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Photo-Fenton reaction at mildly acidic conditions: assessing the effect of bio-organic substances of different compositions through experimental design --Manuscript Draft--

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Abstract:	<p>Urban-waste bio-organic substances (UW-BOS) have been shown to be capable of extending the photo-Fenton reaction to mildly acidic conditions. Nevertheless, a systematic investigation has not yet been carried out to compare UW-BOS of different origins and chemical composition. In this study, solutions containing the model compound sulfadiazine (SDZ) were irradiated in a solar simulator equipped with a 550 W Xenon short arc lamp in the pH range 3-7. The effects of UW-BOS, H₂O₂ and iron concentrations were assessed using the Doehlert design and the response surface methodology for different types of UW-BOS (namely, CVT230 and FORSUD). At pH 3 and 5, without the addition of iron, SDZ removal occurred through the photo-Fenton reaction driven by the iron found in the UW-BOS. With iron added, SDZ removal was greatly enhanced at pH 5, which could be ascertained to Fe(III) complexation with UW-BOS notably for CVT230, which presents lower lipophilic/hydrophilic and aliphatic/aromatic ratios hence maintained in the reaction medium as a photoactive species. In contrast, UW-BOS showed to be detrimental towards TOC abatement, with only 35% mineralization achieved after 90 min of irradiation. The degradation of the pollutant can be efficient if iron availability is increased by complexation with UW-BOS.</p>
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**Photo-Fenton reaction at mildly acidic conditions: assessing the effect of bio-organic
substances of different compositions through experimental design**

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ABSTRACT

1
2 Urban-waste bio-organic substances (UW-BOS) have been shown to be capable of extending the
3
4 photo-Fenton reaction to mildly acidic conditions. Nevertheless, a systematic investigation has
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6 not yet been carried out to compare UW-BOS of different origins and chemical composition. In
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8 this study, solutions containing the model compound sulfadiazine (SDZ) were irradiated in a
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10 solar simulator equipped with a 550 W Xenon short arc lamp in the pH range 3-7. The effects of
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12 UW-BOS, H₂O₂ and iron concentrations were assessed using the Doehlert design and the
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14 response surface methodology for different types of UW-BOS (namely, CVT230 and
15
16 FORSUD). At pH 3 and 5, without the addition of iron, SDZ removal occurred through the
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18 photo-Fenton reaction driven by the iron found in the UW-BOS. With iron added, SDZ removal
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20 was greatly enhanced at pH 5, which could be ascertained to Fe(III) complexation with UW-
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22 BOS – notably for CVT230, which presents lower lipophilic/hydrophilic and aliphatic/aromatic
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24 ratios – hence maintained in the reaction medium as a photoactive species. In contrast, UW-
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26 BOS showed to be detrimental towards TOC abatement, with only 35% mineralization achieved
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28 after 90 min of irradiation. The degradation of the pollutant can be efficient if iron availability is
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30 increased by complexation with UW-BOS.
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41 **KEYWORDS:** Urban-waste bio-organic substances (UW-BOS), sulfadiazine, advanced
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43 oxidation processes, photo-Fenton, Doehlert uniform array, response surface.
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INTRODUCTION

Advanced oxidation processes (AOP), based on the generation of highly reactive species, such as hydroxyl radicals ^[1, 2], have been considered an important treatment alternative to remove pharmaceuticals from water matrices. Among them, the photo-Fenton process has been widely used. ^[3] It is based on the decomposition of hydrogen peroxide into hydroxyl radicals by iron ions, which is accelerated by irradiation. The pH range has a significant effect on the Fenton reaction, and the optimum is around 3. ^[4] At a higher pH, the system efficiency decreases since iron ions precipitate as non-active iron oxides or hydroxides. This issue has been regarded as a serious operational and economical constraint for employing the photo-Fenton process in full-scale water decontamination. ^[3] Iron complexation in the presence of organic compounds, giving photoactive complexes at mild pH, seem promising for extending the optimum pH range; 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]

1 Thus far, the photosensitizing properties of UW-BOS have been demonstrated for the
2 photodegradation of azo dyes, ^[13] phenols, ^[14] and some pharmaceuticals. ^[8] However, owing to
3 light absorption by UW-BOS in a wide wavelength range, the decrease in pollutants removal by
4 the sunlight screening effect should be considered. ^[15] As a result, the search for optimal pH,
5 UW-BOS, H₂O₂ and iron concentrations is needed for each type of bio-organic substance.
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7 Nevertheless, detailed investigations with this aim comparing UW-BOS with different properties
8 are still absent in the literature.
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10 In this study, the role of different UW-BOS in the photo-Fenton degradation of the probe
11 compound sulfadiazine (SDZ), a sulfonamide antibiotic not readily biodegradable and found in
12 water matrices, is investigated for different pH values (3, 5, and 7). The effect of UW-BOS,
13 H₂O₂ and iron concentrations is discussed using the response surface methodology for two
14 different types of UW-BOS (namely, CVT230 and FORSUD), which differ in the iron content,
15 and in the lipophilic/hydrophilic and aliphatic/aromatic ratios. To our knowledge, this is the first
16 work to compare two different types of UW-BOS in the photo-Fenton reaction. Finally, in view
17 of a practical application, an experiment was then scaled-up using natural solar light.
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39 **EXPERIMENTAL**

40 *Reagents*

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44 SDZ (99%) provided by Sigma-Aldrich was employed to prepare the solutions in Milli-Q water.
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48 Fe₂(SO₄)₃·5H₂O, used as source of iron and H₂O₂ (30% v/v) were acquired from Panreac. To
49 prepare the mobile phase for the HPLC system, methanol (HPLC quality) and acetic acid (80%
50 v/v) were acquired from Panreac and Scharlau, respectively.
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1 Two different UW-BOS, identified by the acronyms CVT230 and FORSUD, were employed in
2 this study. They were obtained from urban bio-wastes sampled from the process lines of ACEA
3 Pinerolese waste treatment plant in Pinerolo (Italy) ^[11]. Briefly, these UW-BOS were collected
4 from different biowastes, aged for different times under non-aerobic or aerobic digestion. The
5 main characteristics of the UW-BOS materials used in this study (Table 1), including their
6 surfactant activity, biodegradability and toxicity, was characterized by Gomis et al. ^[8] The
7 authors concluded that CVT230 and FORSUD are poorly-biodegradable, although non-toxic
8 materials.
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22 *Experiments*

