



Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: Optimization of operational variables



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ABSTRACT

The use of soluble bio-based organic substances (SBO) obtained from urban wastes to expand the pH region where the photo-Fenton process can be applied has been investigated in this study. For this purpose, a mixture of six pollutants, namely acetaminophen, carbamazepine, amoxicillin, acetamidrid, clofibric acid and caffeine, at an initial concentration of 5 mg L⁻¹ each, has been employed. Surface response methodology, based on the Doehlert matrix, has shown to be a useful tool to determine the effect of pH (in the range 3–7), concentration of SBO (15–25 mg L⁻¹) and iron (2–6 mg L⁻¹) on the performance of the photodegradation of the studied pollutants, measured by their half-life. Results indicate that, at high SBO concentration, the optimum pH shifts in most cases to a higher value (between 3 and 4) and that a significant loss of efficiency of the process was only observed at pH values above 5. An iron concentration of 4–5 mg L⁻¹ and an amount of SBO of 19–22 mg L⁻¹ have been determined to be the optimal conditions for the degradation of most of the studied pollutants at pH = 5.

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1. Introduction

Wastes have deserved attention from researchers, as they could be a sustainable source of materials with a wide range of potential applications [1]. In particular, soluble bio-based organic substances (SBO) have been isolated from solid organic wastes submitted to aging under aerobic fermentation conditions, following a process that involves extraction of the soluble fraction at basic pH and posterior precipitation at acidic media [2]. SBO are constituted by a mixture of macromolecules, which average molecular weight ranges from 67 to 463 kg mol⁻¹; they consist of long aliphatic chains, aromatic rings and several oxygen and nitrogen-containing functional groups [2]. Hence, these materials show basic structural similarities with some macromolecules found in natural organic matter (NOM), such as humic and fulvic acids, which

play an important role in photochemical processes leading to the self-remediation of ecosystems [3]. In this context, determining the potential use of SBO for water detoxification is meaningful, as this may be considered a green process since it valorises solid wastes as sources of photoactive materials with similar properties as less available NOM. Information on this issue is very scarce, and only some recent papers have been published reporting on the ability of these compounds to act as photocatalysts in the degradation of chlorophenols [4,5], sulphonic acids [6], dyes [7,8] or pharmaceuticals [9]. SBOs action can be related to an enhanced photogeneration of reactive species; however, the strong screen effect produced by these coloured materials negatively affects the degradation of pollutants that can undergo direct photolysis. When simulated sunlight was employed as irradiation source, the screen effect becomes predominant, thus making SBOs unattractive as solar photocatalysts [9].

Alternatively, SBOs might also be employed as complexing agents to drive photo-Fenton processes at mild conditions. Photo-Fenton is based on the ability of iron salts to catalyse

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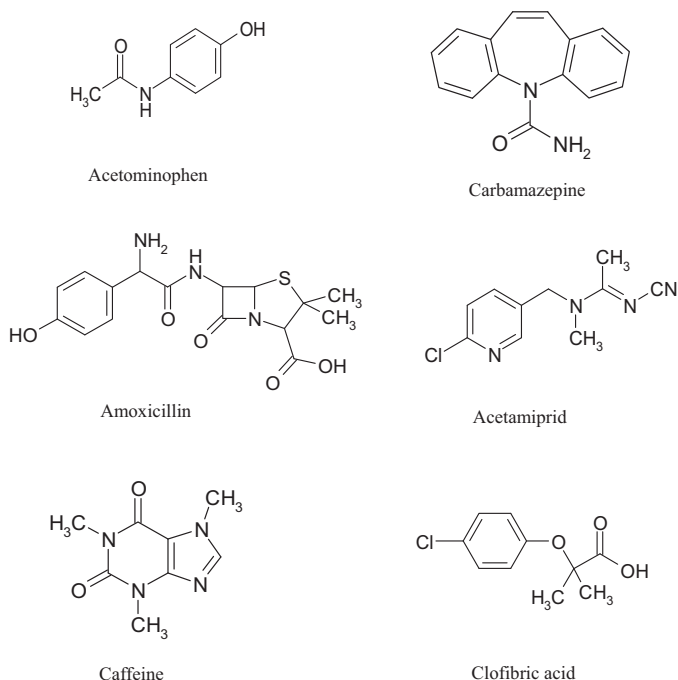


Fig. 1. Chemical structures of EPs used in this study.

decomposition of hydrogen peroxide into highly oxidizing species (mainly hydroxyl radicals, although other species might also contribute) in a process that is accelerated by irradiation [10]. One major drawback of this process is the highly acidic media required to avoid formation of non-active iron oxides or hydroxides. However, some efforts have been recently made for the implementation of photo-Fenton at circumneutral pH. This approach might be especially useful to treat emerging pollutants (EPs) as a certain loss of efficiency in the generation of reactive species might be acceptable in this case, as EPs are commonly found at low concentration, and hence lesser amounts of oxidizing species are necessary [11,12]. This strategy can be improved by using chemical auxiliaries, able to form photoactive complexes, at mild pH, with the iron added [13]. Humic acids are among the materials employed for this purpose, because of their ability for iron complexation [13–16].

