table 3S. Analysis of variance (ANOVA) for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$, min) obtained for the photo-Fenton degradation of SDZ in the presence of CVT230 and $[H_2O_2]_0$ = 244 mg L^{-1}. Experimental conditions: $[SDZ]_0$ = 25 mg L^{-1}, $[CVT230]_0$ = 5-50 mg L^{-1}, $[Fe(III)]_0$ =1-15 mg L^{-1}, pH 3, 5 and 7.

Source	**Sum of Squares**	**Degrees of Freedom**	**Mean Square**	***F*-Ratio**	***p*-Value**
X_1: $[Fe(III)]_0$ (mg L^{-1})	260.8	1	260.8	10.7	0.0223
X_2: $[CVT230]_0$ (mg L^{-1})	436.8	1	436.8	17.9	0.0083
X_3: pH	23904.9	1	23904.9	978.6	0.0000
X_1^2	30.2	1	30.2	1.2	0.3168
$X_1 X_2$	197.4	1	197.4	8.1	0.0361
$X_1 X_3$	222.9	1	222.9	9.1	0.0294
X_2^2	33.9	1	33.9	1.4	0.2917
$X_2 X_3$	279.9	1	279.0	11.4	0.0197
X_3^2	1354.0	1	1354.0	55.4	0.0007
Total Error	122.1	5	24.4		
Total (corr.)	27300.0	14			
R^2	99.55				

Table 4S. Analysis of variance (ANOVA) for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$, min) obtained for the photo-Fenton degradation of SDZ in the presence of CVT230 and $[H_2O_2]_0$ = 61 mg L^{-1}. Experimental conditions: $[SDZ]_0$ = 25 mg L^{-1}, $[CVT230]_0$ = 5-50 mg L^{-1}, $[Fe(III)]_0$ =1-15 mg L^{-1}, pH 3, 5 and 7.

Source	Sum of Squares	Degrees of Freedom	Mean Square	*F*-Ratio	*p*-Value
X_1: $[Fe(III)]_0$ (mg L^{-1})	7452.0	1	7452.0	7.8	0.0380
X_2: $[CVT230]_0$ (mg L^{-1})	4479.5	1	4479.5	4.7	0.0821
X_3: pH	85801.0	1	85801.0	90.3	0.0002
X_1^2	220.3	1	220.3	0.2	0.6505
$X_1 X_2$	3875.1	1	3875.1	4.1	0.0995
$X_1 X_3$	785.9	1	785.9	0.8	0.4049
X_2^2	5854.8	1	5854.8	6.2	0.0557
$X_2 X_3$	990.2	1	990.2	1.0	0.3542
X_3^2	426.0	1	426.0	0.5	0.5329
Total Error	4752.6	5	950.5		
Total (corr.)	114749.0	14			
R^2	95.86				

Table 5S. Analysis of variance (ANOVA) for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$, min) obtained for the photo-Fenton degradation of SDZ in the presence of FORSUD, $[H_2O_2]_0$ = 244 mg L^{-1} and pH 5. Experimental conditions: $[SDZ]_0$ = 25 mg L^{-1}, $[FORSUD]_0$ = 5-50 mg L^{-1} and $[Fe(III)]_0$ =1-15 mg L^{-1}.

Source	**Sum of Squares**	**Degrees of Freedom**	**Mean Square**	***F*-Ratio**	***p*-Value**
X_1: $[Fe(III)]_0$ (mg L^{-1})	65.8	1	65.8	3.9	0.1433
X_2: $[FORSUD]_0$ (mg L^{-1})	241.8	1	241.8	14.3	0.0325
X_1^2	20.3	1	20.3	1.2	0.3532
$X_1 X_2$	167.7	1	167.7	9.9	0.0514
X_2^2	471.2	1	471.2	27.8	0.0133
Total Error	50.8	3	16.9		
Total (corr.)	997.4	8			
R^2	94.91				