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26 Solutions were irradiated in a solar simulator (SUN 2000, model 11014, ABET Technologies)
27 equipped with a 550 W Xenon Short Arc Lamp (maximum irradiance AM 1.5G of 7000 W m⁻²)
28 and a Pyrex glass filter, used to cut off radiation in the range 280-295 nm. The reactions were
29 conducted in a 250-mL beaker under continuous stirring at 30-35 °C, positioned at a working
30 distance of about 125 mm from the lamp. The initial SDZ concentration was 25 mg L⁻¹ (TOC =
31 12 mg L⁻¹), which was selected to allow HPLC quantification without using pre-concentration
32 steps, thus preventing the introduction of variability in the experimental data. Solid UW-BOS
33 (5-50 mg L⁻¹) was dissolved and reactions were run at pH 3, 5 and 7 to check the effect of pH on
34 SDZ degradation. In the case of the photo-Fenton reaction, the H₂O₂ initial concentration was
35 varied between half the stoichiometric amount to mineralize SDZ (61 mg L⁻¹) and twice the
36 amount required for this purpose (244 mg L⁻¹); Fe₂(SO₄)₃·5H₂O was added to achieve a
37 concentration of iron between 1 and 15 mg L⁻¹. Aqueous solutions containing 0.1 mol H₂SO₄ L⁻¹
38 or 0.1 mol NaOH L⁻¹ were used for initial pH correction. The samples were withdrawn from the
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1 solution, filtered through a polypropylene membrane (0.45 μm) and diluted 1:1 with methanol to
2 quench the reaction in the samples when iron and residual H_2O_2 were present.
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6 7 *Analysis* 8 9

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11 The extent of SDZ photodegradation was monitored by an HPLC system (Perkin Elmer Hitachi
12 XL Autosystem D-7000 model) equipped with a RP18 column (Superspher 100 model, 250 mm
13 \times 4.6 mm; 5 μm). Liquid samples were analyzed at room temperature using the following
14 gradient (A: acetic acid 1% v/v; B: methanol): 0-2 min 100% A, 2-12 min 90% A, 12-15 min
15 30% A, 15-20 min 100% A; the flow rate was 1 mL min^{-1} . The injection volume was 30 μL and
16 the detection wavelength was 266 nm. In these conditions, the SDZ retention time was about 10
17 minutes and the SDZ detection limit was 0,044 mg L^{-1} .
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29 Antibiotic mineralization was followed by the decay of TOC concentration using a carbon
30 analyzer (TOC-L from Shimadzu).
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36 *Experimental designs and response surface methodology* 37 38 39 40

41 For the photo-Fenton reaction in the presence of CVT230, an experimental Doehlert uniform
42 array design ^[16] for $k = 3$ variables (pH: 3, 5 and 7; iron: 1-15 mg L^{-1} ; and UW-BOS: 5-50 mg L^{-1})
43 concentrations) at two different H_2O_2 initial concentrations (61 and 244 mg L^{-1}) was used. The
44 response was the irradiation time required to achieve 50% SDZ degradation ($t_{50\%}$). This design
45 comprised 15 experiments (k^2+k+1 plus three replicates of the central point); the conditions are
46 shown in Table 2. Another experimental design was carried out with FORSUD at pH = 5 to
47 study the effect of $[\text{FORSUD}]_0$ (in the range 5-50 mg L^{-1}) and $[\text{Fe}^{3+}]_0$ (1-15 mg L^{-1}) at high
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1 initial H₂O₂ concentration (244 mg L⁻¹) (Table 3). Fitting of the response surface model was
2 carried out using the software Statgraphics Centurion XVI.
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7 **RESULTS AND DISCUSSION**

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10 *Irradiation of SDZ in the presence of UW-BOS*

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17 The photolysis of SDZ was studied at pH 3 and 5 under simulated sunlight. Figure 1A shows
18 that although some direct photolysis occurred, explained by a certain overlap between the
19 emission spectrum of the lamp and the absorption of SDZ (see SUPPORTING MATERIALS,
20 Figure 1S), it was low, as only ca. 20% decrease in SDZ concentration was observed at pH 3 and
21 25% at pH 5 after 180 min of irradiation.
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29 The presence of CVT230 (20 mg L⁻¹) had a negligible effect on the process, as described in a
30 previous publication.^[17] In fact, CVT230 showed very low photochemical activity,
31 compensated by the screen effect of the UW-BOS that decreased direct photolysis. On the other
32 hand, FORSUD seemed to slightly enhance photolysis of the pollutant, although SDZ percent
33 removals were still very low. This can be due to the lower absorption of FORSUD in the UV-vis
34 region, which resulted in a lower screen effect.
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44 The addition of hydrogen peroxide (244 mg L⁻¹) resulted in the acceleration of SDZ removal as
45 shown in Figure 1B. However, in the absence of UW-BOS, more than 60% of the initial amount
46 of antibiotic remained in the solution after 3 hours of irradiation. Therefore, the presence of
47 UW-BOS resulted in the enhancement of the process. As SDZ decreased faster at pH 3, this
48 effect can be attributed to the photo-Fenton process driven by the iron found in the UW-BOS
49 composition, as at this pH the performance of the photo-Fenton reaction is better than at pH 5.
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1 that the photo-Fenton reaction also occurs at mild acidic conditions, as already observed with
2 other pollutants. [8, 10, 17] Under these conditions, CVT230 was more efficient than FORSUD:
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4 this could be due to the presence of higher amounts of iron in its composition (ca. 0.8% w/w)
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6 when compared with FORSUD (0.15% w/w), as shown in Table 1.
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9 When iron(III) and hydrogen peroxide were present in the reaction medium, a very fast SDZ
10 removal was observed at pH 3, in the presence and absence of UW-BOS, as less than 1% of the
11 initial amount remained in the solution after 30 min of irradiation (Fig. 1C). Moreover, it is
12 worth observing that the addition of both CVT230 and FORSUD enhanced the photo-Fenton
13 degradation of SDZ at pH 3 in comparison with the system in the absence of UW-BOS. At pH 5,
14 CVT230 was able to enhance SDZ removal, which was not the case for FORSUD under the
15 conditions studied. This different behaviour might be due to the presence of functional groups in
16 CVT230, such as carboxylic (see Table 1), able to complex iron; this positive effect is able to
17 compensate for the screen effect of the coloured UW-BOS, and also for the competitive effect of
18 the extra amount of organic matter for the reactive species. On the other hand, FORSUD is not
19 able to enhance the photo-Fenton at this pH, most probably due to their limited ability to
20 complex iron because of its high hydrophobicity and low amount of carboxylic moieties, as
21 depicted in Table 1.
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44 *Effect of operational variables on the photo-Fenton process in the presence of UW-BOS*

45 46 47 48 *CVT230*

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53 Two experimental designs, based on the Doehlert matrix were employed to check the effect of
54 iron(III) concentration (in the range 1-15 mg L⁻¹), CVT230 concentration (5-50 mg L⁻¹) and pH
55 (3, 5 and 7) as indicated in Table 2. The experimental designs only differed in the initial amount
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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 H₂O₂ initial concentrations, respectively.