Because of their similarity with humic substances, SBOs are also candidates to extend the application of photo-Fenton to pH conditions where iron ions are normally not soluble. Indeed, photo-Fenton process in the presence of SBOs have been recently shown to be able to remove a mixture of EPs at pH = 5.2 [9]. Hence, a logical step beyond is to determine the role of the operational parameters on the efficiency of the process. For this purpose, a response surface methodology based on Doehlert design has been chosen in this work in order to determine the effect of SBOs and iron concentrations at the pH interval between 3, close to the optimal value, and 7. The Doehlert design has been commonly employed as a chemometric tool, enabling to minimize the number of experiments required to obtain the response surface [17,18]. The mixture of EPs employed in previous work [9,16] has been chosen as target solution: acetaminophen, carbamazepine, amoxicillin, acetamiprid, clofibric acid and caffeine (see Fig. 1 for structures).

2. Experimental

2.1. Reagents

Acetaminophen, caffeine, amoxicillin, clofibric acid, carbamazepine and acetamiprid were purchased from Sigma-Aldrich

and used as received. Hydrogen peroxide (30% v/v), ferric chloride, sulphuric acid and sodium hydroxide, were obtained from Panreac. Water was Milli-Q grade.

The SBO employed in this work, namely CVT230, was obtained from urban biowastes supplied by ACEA Pinerolese waste treatment plant (Pinerolo, Italy) following a procedure detailed elsewhere [2,19]. Briefly, the starting material was compost from gardening-park trimming residues matured for 230 days; it was digested 4 h at 60 °C at alkaline conditions (pH = 13) and 4 v/w water/solid ratio to favour hydrolysis of organics. Alkaline hydrolyzed solution have been recognized as very similar to the humic matter, in turn characterized by the presence of a dimensionally smaller fraction (fulvic acid) soluble in all the pH range, and of a larger one (humic acid), not soluble below pH 3. Instead of separating the two fractions by means of pH variation, the size difference was exploited. The recovered liquid phase was therefore circulated through a polysulfone ultrafiltration membrane with 5 kD molecular weight cut-off to yield a retentate with 5–10% dry matter content. The membrane retentate was dried at 60 °C to yield the final water soluble bio-based product (SBO). It contained 72.1% (w/w) of volatile solids and the carbon content was 38.3% (see [8] for further details).

2.2. Reactions

Experiments were performed in a 250 mL cylindrical Pyrex vessel irradiated with a solar simulator (Sun 2000, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp. A pyrex glass filter was used to cut off radiation below 300 nm (which only accounted for a residual fraction of the lamp irradiance). The vessel was loaded with an aqueous solution containing the six EPs at an initial concentration of 5 mg L⁻¹ each. SBO concentration was varied in the range 15–25 mg L⁻¹; FeCl₃ was added to reach a concentration of iron between 2 and 6 mg L⁻¹. The initial amount of hydrogen peroxide was 2.2 mmol L⁻¹ in all cases, which is half the stoichiometric amount required to mineralize the EPs; this concentration was employed in order to obtain a relatively slow kinetics, which allows a better determination and comparison of illumination times required to remove the EPs under the different conditions that have been studied. The pH was adjusted to the desired value (3–7) by dropwise addition of either 0.1 mmol L⁻¹ NaOH or 0.1 mmol L⁻¹ H₂SO₄. Temperature was kept in the range 30–35 °C throughout the reaction. Samples were periodically taken from the solution, filtered through a polypropylene membrane (0.45 μm) and diluted 1:1 with methanol.

Control experiments showed that direct photolysis of the pollutants was negligible under the employed conditions and irradiation in the presence of H₂O₂ solely resulted in a moderate degradation of amoxicillin (less than 20% after 200 min of irradiation).

2.3. Analysis

The concentration of each EP was determined by UPLC (Perkin Elmer model Flexar UPLC FX-10). A Brownlee Analytical column (DB-C18) was employed as stationary phase. The eluent consisted in a mixture of acetonitrile (A) and a 0.1% formic acid aqueous solution (B); the relative amount of each solvent was changed following a linear gradient, from 3% A to 70% A in 8 min; the flow rate was 0.3 mL min⁻¹. Detection wavelengths were 205 nm (acetaminophen, amoxicillin, caffeine and carbamazepine), 225 nm (clofibric acid) and 245 nm (acetamiprid). Identification and quantification of the EPs were performed by comparison with standards.

2.4. Surface response methodology

In order to gain further insight into the effect of the studied operational variables (pH, SBO and iron concentration), an

Table 1

Experimental points used to obtain the response surface (Doehlert matrix). The concentrations of SBO and iron are expressed as mg L^{-1} ; data given in the last six columns correspond to the time (in min) required to decrease concentration of each EP to 50% of the initial value for carbamazepine (A), acetaminophen (B), amoxicillin (C), acetamiprid (D), clofibrac acid (E) and caffeine (F).

