APPLICATION OF SOLUBLE BIO-ORGANIC SUBSTANCES (SBO) IN PHOTOCHEMICAL PROCESSES FOR THE DEGRADATION OF SULFADIAZINE CONTAMINATING WATER

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ABSTRACT – Soluble bio-organic substances (SBO) obtained from urban bio-wastes have been investigated as chemical auxiliaries in photochemical processes. For this purpose, photodegradation of the antibiotic sulfadiazine (SDZ) (25 mg L^{-1}) was studied under simulated sunlight. Experiments were performed to check the role of the SBO as additives for the photo-Fenton process ($[SBO]_0 = 20$ mg L^{-1}, $[H_2O_2]_0 = 244$ mg L^{-1}, $[Fe^{3+}]_0 = 5$ mg L^{-1}) at pH 3, 5.2 and 7. The results show that in slightly acidic conditions (pH = 5.2) the SBO improve the photo-Fenton process. Organic compounds present in the SBO are able to complex iron cations and hence, iron precipitation could be avoided. Finally, the results of a Doehlert uniform array design were used to fit a neural network model, which was found to be an effective, simple approach to successfully modeling the photo-Fenton degradation using SBO within the range of experimental conditions. This model might be useful in process optimization.

1. INTRODUCTION

Large amounts of antibiotics have been detected in different aqueous matrices throughout the world. However, some of these pharmaceutical products are not eliminated completely by conventional biological and physicochemical-based treatments in sewage treatment plants. Among them, sulfadiazine (SDZ) is not readily biodegradable and has been frequently detected in drinking water, surface water, groundwater and wastewater from treatment plants (Holm *et al.*, 1995).

Advanced oxidation processes (AOP) are highly promising for the remediation of contaminated aqueous systems; among them the photo-Fenton process has been widely used. The change of pH has significant effects on Fenton reaction and the optimum is around 3 (Pignatello *et al.*, 2006). At higher pH, the system efficiency is decreased since iron ions precipitate as iron hydroxide. This issue is a constraint for the employment of the photo-Fenton process in full-scale operation. Therefore, iron complexation in the presence of organics seem promising for extending the optimum pH range, as reported for humic acids (Gomis *et al.*, 2013).

Soluble bio-organic substances (SBO) obtained from urban bio-wastes have been used as chemical auxiliaries in photochemical processes for environmental remediation (Avetta *et al.*, 2012; Gomis *et al.*, 2013). They contain a significant mineral portion, in particular iron. For this reason, the photo-Fenton process might be driven with these compounds. The purpose of this study is to investigate the role of SBO in photochemical processes for the degradation of SDZ contaminating water. The use of SBO as photosensitizer and as complexing agent to drive photo-Fenton processes at non acid conditions was examined.

2. MATERIALS AND METHODS

Chemicals: SDZ (99%) provided from Sigma-Aldrich was employed to prepare the solutions in distilled water. Solutions of 0.1 mol L^{-1} H_2SO_4 (95-97%) and/or 0.1 mol L^{-1} NaOH (99%) from Sigma-Aldrich was used for initial pH correction. Solution pH was not corrected over time due to the peculiarities of the reactor. As mobile phase for HPLC system, methanol (HPLC quality) and acetic acid (80% v/v) were purchased from Panreac and Scharlau, respectively. Other reagents used were $Fe_2(SO_4)_3.5H_2O$ (75%) and H_2O_2 (30%) acquired from Panreac and furfuryl alcohol (98%) and 2-propanol (99.7%) purchased from Acros Organics and Merck Eurolab, respectively. The SBO, identified by the acronym CVT230 and obtained from urban bio-wastes sampled from the process lines of ACEA Pinerolese waste treatment plant in Pinerolo (Italy) was studied. Actually this SBO is the most soluble and easy to be dissolved in water. The CVT230 has been isolated from home gardening and park trimming residues piles aerated for 230 days and contain a significant mineral portion, in particular iron.

Experimental conditions: Solutions were irradiated with a solar simulator (SUN 2000, ABET Technologies) equipped with a 500 W Xenon Short ARC Lamp and a water filter employed to cut off radiation in the range 280-295 nm. The initial SDZ concentration was 25 mg L^{-1} and the reactions were performed in a 250 mL cylindrical Pyrex vessel under continuous stirring at 30-35 °C. SBO (5-50 mg L^{-1}) was added and reactions were run at pH 3, 5, 5.2 and 7 to check the pH effect on SDZ degradation. In the case of photo-Fenton reactions, concentrations of H_2O_2 higher than the stoichiometric were used ($[H_2O_2]_0/[SDZ]_0$ molar ratio: 2 or $[H_2O_2]_0 = 244$ mg L^{-1}).