Quadratic response surface models were obtained to predict the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$). In the case of high initial H₂O₂ initial concentration, a good correlation was obtained (Equation 1, $R^2 = 0.99$). The corresponding ANOVA tables (see SUPPORTING MATERIALS, Table 1S) 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 correlation was $R^2 = 0.95$ (Equation 2) and only pH and iron concentrations showed significant effects, as indicated by the corresponding ANOVA tables (see SUPPORTING MATERIALS, Table 2S) 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.

$$\begin{aligned}
 t_{50\%}(\text{min}) = & 48.87 - 8.08 \times [Fe] - 10.45 \times [CVT230] + 77.26 \times pH - 5.02 \times [Fe]^2 - \\
 & 5.32 \times [CVT230]^2 + 31.83 \times pH^2 + 16.22 \times [Fe] \times [CVT230] - 19.26 \times [Fe] \times pH - \\
 & 21.55 \times [CVT230] \times pH
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 t_{50\%}(\text{min}) = & 153.0 - 43.16 \times [Fe] + 33.47 \times [CVT230] + 146.36 \times pH - 13.55 \times [Fe]^2 - \\
 & 69.85 \times [CVT230]^2 - 17.87 \times pH^2 - 71.88 \times [Fe] \times [CVT230] + 36.20 \times [Fe] \times pH + \\
 & 40.66 \times [CVT230] \times pH
 \end{aligned} \tag{2}$$

1 Taking into account that the best results were achieved for the higher peroxide concentration, all
2 the discussion will be focused on this case ($[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$). Bi-dimensional plots were
3 obtained by fixing a parameter at the desired value. Figure 3 shows the plots of $t_{50\%}$ as a
4 function of $[\text{CVT230}]$ vs. pH at the fixed lowest (1 mg L^{-1}), central (8 mg L^{-1}) and highest (15
5 mg L^{-1}) iron concentrations. As expected, the performance of the degradation process increases
6 with decreasing pH; however, for pH values up to about 5, the loss of efficiency would be
7 acceptable since the increase in the irradiation time can be compensated by the decrease in the
8 amount of acid solution required to lower the pH. Similar plots can be observed for $[\text{Fe}^{3+}]_0$ vs.
9 pH at fixed $[\text{CVT230}]_0$ values.

10 Figure 4 shows the plots of $t_{50\%}$ as a function of $[\text{Fe}^{3+}]_0$ and $[\text{CVT230}]_0$ at pH of 3, 5 and 7 for
11 $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$.

12 At pH 3, the reaction is very fast in the entire domain studied, with a certain loss of efficiency
13 for high iron and CVT230 concentrations. This effect can be associated to the scavenging of
14 hydroxyl radicals by organic matter and iron at higher concentrations, ^[8] limiting SDZ
15 degradation rate.

16 At pH 5, the reaction rate increases with iron and CVT230 concentrations, achieving the best
17 performance for $[\text{Fe}^{3+}]_0 > 12 \text{ mg L}^{-1}$ and $[\text{CVT230}]_0 > 35 \text{ mg L}^{-1}$. In this case, the process is
18 ruled by iron availability, as this species is known to form non-active oxides or hydroxides at pH
19 > 3 . Hence, the presence of UW-BOS is beneficial towards iron complexation to form
20 photochemically active chelates. Finally, at pH 7, the process is very inefficient ($t_{50\%}$ values
21 systematically above 100 minutes) as even UW-BOS is not able to prevent iron removal.

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

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

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22 The results of the second experimental design performed with FORSUD at pH = 5 are shown in
23 Table 3. With these data, a second order response surface model describing the behaviour of
24 $t_{50\%}$ as a function of $[FORSUD]_0$ and $[Fe^{3+}]_0$ was obtained (Equation 3). The determination
25 coefficient R^2 was 0.94 and the Pareto chart shows that only the FORSUD initial concentration
26 was significant at 95% confidence level (see SUPPORTING MATERIALS, Figure 2S and Table
27 3S). The average value of the response variable ($t_{50\%}$) at the central point of the experimental
28 design was (38.3 ± 3.4) min.
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$$41 \quad t_{50\%}(\text{min}) = 38.33 - 4.68 \times [Fe] + 8.98 \times [FORSUD] + 4.12 \times [Fe]^2 + 19.82 \times$$
$$42 \quad [FORSUD]^2 + 14.95 \times [Fe] \times [FORSUD] \quad (3)$$

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49 The contour plot corresponding to Equation 3 is shown in Figure 6. The trends are similar to
50 CVT230 at high initial H_2O_2 concentrations. However, a significant difference is observed
51 regarding the FORSUD concentration: in the range 5-30 mg L⁻¹, an increase in the concentration
52 results in better SDZ removal; nevertheless, beyond this point, extra addition of FORSUD
53 results in higher $t_{50\%}$ values. This behaviour was observed in all cases and can be attributed to a
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1 competitive effect with the pollutant for the reactive species when the FORSUD concentration is
2 high. The presence of higher amounts of iron accelerates the process, in agreement with iron
3 availability limiting the photo-Fenton reaction.
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7 The aforementioned results indicate that the elimination of SDZ can be efficient if iron
8 availability is increased (if necessary, by complexing with UW-BOS) and the concentration of
9 UW-BOS is not detrimental, be it by reducing the availability of the oxidizing agent or by
10 decreasing the number of photons reaching the catalyst by the inner-screen effect. However, it is
11 also worth studying the type of UW-BOS; for that reason, the effects of iron and UW-BOS
12 concentrations at pH 5 were checked using FORSUD. This type of UW-BOS has the advantage
13 of being less coloured, despite showing lower ability to complex iron. In fact, the systematic
14 experimental design study of the present work confirms the hypothesis presented in a previous
15 investigation,^[8] according to which FORSUD was suggested to be less photochemically active
16 and less prone to complex iron owing to the higher amount of aliphatic carbon in its structure
17 (Table 1). In contrast, the structure of CVT230 presents lower amounts of aliphatic carbon,
18 which increases iron complexation and may therefore compensate for inner filter effects
19 resulting from the stronger colour of this UW-BOS as well as the competition for reactive
20 species.
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43 ***TOC removal***

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48 In contrast to the aforementioned SDZ removal results, TOC analysis showed that less than 35%
49 mineralization was achieved after 90 min of irradiation for both UW-BOS (Fig. 7); in the
50 absence of UW-BOS, ca. 50% of mineralization was achieved. Additionally, less than 5%
51 mineralization was achieved after 90 min of irradiation in the solutions containing only UW-
52 BOS (results not shown). These results are associated with the formation of more recalcitrant
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1 compounds during the photo-Fenton process in all the systems studied. Probably, the remaining
2 amount of oxidant did not limit TOC abatement in the presence of UW-BOS, since the initial
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4 H₂O₂ concentration was the same in these experiments (244 mg L⁻¹) and the increase in the
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6 organic matter content with the addition of UW-BOS was small – from 14.9 mg L⁻¹ to 18.8 mg
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8 L⁻¹ (CVT230) and 17.9 mg L⁻¹ (FORSUD). The formation of distinct degradation products and
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10 the screening effect caused by UW-BOS may be hypothesized as possible reasons to explain the
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12 TOC-time patterns obtained, and should be investigated.
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19 *Photo-Fenton process under natural sunlight*