Exp number	[Fe(III)]	[SBO]	pH	A	B	C	D	E	F
1	4	20	5	21.6	25.8	14.4	57.6	24.3	25.5
1'	4	20	5	18.1	24.9	16	54.1	24.6	26.6
1''	4	20	5	15	22	10	48.8	20.4	23.2
2	6	20	5	23.8	26.6	12.8	59.5	28.2	31.3
3	5	25	5	27.8	33.8	22	68.9	32.1	36.4
4	2	20	5	27.9	28.4	24.4	57	29.5	35.1
5	3	15	5	34.4	41.6	26.3	83.9	40.3	47.1
6	5	15	5	33.3	36.4	24.4	68.9	36.1	39.6
7	3	25	5	27.5	33	22.3	65.8	33.7	35.8
8	5	21.7	7	129.4	86.3	111.5	320	133.3	207.5
9	3	21.7	7	88.4	82.1	62.4	218	87.4	109.7
10	4	16.7	7	154	75.5	174.3	242.7	156.4	150
11	3	18.3	3	2.3	3.3	2.3	6.4	2.7	3.1
12	5	18.3	3	1.7	1.5	1	3.9	2.1	1.8
13	4	23.3	3	1.3	2.4	1.3	4.6	1.8	2.1

experimental design methodology based on a Doehlert array [20] was used. In this case, a total of 15 experiments ($k^2 + k + 1$, where k is the number of analyzed variables, 3 in this study, plus two replicates of the central point) were performed. Experimental conditions of all experiments are found in Table 1. The software Statgraphics Centurion XVI was used for response surface model fitting by means of the least squares method. The illumination time required to degrade each pollutant to 50% of its initial concentration ($t_{50\%}$) was used as response, which was obtained from the plot of the relative EP concentration vs. illumination time.

3. Results and discussion

Plots of the relative concentration of each EP vs. illumination time were obtained for each experiment (see Fig. 2 for an example). Considering an illumination time of 90 min, the results show complete removal of all EPs for the experiments carried out at pH 3. At pH 5, removals between 90 and 100% were obtained for all EPs except acetamiprid, for which removals in the range 54–68.5% were obtained. These results confirm the efficiency of the photo-Fenton reaction under acidic and mild acidic conditions, the later favoured by the presence of SBOs. Finally, maximum percent removals between 5.7 and 64.7% were obtained for the experiments carried out at pH 7, again the lowest removals after 90 min of illumination (5.7–21%) corresponding to acetamiprid. These trends show that the choice of a response like the illumination time necessary

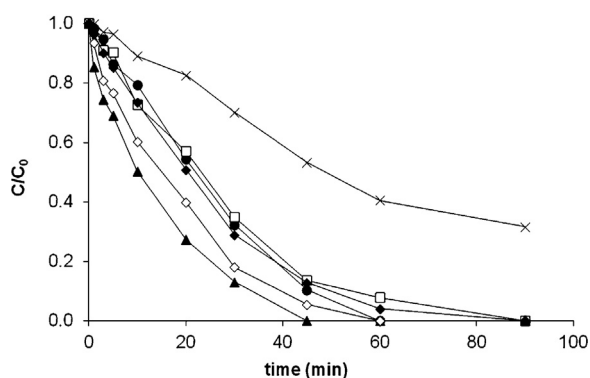


Fig. 2. Example of the photodegradation of a mixture of 6 EPs by means of the photo-Fenton reaction. Plot of the relative concentration vs. time: amoxicillin (▲), acetaminophen (●), acetamiprid (×), caffeine (□), clofibrac acid (◆) and carbamazepine (◇). Data correspond to the central point ([SBO]=20 mg L^{-1} , [Fe(III)]=4 mg L^{-1} , pH=5).

to obtain pollutant removals of 90% or greater could not be considered for all EPs and pH for the conditions used in the present study (pollutants initial concentrations, H_2O_2 and iron concentrations) and in some cases would require too long illumination times to be observed.

As a result, the illumination time required for the removal of 50% of each pollutant ($t_{50\%}$) was considered for every experiment (Table 1). From the practical point of view, the response $t_{50\%}$ is not submitted to phenomena such as lack of hydrogen peroxide or changes in the experimental conditions that can affect the kinetic behaviour and/or reproducibility (mainly under the less efficient conditions, where too long illumination times would be required). Based on the response values in Table 1, six three-dimensional full quadratic response surface models were obtained, one for each EP (see Table 2, Eqs. I-A to I-F). For all EPs the values of the determination coefficient (R^2) were high (92.4; 97.4; 98.1; 97.1; 95.9; and 99.4% for amoxicillin, carbamazepine, acetamiprid, clofibrac acid, caffeine, and acetaminophen, respectively), indicating good agreement between experimental and calculated values of the response variable. In each case, the values of the residuals (differences between calculated and measured values of $t_{50\%}$) as a function of measured values were randomly distributed around error zero with zero mean.