High performance liquid chromatography (HPLC): 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 using (B) methanol and (A) acid acetic 1% (v/v) as the mobile phase at 1 mL min^{-1} and room temperature. The injection volume was 30 µL and detection was achieved at 266 nm.

3. RESULTS AND DISCUSSION

3.1. Irradiation of SDZ in the presence of CVT230

The UV-vis absorption spectra of SDZ and CVT230 and the emission spectrum of the Xenon lamp used in this study are shown in Figure 1. The absorption of SDZ solutions at different pH is overlapped with the irradiance of the lamp. Control experiments in the dark showed that SDZ concentration did not change significantly after 48 h, indicating negligible hydrolysis under such conditions.

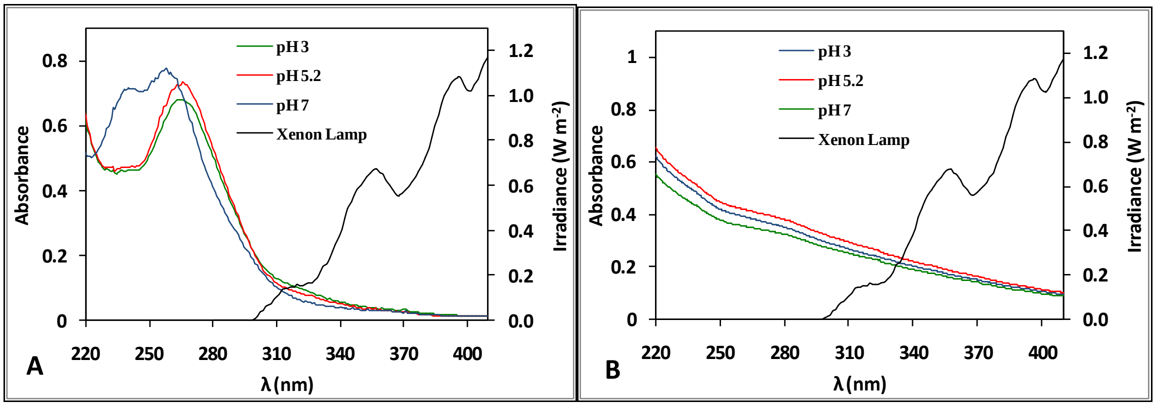

Figure 1 - Emission spectrum of the xenon lamp and UV-vis absorption spectra of (A) SDZ (25 mg L^{-1} and (B) CVT230 (20 mg L^{-1}) at pH 3, 5.2 and 7.

SDZ photolysis was studied using artificial sunlight at different pH (3, 5.2 and 7). Despite the pH value, experiments showed that SDZ concentration decreased when the solutions ($[SDZ]_0$=25 mg L^{-1}) were irradiated. The highest SDZ removal after 180 minutes was 28.4% at pH 7. At pH 3 and 5.2, the percent removals were 17.4% and 26.2%, respectively. SDZ removals followed pseudo first-order kinetics with rate constants of 0.5×10^{-3} (R^2=0.960), 1.7×10^{-3} (R^2=0.989) and 1.9×10^{-3} (R^2=0.996) min^{-1} for pH 3, 5.2 and 7, respectively.

Another series of experiments was performed to investigate the role of CVT230 (20 mg L^{-1}) on SDZ photolysis (25 mg L^{-1}) at different pH (3, 5.2 and 7). The highest antibiotic degradation after 180 minutes in the presence of CVT230 was 26.5% at pH 7 with pseudo first-order rate constant of 1.2×10^{-3} (R^2=0.992). The percent removals at pH 3 and 5.2 were 19.7% and 21.2%, respectively. In all cases SDZ decay followed a pseudo first-order behavior with rate constants of 0.7×10^{-3} (R^2 = 0.988) and 0.9×10^{-3} (R^2 = 0.997) min^{-1} for pH solutions of 3 and 5.2, respectively.