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24 An experiment was performed in a CPC reactor (Solardetox Acadus-2001, Ecosystem) under
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26 natural sunlight in Alcoy (Eastern Spain, 38°42' N–0°28' W), in order to evaluate the photo-
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28 Fenton-driven SDZ removal for a set of adequate conditions; the experimental set-up has been
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30 described elsewhere. [18] Briefly, the CPC consists of four borosilicate glass tubes, with an
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32 irradiated volume of 1.83 L and an irradiated CPC surface of 0.26 m², tilted 30° with the
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34 horizon. The liquid flows through the system by using a centrifugal pump with a flow rate that
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36 guarantees a turbulent regime. Solar irradiance was measured using a spectroradiometer Acadus
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38 85. The reservoir tank was fed with 4 L of SDZ solution (25 mg L⁻¹), UW-BOS (20 mg L⁻¹),
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40 Fe³⁺ (5 mg L⁻¹), H₂O₂ (244 mg L⁻¹) at pH 5, prepared with Milli-Q water. In these experiments,
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42 1.68-mL aliquots of hydrogen peroxide solution (30% v/v) were added at variable time intervals
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44 in order to keep H₂O₂ concentration around 100-1000 mg L⁻¹ (measured with MQuant™ H₂O₂
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46 test strips). Figure 8 shows that more than 80% SDZ removal was achieved after about $t_{30W} = 75$
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48 min (which correspond to 180 minutes of sunlight exposure); the corresponding TOC removed
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50 was about 70%. This experiment suggests that the UW-BOS-assisted photo-Fenton treatment of
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1 antibiotic-containing wastewater without previous acidification to pH = 3 would be a feasible
2 alternative for practical applications.
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6 7 **CONCLUSIONS**

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11 The use of soluble bio-organic substances (UW-BOS) as photosensitizers and/or for
12 implementing circumneutral photo-Fenton processes may be considered in photochemical
13 wastewater treatment processes. The effects of UW-BOS, H₂O₂ and iron concentrations were
14 assessed using the Doehlert design and the response surface methodology for two different types
15 of UW-BOS (namely, CVT230 and FORSUD). The presence of CVT230 (20 mg L⁻¹) had a
16 negligible effect on SDZ photolysis. Therefore, the very low photochemical activity of this UW-
17 BOS was overcome by its screen effect. In contrast, FORSUD seemed to slightly enhance
18 photolysis of the pollutant, although SDZ percent removals were still very low. When UW-BOS
19 were present in the photo-Fenton processes, however, the reaction rate was greatly enhanced at
20 milder pH (5), which could be ascertained for the complexation of iron with UW-BOS –
21 particularly in the case of CVT230, which presents lower amounts of aliphatic carbon – hence
22 maintained in the reaction medium as a photoactive species. This is advantageous for possible
23 engineered applications, including solar-driven processes, such as the treatment of
24 sulfonamides-containing wastewater without previous pH correction and/or hybrid (chemical-
25 biological) remediation systems.
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FIGURE CAPTIONS

Figure 1. SDZ removal by different processes. (A) Photolysis ($[\text{SDZ}]_0 = (26.2 \pm 0.3) \text{ mg L}^{-1}$). (B) $\text{H}_2\text{O}_2/\text{UV}$ ($[\text{SDZ}]_0 = (25.8 \pm 1.3) \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$). (C) Photo-Fenton ($[\text{SDZ}]_0 = (26.3 \pm 1.1) \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$; $[\text{Fe}^{3+}]_0 = 5 \text{ mg L}^{-1}$). Experimental conditions: (Δ) without UW-BOS at pH 3; (\blacktriangle) without UW-BOS at pH 5; (\square) with CVT230 (20 mg L^{-1}) at pH 3; (\blacksquare) with CVT230 (20 mg L^{-1}) at pH 5; (\circ) with FORSUD (20 mg L^{-1}) at pH 3; (\bullet) 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 $[\text{Fe}]_0$ and $[\text{CVT230}]_0$ represent the uncoded factors. (A) $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$. (B) $[\text{H}_2\text{O}_2]_0 = 61 \text{ mg L}^{-1}$. Experimental conditions: $[\text{SDZ}]_0 = (25.4 \pm 1.1) \text{ mg L}^{-1}$, $[\text{CVT230}]_0 = 5\text{-}50 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}]_0 = 1\text{-}15 \text{ mg L}^{-1}$, pH 3, 5 and 7

Figure 3. Contour plots of $t_{50\%}$ (min) as a function of $[\text{CVT230}]_0$ and pH for the photo-Fenton degradation of SDZ for $[\text{Fe}^{3+}]_0 = 1, 8$ and 15 mg L^{-1} and $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$

Figure 4. Contour plots of $t_{50\%}$ (min) as a function of $[\text{Fe}^{3+}]_0$ and $[\text{CVT230}]_0$ for the photo-Fenton degradation of SDZ at pH 3, 5 and 7 and $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$

Figure 5. Contour plots of $t_{50\%}$ (min) as a function of $[\text{Fe}^{3+}]_0$ and $[\text{CVT230}]_0$ for the photo-Fenton degradation of SDZ at pH 5 for low and high H_2O_2 initial concentrations

1 **Figure 6.** Contour plots of $t_{50\%}$ (min) as a function of $[\text{UW-BOS}]_0$ and $[\text{Fe}^{3+}]_0$ for CVT230 and
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3 FORSUD for $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$ and pH 5
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7 **Figure 7.** TOC removal by the photo-Fenton process in the absence of UW-BOS (\circ , $[\text{TOC}]_0 =$
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9 14.9 mg L^{-1}) and in the presence of CVT230 (\triangle , $[\text{TOC}]_0 = 18.8 \text{ mg L}^{-1}$) and FORSUD (\square ,
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11 $[\text{TOC}]_0 = 17.9 \text{ mg L}^{-1}$). Experimental conditions: $[\text{SDZ}]_0 = (25.7 \pm 1.76) \text{ mg L}^{-1}$, $[\text{UW-BOS}]_0 =$
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13 20 mg L^{-1} , $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}]_0 = 5 \text{ mg L}^{-1}$, pH 5
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19 **Figure 8.** SDZ degradation (\bullet , $[\text{SDZ}]_0 = 24.4 \text{ mg L}^{-1}$) and TOC removal (\circ , $[\text{TOC}]_0 = 15.1 \text{ mg}$
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21 L^{-1}) by the photo-Fenton process in the presence of CVT230 in a CPC reactor under natural
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23 sunlight. Experimental conditions: $[\text{CVT230}]_0 = 20 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}]_0 = 5$
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25 mg L^{-1} , pH 5. Accumulated UV radiation is expressed as $t_{30\text{W}}$ to normalize the intrinsically
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27 changing irradiation conditions ^[17]
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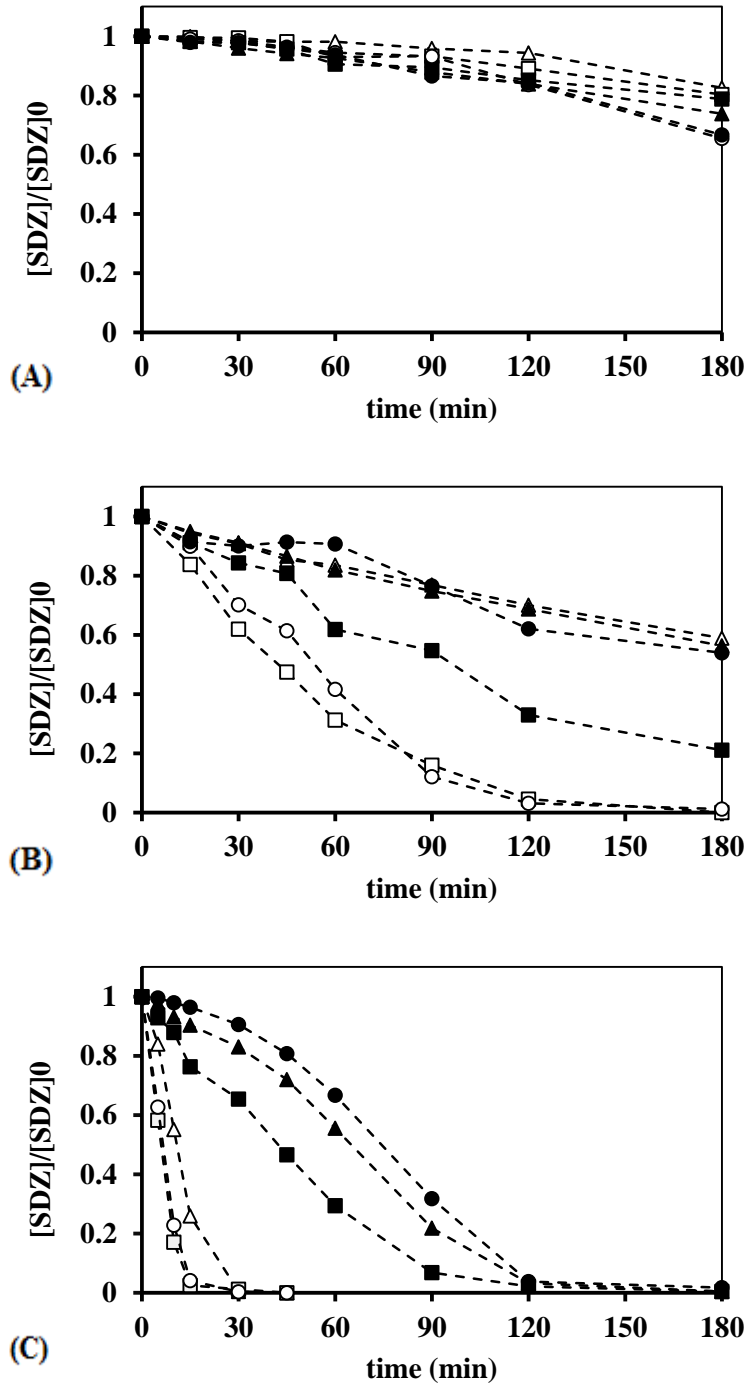