The corresponding ANOVA tables (see Supplementary data, Tables T1–T6) and the Pareto charts (Fig. 3) show that except for acetaminophen, the only significant effect on $t_{50\%}$ at 95% confidence level (p -values <0.05) was due to pH, as expected, being the reaction faster at lower pH values; the quadratic effect of this variable was significant, indicating the important curvature of the response surfaces. For acetaminophen, the quadratic effect of SBO concentration was also significant. Therefore, simplified model equations for $t_{50\%}$ were fitted by considering the effect of pH only, as presented in Table 2 (cf. Eqs. II-A to II-F) (see Supplementary data, Tables T7–T12 for the corresponding ANOVA tables). In comparison with the complete model equations, in most cases the values of R^2 decreased as the simplified fitted models exhibit lack-of-fit and fail to predict $t_{50\%}$ for the experiments in which the effects of SBO and Fe(III) concentrations on the response are important (see Supplementary data, Figs. F1–F6). In other words, the effect of pH on the response is so pronounced that it masks the effects of the other variables, especially that of SBO concentrations for some pH conditions. For that reason, in order to discuss some trends concerning the effects of SBO and Fe(III) concentrations and to better determine the pH domain where the photo-Fenton could be applied, the complete fitted response surface models were considered, and two-dimensional contour plots were built for each EP by fixing [SBO] at the higher and lower values.

Table 2
Response surface models obtained for each EP, where the values of the variables are specified in their original units. (I) Refer to the complete fitted model, (II) to the simplified fitted model without the non-significant variables, and (III) to the fitted model considering only the experiments performed at pH 5.

Compound	Equation
Carbamazepine	$t_{50\%}(\text{min}) = 248.38 - 40.37 \cdot [\text{Fe}] - 8.52 \cdot [\text{SBO}] - 51.39 \cdot \text{pH} + 1.90 \cdot [\text{Fe}]^2 + 0.07 [\text{Fe}] [\text{SBO}] + 5.14 \cdot [\text{Fe}] \cdot \text{pH} + 0.43 [\text{SBO}]^2 - 2.08 \cdot [\text{SBO}] \cdot \text{pH} + 10.28 \cdot \text{pH}^2$ ($R^2 = 0.974$) (I-A) $t_{50\%}(\text{min}) = 106.29 - 62.86 \cdot \text{pH} + 9.34 \cdot \text{pH}^2$ ($R^2 = 0.915$) (II-A) $t_{50\%}(\text{min}) = 239.50 - 17.38 \cdot [\text{Fe}] - 17.88 [\text{SBO}] + 1.90 [\text{Fe}]^2 + 0.43 [\text{SBO}]^2 + 0.07 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.930$) (III-A)
Acetaminophen	$t_{50\%}(\text{min}) = 318.33 - 15.36 \cdot [\text{Fe}] - 22.79 \cdot [\text{SBO}] - 32.82 \cdot \text{pH} + 0.82 \cdot [\text{Fe}]^2 + 0.30 [\text{Fe}] [\text{SBO}] + 0.50 [\text{Fe}] \cdot \text{pH} + 0.45 [\text{SBO}]^2 + 0.71 \cdot [\text{SBO}] \cdot \text{pH} + 3.64 \cdot \text{pH}^2$ ($R^2 = 0.994$) (I-B) $t_{50\%}(\text{min}) = 3.98 - 9.21 \cdot \text{pH} + 2.89 \cdot \text{pH}^2$ ($R^2 = 0.963$) (II-B) $t_{50\%}(\text{min}) = 253.57 - 13.20 \cdot [\text{Fe}] - 19.60 [\text{SBO}] + 0.82 [\text{Fe}]^2 + 0.45 [\text{SBO}]^2 + 0.3 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.972$) (III-B)
Amoxicillin	$t_{50\%}(\text{min}) = 56.92 - 41.63 \cdot [\text{Fe}] + 3.80 \cdot [\text{SBO}] - 19.34 \cdot \text{pH} + 1.28 \cdot [\text{Fe}]^2 + 0.08 [\text{Fe}] [\text{SBO}] + 6.23 \cdot [\text{Fe}] \cdot \text{pH} + 0.36 [\text{SBO}]^2 - 4.19 \cdot [\text{SBO}] \cdot \text{pH} + 10.69 \cdot \text{pH}^2$ ($R^2 = 0.924$) (I-C) $t_{50\%}(\text{min}) = 123.65 - 70.42 \cdot \text{pH} + 9.91 \cdot \text{pH}^2$ ($R^2 = 0.794$) (II-C) $t_{50\%}(\text{min}) = 199.27 - 13.98 \cdot [\text{Fe}] - 15.04 [\text{SBO}] + 1.28 [\text{Fe}]^2 + 0.36 [\text{SBO}]^2 + 0.08 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.879$) (III-C)
Acetamidrid	$t_{50\%}(\text{min}) = 966.42 - 83.28 \cdot [\text{Fe}] - 40.02 \cdot [\text{SBO}] - 206.76 \cdot \text{pH} + 1.19 \cdot [\text{Fe}]^2 + 0.91 \cdot [\text{Fe}] \cdot [\text{SBO}] + 12.29 \cdot [\text{Fe}] \cdot \text{pH} + 0.69 \cdot [\text{SBO}]^2 + 1.77 \cdot [\text{SBO}] \cdot \text{pH} + 18.59 \cdot \text{pH}^2$ ($R^2 = 0.981$) (I-D) $t_{50\%}(\text{min}) = 180.38 - 110.88 \cdot \text{pH} + 17.47 \cdot \text{pH}^2$ ($R^2 = 0.946$) (II-D) $t_{50\%}(\text{min}) = 440.30 - 28.18 \cdot [\text{Fe}] - 32.03 [\text{SBO}] + 1.19 [\text{Fe}]^2 + 0.69 [\text{SBO}]^2 + 0.91 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.915$) (III-D)
Clofibric acid	$t_{50\%}(\text{min}) = 242.78 - 40.30 \cdot [\text{Fe}] - 9.39 \cdot [\text{SBO}] - 44.58 \cdot \text{pH} + 1.44 \cdot [\text{Fe}]^2 + 0.13 [\text{Fe}] [\text{SBO}] + 5.70 \cdot [\text{Fe}] \cdot \text{pH} + 0.44 [\text{SBO}]^2 - 2.06 \cdot [\text{SBO}] \cdot \text{pH} + 9.40 \cdot \text{pH}^2$ ($R^2 = 0.971$) (I-E) $t_{50\%}(\text{min}) = 88.28 - 54.22 \cdot \text{pH} + 8.51 \cdot \text{pH}^2$ ($R^2 = 0.907$) (II-E) $t_{50\%}(\text{min}) = 246.10 - 14.80 \cdot [\text{Fe}] - 18.67 [\text{SBO}] + 1.44 [\text{Fe}]^2 + 0.44 [\text{SBO}]^2 + 0.13 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.955$) (III-E)
Caffeine	$t_{50\%}(\text{min}) = 702.53 - 79.39 \cdot [\text{Fe}] - 25.36 \cdot [\text{SBO}] - 147.13 \cdot \text{pH} + 2.02 \cdot [\text{Fe}]^2 + 0.41 [\text{Fe}] [\text{SBO}] + 12.04 \cdot [\text{Fe}] \cdot \text{pH} + 0.50 \cdot [\text{SBO}]^2 + 0.65 [\text{SBO}] \cdot \text{pH} + 12.44 \cdot \text{pH}^2$ ($R^2 = 0.959$) (I-F) $t_{50\%}(\text{min}) = 126.86 - 75.73 \cdot \text{pH} + 11.41 \cdot \text{pH}^2$ ($R^2 = 0.890$) (II-F) $t_{50\%}(\text{min}) = 310.83 - 25.51 \cdot [\text{Fe}] - 22.51 [\text{SBO}] + 2.03 [\text{Fe}]^2 + 0.50 [\text{SBO}]^2 + 0.41 [\text{Fe}] [\text{SBO}]$ ($R^2 = 0.984$) (III-F)