The presence of CVT230 was irrelevant towards SDZ photodegradation. Similar results were obtained by other authors who reported this effect for the photolysis of emerging pollutants mixed in solution in the presence of humic acid (20 mg L^{-1}), which can be attributed to the light screening effect (Carlos *et al.*, 2012). However, other processes like the scavenging of generated reactive species by SBO and/or the formation of photoactive complexes between SBO and SDZ should be considered (Gomis *et al.*, 2013). For this reason, the real applicability of SBO as solar photocatalysts might be unattractive. However they might be of interest as Fenton additives at slightly acid conditions.

3.2. Photo-Fenton process in the presence of CVT230

Different experiments were performed to check the possible use of CVT203 as Fenton additive, as shown in Table 1 and Figure 2. In order to obtain more quantitative data, the photodegradation of SDZ was fitted in all cases to a pseudo first-order law and the rate constant was calculated. This simple model can be used for comparison purposes only owing to other factors that need to be evaluated considering the complexity of the reactions involved.

Table 1 – Pseudo first-order rate constants (k×10^3 min^{-1}) for SDZ photodegradation under different conditions ($[SDZ]_0$ = 25 mg L^{-1}, $[CVT230]_0$ = 20 mg L^{-1}, $[Fe^{3+}]_0$ = 5 mg L^{-1}, $[H_2O_2]_0$ = 244 mg L^{-1})

Conditions (without CVT230)	**pH 3**	**pH 5.2**	**pH 7**
UV-vis	0.5	1.7	1.9
UV-vis/H_2O_2	2.9	3.2	1.1
UV-vis/H_2O_2/Fe^{3+}	89.4	9.7	2.8
Conditions (with CVT230)	**pH 3**	**pH 5.2**	**pH 7**
UV-vis/SBO	0.7	0.9	1.2
UV-vis/SBO/H_2O_2	26.1	7.0	3.1
UV-vis/SBO/H_2O_2/Fe^{3+}	151.2	32.5	5.5