Fig. 1

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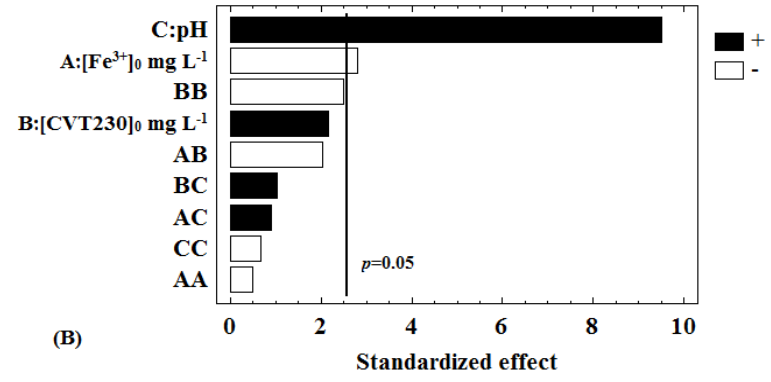
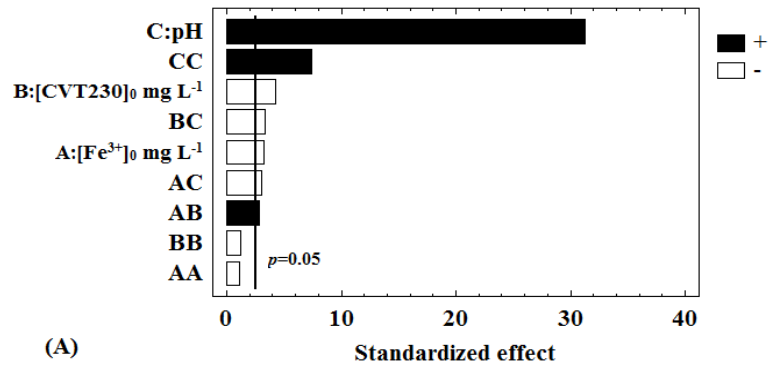
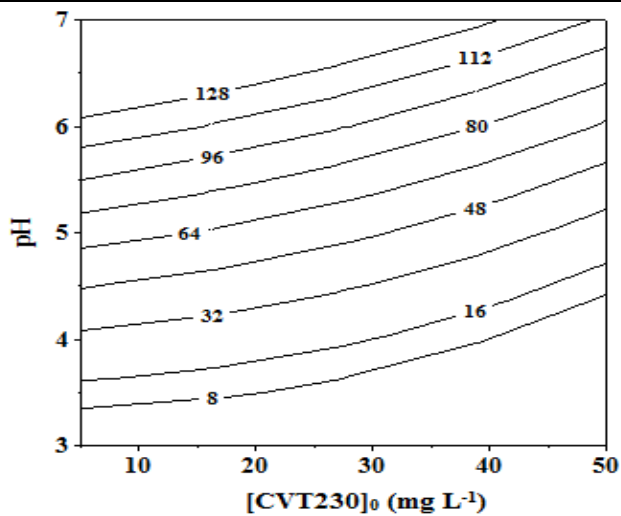


Fig. 2

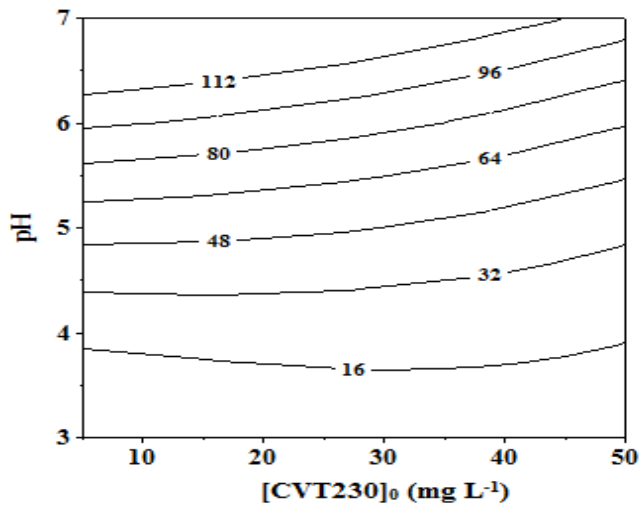
[Fe³⁺]₀ (mgL⁻¹)

Contour Plots of $t_{50\%}$ (min)