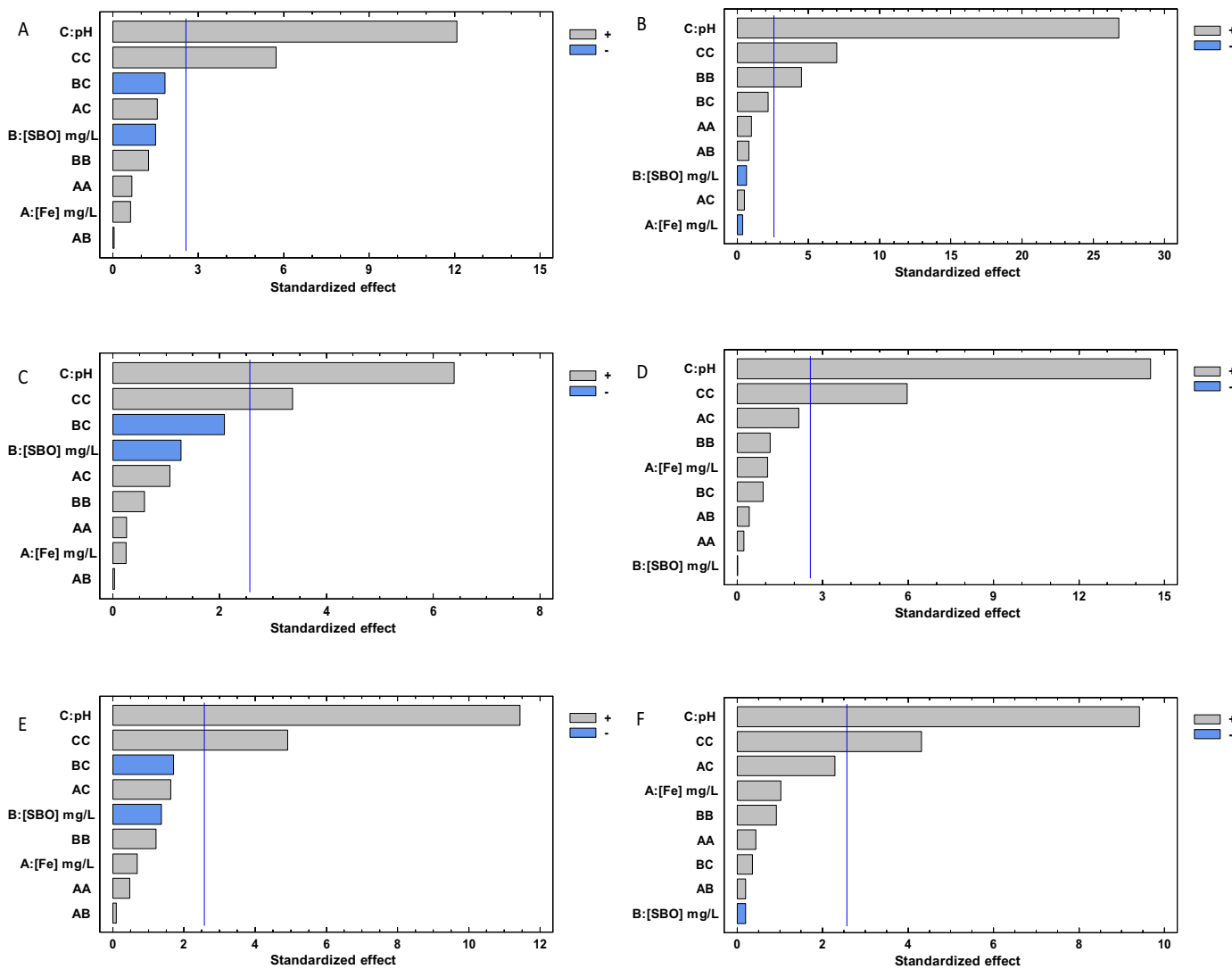


Fig. 3. Pareto charts for the response $t_{50\%}$ (min) obtained for the photo-Fenton degradation of EPs in the presence of SBO. The EPs are carbamazepine (A), acetaminophen (B), amoxicillin (C), acetamidrid (D), clofibric acid (E) and caffeine (F).