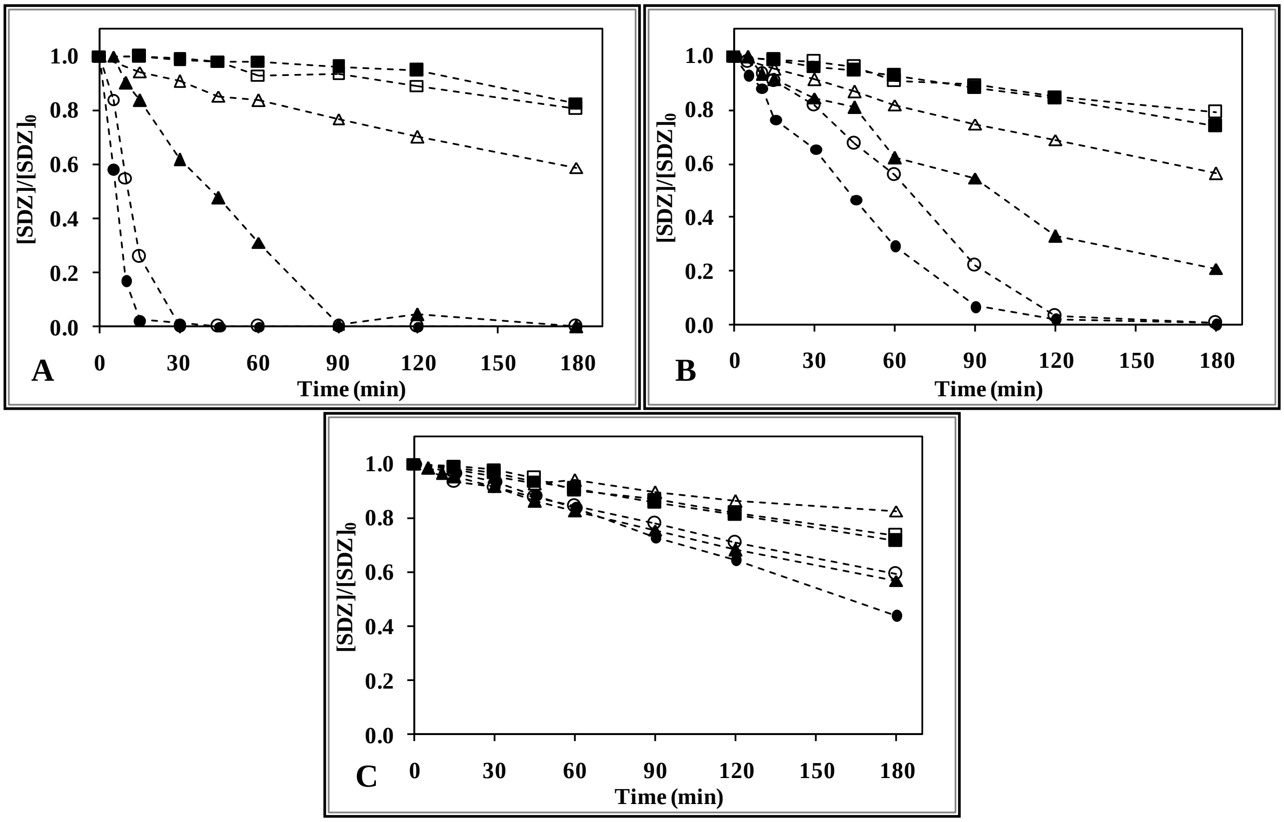

Figure 2 - SDZ removal by different processes ($[SDZ]_0$ = 25 mg L^{-1}, $[CVT230]_0$ = 20 mg L^{-1}, $[Fe^{3+}]_0$ = 5 mg L^{-1}, $[H_2O_2]_0$ = 244 mg L^{-1}) at: (A) pH = 3; (B) pH = 5.2 and (C) pH = 7. (■) UV-vis, (□) UV-vis/SBO, (Δ) UV-vis/H_2O_2, (▲) UV-vis/SBO/H_2O_2, (○) UV-vis/H_2O_2/Fe^{3+}, (●) UV-vis/SBO/H_2O_2/Fe^{3+}.

At pH 5.2 and 7, experiments with the Fenton reagent without SBO have scarce effect on SDZ degradation, compared with pH 3. However, photo-Fenton degradation of SDZ is faster than in the case of photolysis at all conditions. Additionally, except for pH 3, the use of H_2O_2 was irrelevant towards SDZ photodegradation. In contrast, when SBO were present in the photo-Fenton process, the reaction rate was greatly enhanced at all pH values. This behavior could be due to the complexation of iron by SBO at pH 5.2 and 7. Recently, Gomis *et al.* (2012) studied the applicability of SBO in the photobleaching of crystal violet solutions, a cationic dye. They observed that the presence of CVT230 greatly improved the rate of reaction in the case of the photo-Fenton process and explain that iron ions can be complexed by the SBO at pH 7. Despite the pH value, the extent of SDZ degradation was higher for the UV-vis/SBO/H_2O_2/Fe^{3+} process as compared to UV-vis, UV-vis/H_2O_2, UV-vis/SBO, UV-vis/SBO/H_2O_2 and UV-vis/H_2O_2/Fe^{3+}, as shown in Figure 2.

3.3. PHOTODEGRADATION OF SDZ IN THE PRESENCE OF RADICAL SCAVENGERS

To gain a better understanding about the nature of the reactive species formed, radical scavengers can be added to the reaction mixture. Alcohols such as *n*-butanol and *2*-propanol are well-known $^\bullet$OH radical scavengers (Vione *et al.*, 2001) and furfuryl alcohol is a trapping agent of singlet oxygen (Haag *et al.*, 1984). For this purpose, solutions of SDZ containing the Fenton reagent and CVT230 were irradiated in the presence of either *2*-propanol or furfuryl alcohol at pH 5.2.

In our case, the presence of *2*-propanol (20 mM) resulted in 40.5% SDZ removal after 180 minutes and a pseudo first-order rate constant of 2.8×10^{-3} min^{-1}; the corresponding values in the presence of furfuryl alcohol (1 mM) were 27.3% and 1.9×10^{-3} min^{-1}. In the absence of these scavengers, SDZ removal was 99.6% and occurred with a rate of 32.5×10^{-3} min^{-1}. Figure 3 shows that addition of these scavengers has a noticeable effect on SDZ removal. However, the inhibition was slightly more pronounced with furfuryl alcohol suggesting that SDZ degradation proceed by a singlet oxygen mechanism, fundamentally. Nevertheless, the attack of $^\bullet$OH radicals cannot be ruled out.