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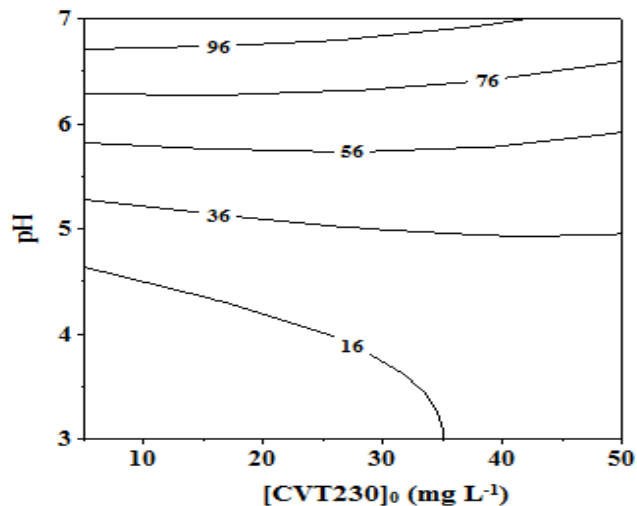
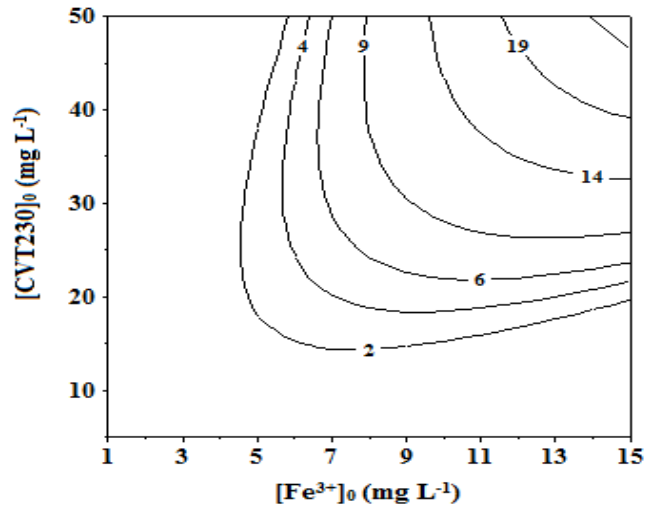


Fig. 3

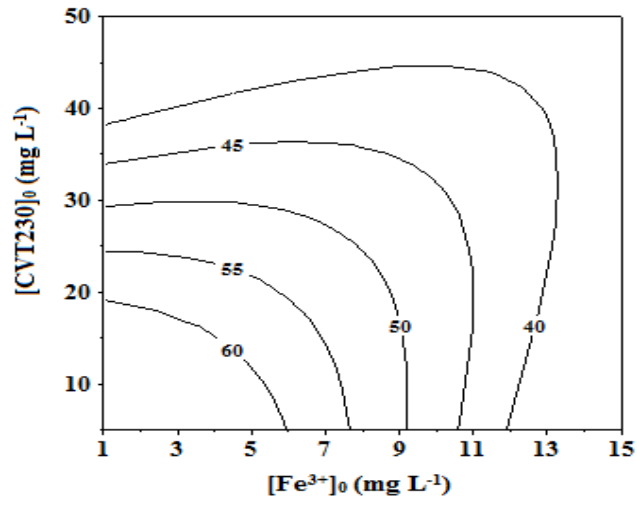
pH

Contour Plots of $t_{50\%}$ (min)

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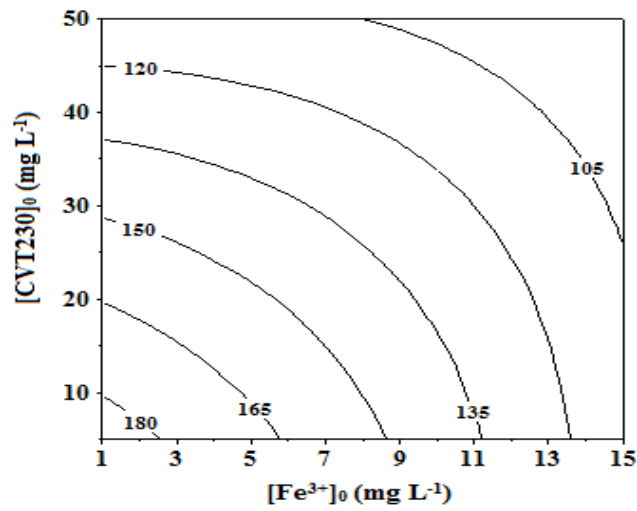
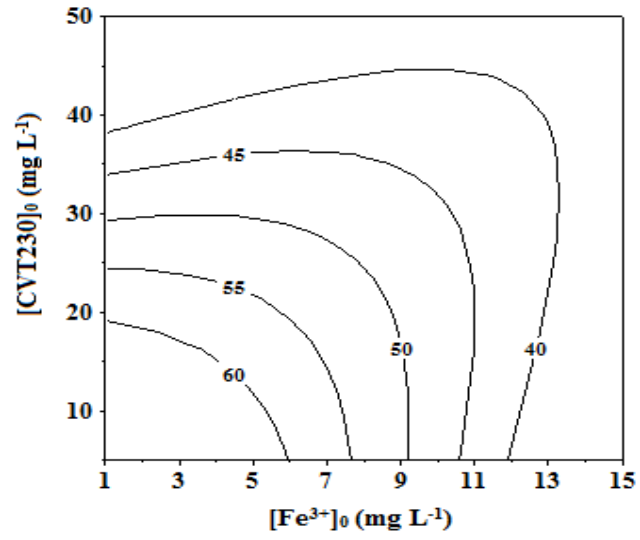


Fig. 4

[H₂O₂]₀

Contour Plots of $t_{50\%}$ (min)

High [H₂O₂]₀
(244 mg L⁻¹)



Low [H₂O₂]₀
(61 mg L⁻¹)

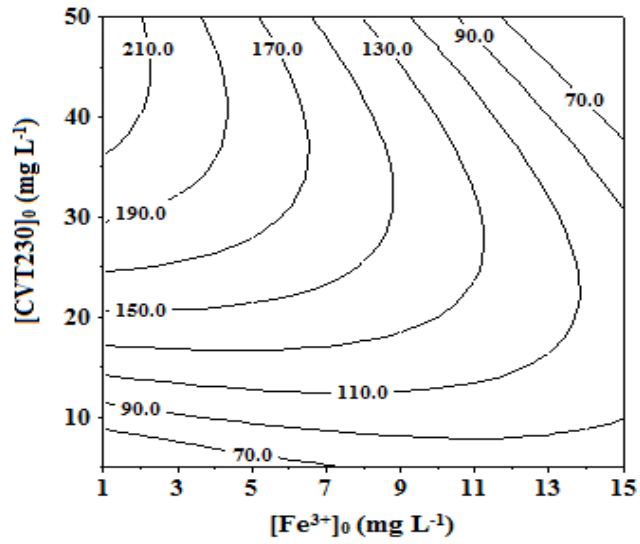
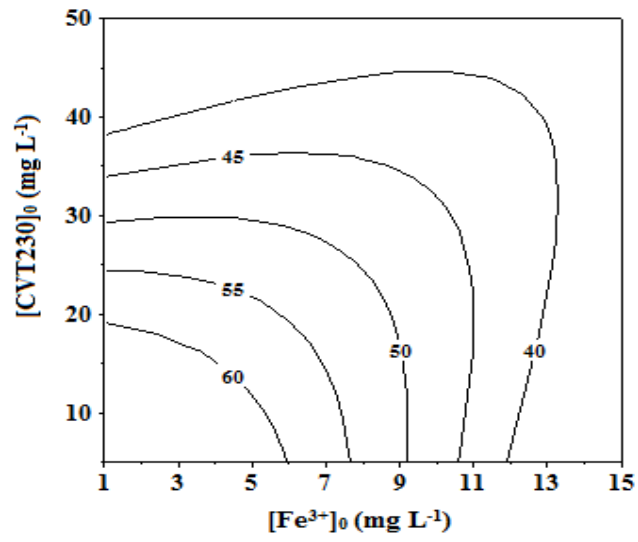