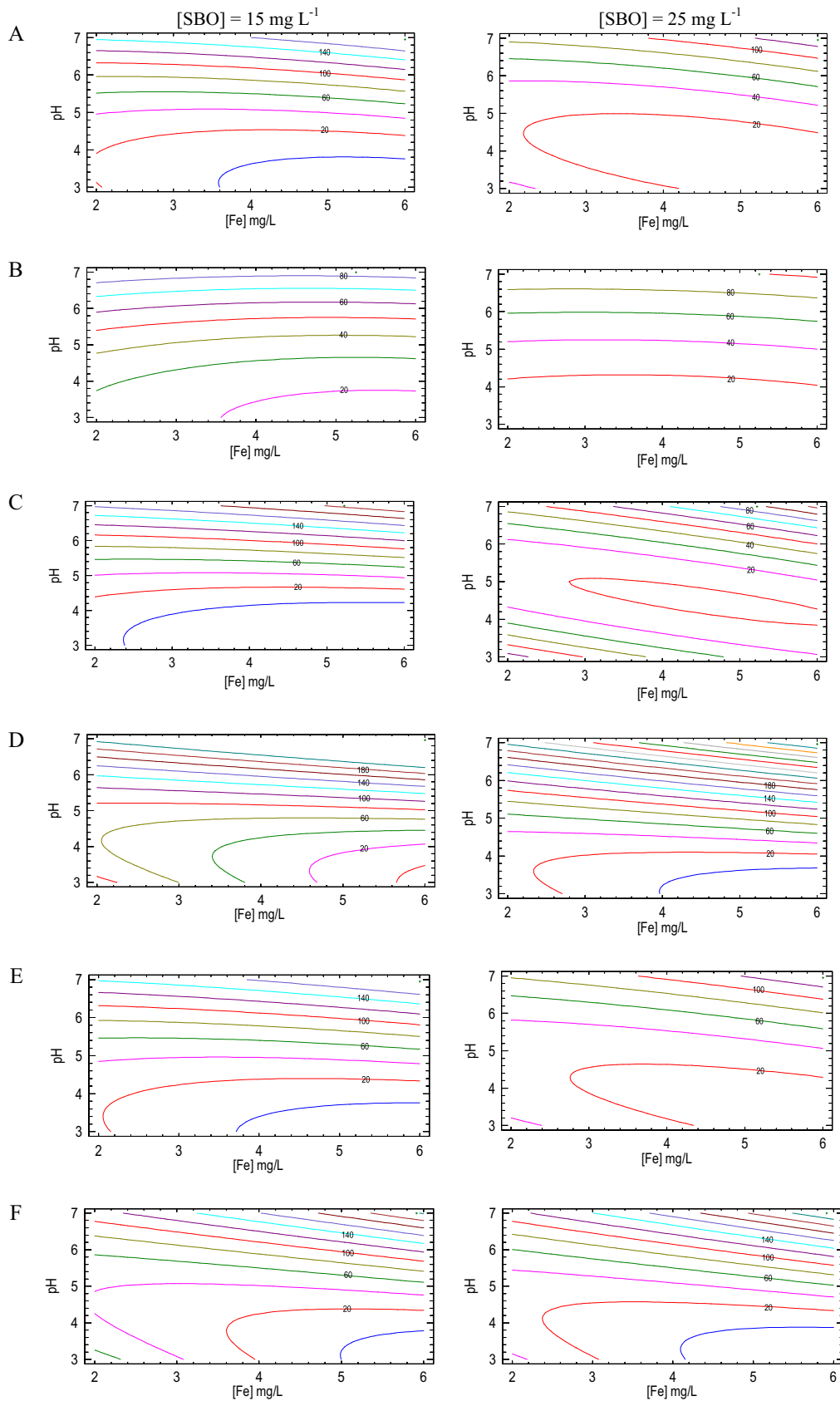


Fig. 4. Contour plots for $t_{50\%}$ (min) obtained for the photo-Fenton degradation of EPs in the presence of SBO. The EPs are carbamazepine (A), acetaminophen (B), amoxicillin (C), acetamiprid (D), clofibrac acid (E) and caffeine (F).