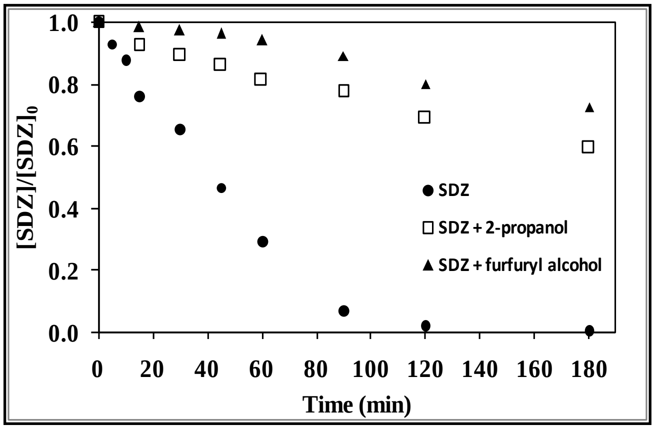

Figure 3 - Scavenging experiments ($[SDZ]_0$= 25 mg L^{-1}, $[CVT230]_0$ = 20 mg L^{-1}, $[Fe^{3+}]_0$ = 5 mg L^{-1}, $[H_2O_2]_0$ = 244 mg L^{-1}, $[2\text{-propanol}]_0$= 20 mM, $[\text{furfuryl alcohol}]_0$ = 1 mM, pH 5.2).

3.4. NEURAL NETWORKS

A Doehlert uniform array design was used to detail the effects of $[Fe^{3+}]_0$, $[SBO]_0$ and pH by means of 15 experiments. The results of this design were used to fit a neural network (NN) model with three-layer feed-forward, sigmoidal response function and 7 hidden layers. The input variables were $[Fe^{3+}]_0$ (1-15 mg L^{-1}), $[SBO]_0$ (5-50 mg L^{-1}), pH (3, 5 and 7) and $[H_2O_2]_0$ (61 and 244 mg L^{-1}). The model enabled to predict the relative SDZ concentration at a given irradiation time with $R^2 > 0.97$. The whole set of experimental data consisted of 300 input-output data pairs, of which 75% was used in the training procedure.

The model shows similar effects of $[Fe^{3+}]_0$, $[SBO]_0$ and $[H_2O_2]_0$ on SDZ removal, while the effect of pH was almost four times higher. Simulations of selected experiments of the Doehlert design confirm the good agreement between experimental and predicted $[SDZ]/[SDZ]_0$ values, as shown in Figure 4.

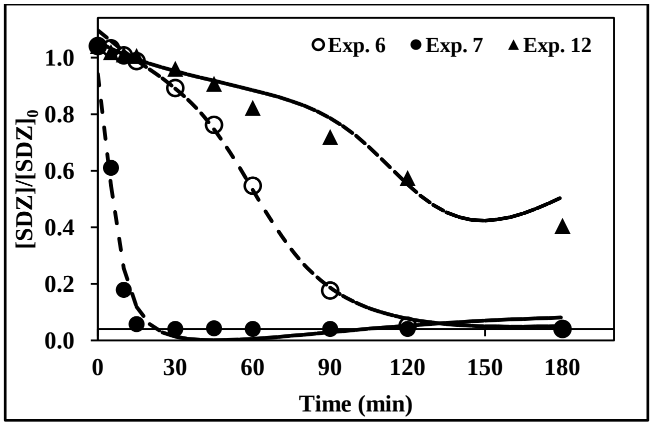

Figure 4 - Comparison between experimental and predicted $[SDZ]/[SDZ]_0$ values. Experimental conditions for: Exp. 6 ($[CVT230]_0$ = 5 mg L^{-1}, $[Fe^{3+}]_0$ = 4.5 mg L^{-1}, pH 5); Exp. 7 ($[CVT230]_0$ = 20 mg L^{-1}, $[Fe^{3+}]_0$ = 4.5 mg L^{-1}, pH 3) and Exp. 12 ($[CVT230]_0$ = 35 mg L^{-1}, $[Fe^{3+}]_0$ = 4.5 mg L^{-1}, pH 7); at $[SDZ]_0$= 25 mg L^{-1} and $[H_2O_2]_0$ = 244 mg L^{-1}.

4. CONCLUSIONS

In this study, the real applicability of CVT230 as solar photocatalyst might be unattractive. However, the use of this SBO as Fenton additive has a remarkable influence in SDZ photodegradation at slightly acid conditions (pH 5.2). In the presence of radical scavengers, SDZ inhibition was slightly more pronounced with furfuryl alcohol suggesting that antibiotic degradation proceed by a singlet oxygen mechanism, fundamentally. The neural network model fitted to experimental data was able to reproduce the complexity of the photo-Fenton reaction in the presence of SBO.

5. REFERENCES

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