Fig. 5

UW-BOS

Contour Plots of $t_{50\%}$ (min)

CVT230



FORSUD

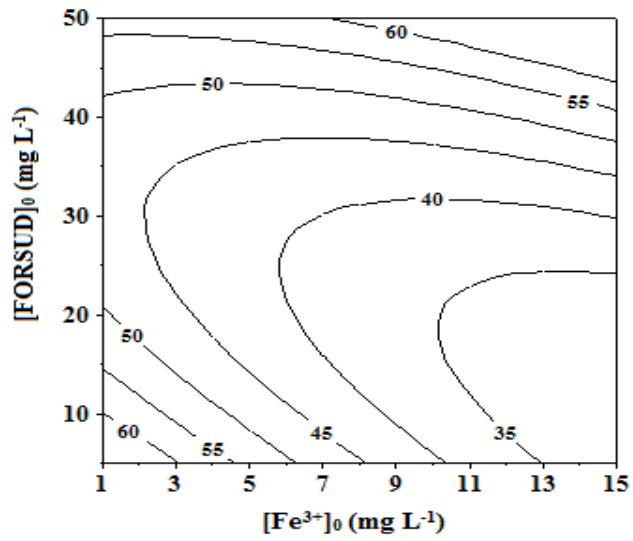


Fig. 6

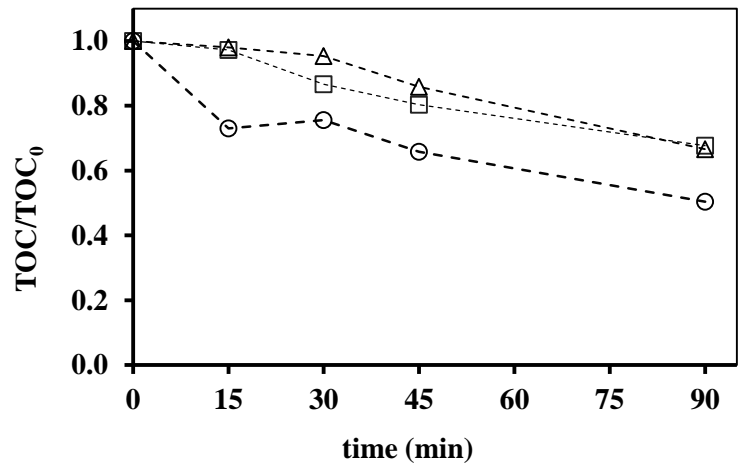


Fig. 7

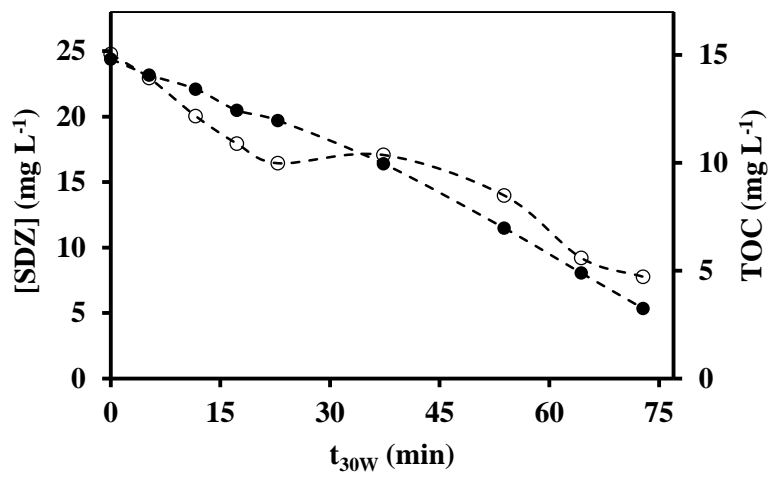


Fig. 8

Table 1. 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
Fe (% w/w)	0.77	0.16
Aliphatic carbon (%)	37	43
Aromatic (%)	13	10
Carboxylic (%)	12	7
Lipophilic/hydrophilic ratio	3.6	9.3
Aliphatic/aromatic ratio	1.8	3.3

Table 2. Doehlert design matrix for three factors and two different H₂O₂ initial concentrations.

Variables X_1 , X_2 , and X_3 represent the coded values of $[\text{Fe}^{3+}]_0$, $[\text{CVT230}]_0$ and pH, respectively.

$$[\text{SDZ}]_0 = (25.4 \pm 1.1) \text{ mg L}^{-1}$$

Exp. number	X_1	X_2	X_3	$[\text{Fe}^{3+}]_0$ (mg L ⁻¹)	$[\text{CVT230}]_0$ (mg L ⁻¹)	pH	$t_{50\%}$ (min)	
							$[\text{H}_2\text{O}_2]_0=244 \text{ mg L}^{-1}$	$[\text{H}_2\text{O}_2]_0=61 \text{ mg L}^{-1}$
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 3. Doehlert design matrix for two factors at pH 5 and $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$. Variables X_1 and X_2 represent the coded values of $[\text{Fe}^{3+}]_0$ and $[\text{FORSUD}]_0$, respectively. $[\text{SDZ}]_0 = (24.6 \pm 1.0)$

mg L⁻¹

Exp. number	X_1	X_2	$[\text{Fe}^{3+}]_0$ (mg L ⁻¹)	$[\text{FORSUD}]_0$ (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

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5 **Figure 1S.** Emission spectrum of the xenon lamp and UV-vis absorption spectra of (A) SDZ (25
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7 mg L⁻¹ and (B) CVT230 (20 mg L⁻¹) at pH 3, 5 and 7
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12 **Figure 2S.** Pareto chart for the irradiation time required to achieve 50% SDZ removal ($t_{50\%}$,
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14 min) obtained for the photo-Fenton degradation of SDZ in the presence of FORSUD for $[\text{H}_2\text{O}_2]_0$
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16 = 244 mg L⁻¹ and pH 5; where $[\text{Fe}^{3+}]_0$ and $[\text{FORSUD}]_0$ represent the uncoded factors
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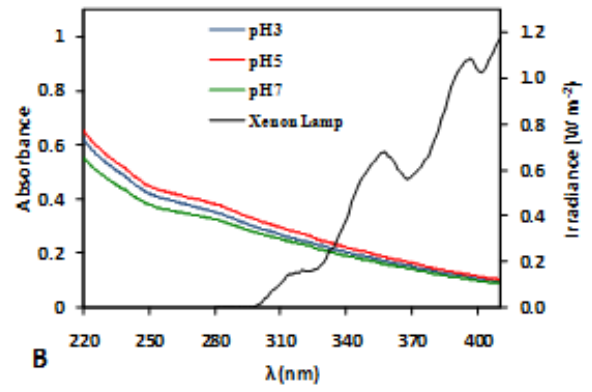
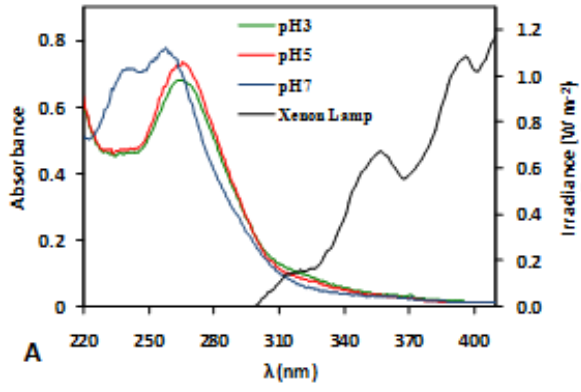