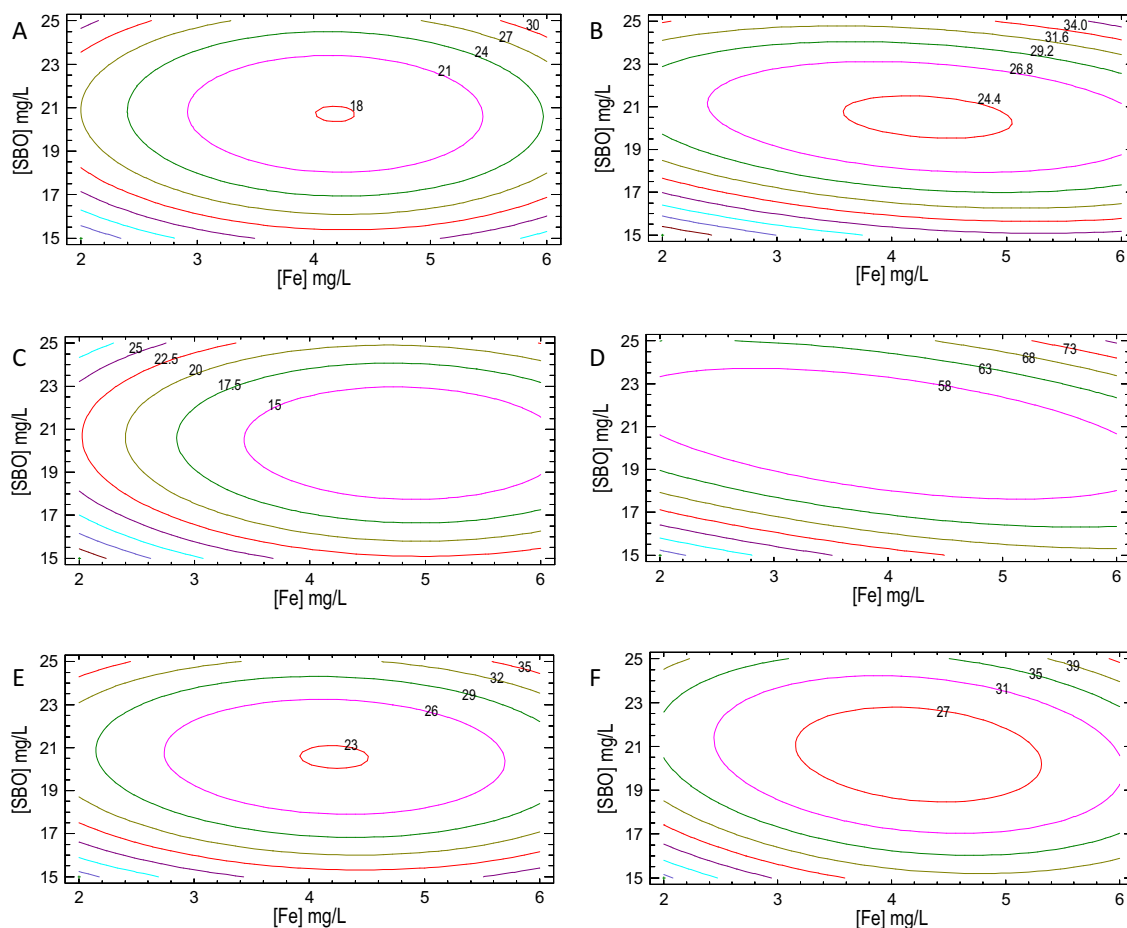


Fig. 5. Contour plots for $t_{50\%}$ (min) obtained for the photo-Fenton degradation of EPs at pH = 5. The EPs are carbamazepine (A), acetaminophen (B), amoxicillin (C), acetamidrid (D), clofibrac acid (E) and caffeine (F).

Fig. 4A shows data obtained for carbamazepine. At low SBO concentration, a fast decrease in the efficiency of photo-Fenton with increasing pH is observed, as the line corresponding to $t_{50\%} = 20$ min can be found at a pH of ca. 4 and that of 60 min at a pH of approximately 5.5. At low pH (below 4) an increase in $[\text{Fe(III)}]$ results in a slight enhancement of the process. This behaviour could be attributed to differences in iron availability: at acidic medium, higher amounts of iron can be kept in solution, what results in a faster degradation reaction; however, above pH = 4, SBOs are not able to prevent efficiently iron precipitation and reaction rate decreases.

In contrast, at the highest SBO concentration (25 mg L^{-1}) a different trend can be found: the loss of efficiency of the process occurs at higher pH, as differences are not acute in the pH range 3–5.5, what suggests that SBOs are useful materials to apply the photo-Fenton reaction at milder pH conditions. Furthermore, the optimum pH shifted to higher values (ca. 4). This might indicate a change in the photo-Fenton mechanism, in which the key species is not only Fe(OH)^{2+} (responsible for the optimal pH value of 2.8), but photoactive iron-SBO complexes might also contribute. Modification of the optimum pH has already been described when species able to modify iron complexation are present. For instance, at high concentration of chloride, photo-Fenton exhibits the best performance at a pH slightly above 3 [21]. In addition, changes in photo-Fenton mechanism at circumneutral values and/or in the presence of chelating agents, such as EDTA [22,23] or citrate [24,25], have been proposed, eventually changing the key species [26]. Interestingly, when ethylenediamine-*N,N'*-disuccinic acid (EDDS)

was used as complexing agent, best results were reached at neutral or even slightly basic medium; this variation was attributed to a completely different mechanism in which superoxide plays a key role [27]. In the case of SBOs, experiments carried out with chemical probes have shown that other species, in addition to $\bullet\text{OH}$ radicals, are responsible for pollutants degradation [8,9].

Results obtained with clofibrac acid (Fig. 4E) and caffeine (Fig. 4F) are very similar to carbamazepine and for these compounds the photo-Fenton reaction showed to be efficient until pH slightly above 5 at $[\text{SBO}] = 25 \text{ mg L}^{-1}$. In fact, previous experiments involving mild photo-Fenton conditions with non-complexed iron or in the presence of humic substances or SBOs have demonstrated that they follow similar behaviour with only quantitative differences. Acetamidrid (Fig. 4D) is the most recalcitrant compound towards the photo-Fenton process [8,9]. This low reactivity results in a poor efficiency of photo-Fenton, which quickly decreases with increasing pH (the line of $t_{50\%} = 60$ min is at pH ca. 5 at low and high SBO concentrations). Amoxicillin, on the other hand, is the most reactive among the EPs towards photo-Fenton and at initial $[\text{SBO}] = 25 \text{ mg L}^{-1}$ shows the highest efficiency at pH = 5 and reaction rate did not decrease significantly until values close to 7 (Fig. 4C). Finally, for acetaminophen (Fig. 4B) a slow but continuous decrease in reaction rate with increasing pH is observed (line $t_{50\%} = 60$ min at pH = 6). In fact, in a previous study [9] this compound has been shown to have a different reactivity in comparison to the other EPs, in which other species than $\bullet\text{OH}$ play an important role.

Based on those results, it could be hypothesised that the presence of SBOs modifies the photo-Fenton mechanism and, although

some differences in the individual behaviour of each EP have been evidenced, the process can be extended, in most cases, at least up to pH=5. Hence it is interesting to determine at this pH value the role of [Fe(III)] and [SBO] in view of optimizing these variables. Contour plots obtained at pH=5 for all six EPs can be observed in Fig. 5; the corresponding fitted equations are shown in Table 2 (cf. Table 2, Eqs. III-A to III-F) (see Supplementary data for the ANOVA tables, Tables T13–T18). In general, an optimum can be found in the region 4–5 mg L⁻¹ of iron and 19–22 mg L⁻¹ of SBO, which should be considered as the best conditions for the removal of the EPs from water by the photo-Fenton process. Under those conditions, *t*_{50%} was ca. 20 min for all EPs, except for amoxicillin (*t*_{50%} < 10 min) and for acetamiprid, which was the most refractory; in fact, acetamiprid was the only compound which did not show a minimum for *t*_{50%} in the studied region.

The behaviour of SBO can be explained by considering that this species is necessary to keep iron in solution and to allow the photo-Fenton process at pH=5. However, beyond a given point the role of SBO might be detrimental because it can act as scavenger of the reactive species, competing with the pollutants, or because of a light screening effect related to its brown colour. In the case of iron, it seems that amounts above 4 mg L⁻¹ play a negative role; this can be attributed to the faster precipitation of iron to form oxides/hydroxides, which, in turn, decrease the photo-Fenton efficiency.

4. Conclusions

SBOs have been demonstrated as useful materials to allow the implementation of the photo-Fenton processes at higher pH values (at least 5). This can be due to the ability of these materials to complex iron, thus avoiding its precipitation as oxides or hydroxides. The surface response methodology enabled to study the effect of iron, SBO and pH on the process. Surface responses obtained at pH=5 showed that optimal conditions of Fe(III) and SBO concentrations were in the range 4–5 mg L⁻¹ and 19–22 mg L⁻¹ respectively. Extending this methodology to other variables (e.g. H₂O₂ concentration) or other compounds is a logical step forward.

Although a mechanistic study for such a complex system falls beyond the aim of this study, our results seem to point to a modification of the photo-Fenton mechanism in which the optimum pH shifts to higher values (in most cases in the range 3–4, slightly above the optimal value described for photo-Fenton, 2.8). Furthermore, some differences in the behaviour of each EP have been identified, which may be explained by their reactivity with the new species formed, whose nature remains to be elucidated. Hence, further research on the mechanistic issues of the process seems meaningful.

Finally, future work is also required to study the process at pH=5 under real sunlight at pilot plant with more realistic aqueous matrices, estimating values such as H₂O₂ consumption, irradiation time or changes in biocompatibility, in order to better assess the real applicability of this methodology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2014.03.034>.

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