Fig. 1S

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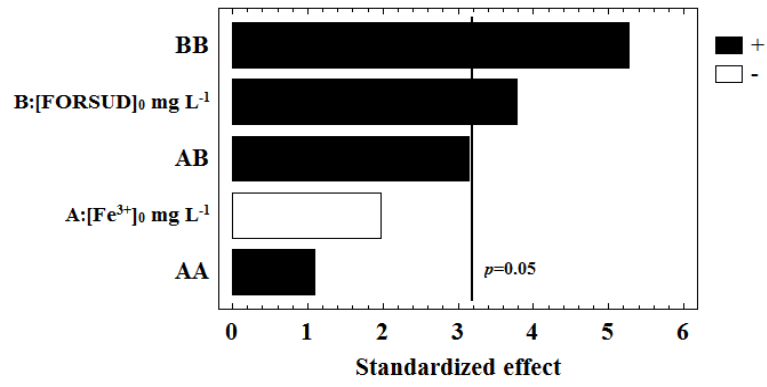


Fig. 2S

Table 1S. 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 $[\text{H}_2\text{O}_2]_0 = 244 \text{ mg L}^{-1}$. Experimental conditions: $[\text{SDZ}]_0 = 25 \text{ mg L}^{-1}$, $[\text{CVT230}]_0 = 5\text{-}50 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}]_0 = 1\text{-}15 \text{ mg L}^{-1}$, pH 3, 5 and 7

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio	p-Value
A: $[\text{Fe}^{3+}]_0$ (mg/L)	260.8	1	260,8	10,7	0,0223
B: $[\text{CVT230}]_0$ (mg/L)	436.8	1	436,8	17,9	0,0083
C: pH	23904.9	1	23904,9	978,6	0,0000
AA	30.2	1	30,2	1,2	0,3168
AB	197.4	1	197,4	8,1	0,0361
AC	222.9	1	222,9	9,1	0,0294
BB	33.9	1	33,9	1,4	0,2917
BC	279.9	1	279,0	11,4	0,0197
CC	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 2S. 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 $[\text{H}_2\text{O}_2]_0 = 61 \text{ mg L}^{-1}$. Experimental conditions: $[\text{SDZ}]_0 = 25 \text{ mg L}^{-1}$, $[\text{CVT230}]_0 = 5\text{-}50 \text{ mg L}^{-1}$, $[\text{Fe}^{3+}]_0 = 1\text{-}15 \text{ mg L}^{-1}$, pH 3, 5 and 7

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio	p-Value
A: $[\text{Fe}^{3+}]_0$ (mg/L)	7452.0	1	7452.0	7.8	0.0380
B: $[\text{CVT230}]_0$ (mg/L)	4479.5	1	4479.5	4.7	0.0821
C: pH	85801.0	1	85801.0	90.3	0.0002
AA	220.3	1	220.3	0.2	0.6505
AB	3875.1	1	3875.1	4.1	0.0995
AC	785.9	1	785.9	0.8	0.4049
BB	5854.8	1	5854.8	6.2	0.0557
BC	990.2	1	990.2	1.0	0.3542
CC	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 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 FORSUD, $[H_2O_2]_0 = 244 \text{ mg L}^{-1}$ and pH 5. Experimental conditions: $[SDZ]_0 = 25 \text{ mg L}^{-1}$, $[FORSUD]_0 = 5\text{-}50 \text{ mg L}^{-1}$ and $[Fe^{3+}]_0 = 1\text{-}15 \text{ mg L}^{-1}$

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio	p-Value
A: $[Fe^{3+}]_0$ (mg/L)	65.8	1	65.8	3.9	0.1433
B: $[FORSUD]_0$ (mg/L)	241.8	1	241.8	14.3	0.0325
AA	20.3	1	20.3	1.2	0.3532
AB	167.7	1	167.7	9.9	0.0514
BB	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				



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São Paulo, October 28th, 2018.

To

Prof. Shahamat U. Khan

Editor-in-Chief – Journal of Environmental Science and Health, Part A

Dear Prof. Khan,

Please find attached the manuscript entitled “**Photo-Fenton reaction at mildly acidic conditions: assessing the effect of bio-organic substances of different compositions through experimental design**”, for publication in the **Journal of Environmental Science and Health, Part A**.

Urban-waste bio-organic substances (UW-BOS), derived from solid urban residues, are solid materials containing a mixture of macromolecules characterized by long aliphatic carbon chains, aromatic rings, and numerous functional groups such as carboxylic, amide, carbonyl, phenolic, alkoxy or amine. They compare with macromolecules present in natural organic matter (NOM) in terms of chemical nature and good properties as complexing agents and surfactants.

To our knowledge, this is the first research work in which two different types of UW-BOS (namely, CVT230 and FORSUD) are compared, regarding their use as promoters in the photo-Fenton reaction. The effects of UW-BOS, H₂O₂ and iron concentrations upon the removal of sulfadizine (SDZ, an antibiotic selected as a model pollutant of emerging concern), were assessed using a Doehlert experimental design and the response surface methodology.

The results show that at pH 3 and 5, SDZ removal occurred through the photo-Fenton-like reaction driven by the iron found in the UW-BOS, particularly in the case of CVT230. With iron added, SDZ removal was greatly enhanced at pH 5 and 7, which could be ascertained to Fe(III) complexation by the UW-BOS, which strongly depends on the lipophilic/hydrophilic and aliphatic/aromatic ratios of the UW-BOS sample. This is clearly advantageous for possible engineered applications, including solar-driven

processes without previous pH correction and/or hybrid (chemical-biological) remediation systems. It is worth mentioning that until now, the pH range has been regarded as a serious operational and economical constraint for employing the photo-Fenton process in full-scale wastewater decontamination.

For these reasons, we believe that the **Journal of Environmental Science and Health, Part A**, is the ideal vehicle to share the results we present which may be of interest to a wider audience concerned with the use of green processes for water detoxification, since UW-BOS valorizes solid waste as a material of technological application.

We confirm that all the authors have approved the manuscript and agree with its submission.

We add that the guidelines for authors available were followed.

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Sincerely,

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