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Photo-Fenton degradation of phenol, 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol mixture in saline solution using a falling-film solar reactor

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In this work, a saline aqueous solution of phenol, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP) was treated by the photo-Fenton process in a falling-film solar reactor. The influence of the parameters such as initial pH (5–7), initial concentration of Fe^{2+} (1–2.5 mM) and rate of H_2O_2 addition (1.87–3.74 mmol min^{-1}) was investigated. The efficiency of photodegradation was determined from the removal of dissolved organic carbon (DOC), described by the species degradation of phenol, 2,4-D and 2,4-DCP. Response surface methodology was employed to assess the effects of the variables investigated, i.e. [Fe^{2+}], [H_2O_2] and pH, in the photo-Fenton process with solar irradiation. The results reveal that the variables' initial concentration of Fe^{2+} and H_2O_2 presents predominant effect on pollutants' degradation in terms of DOC removal, while pH showed no influence. Under the most adequate experimental conditions, about 85% DOC removal was obtained in 180 min by using a reaction system employed here, and total removal of phenol, 2,4- and 2,4-DCP mixture in about 30 min.

Keywords: photo-Fenton; phenol; dichlorophenoxyacetic acid; 2,4-dichlorophenol; sunlight; falling-film reactor

1. Introduction

2,4-Dichlorophenoxiacetic acid (2,4-D) is a systemic herbicide widely spread in Brazilian agriculture.[1] Several data have been issued about the toxicity of the herbicide 2,4-D, its salts and esters, which are classified as harmful substances in countries such as the USA and New Zealand.[2–4] 2,4-D (CAS 94-75-7) is produced by condensation of MCA (monochloroacetic acid, CAS 79-11-8) and 2,4-DCP (2,4-dichlorophenol, CAS 120-83-2) in alkaline medium. Reagents in excess, by-products and impurities formed in the condensation are accumulated in an alkaline aqueous waste. This raw effluent contains phenol (500–600 mg L^{-1}), 2,4-DCP (800–1200 mg L^{-1}) and 2,4-D (600–800 mg L^{-1}) in a solution highly saline (about 60 g L^{-1} of NaCl) and alkaline.[5] These three organic compounds have biocide action and when combined in high concentration can inhibit the microbial growth in biological treatment systems. Oxidation processes catalysed by Fe(II)/Fe(III) ions (Fenton and photo-Fenton) have been applied in the removal of several pollutants. These processes have shown to be of remarkable interest in the degradation of phenol under sunlight,[6] herbicides such as tebuthiuron, diuron and 2,4-D under artificial UV light [7] and 2,4-D, 2,4-DCP and phenol mixture under artificial UV light.[5] In the presence of chloride ions, the photo-Fenton reaction is inhibited when in acid pH, due to the combination of the competitive complexation of Fe^{3+} by Cl^{-1} and pH-dependent scavenging of the HO by Cl^{-1} ions.[8] Luna et al. [5,9] conducted experiments involving photochemical degradation of 2,4-D, 2,4-DCP and phenol mixture in the presence of high concentration of NaCl and observed that the pH 7 is the more adequate initial condition to develop the pH-independent photodegradation of this mixture. The mechanisms for the degradation of phenol, 2,4-D and 2,4-DCP by photo-Fenton reactions [10–12] and other advanced oxidative processes [13–15] have been previously reported in the literature. The rising development of Fenton-like processes to the total oxidation of herbicides can be attributed to its economical importance for many countries, and also because of its wide applicability to control weeds in sugar cane and crops.[16–20] The photo-Fenton process is much useful for the abatement of organic compounds of hard degradation, mainly when it is photo-irradiated by UV light and initial pH is of around 3. For UV–Vis light, $Fe^{2+}/Fe^{3+}/C_2O_4^{2-}$ systems have demonstrated the best results.[21] However, at the best of our knowledge, there are no reports in the literature concerning the photo-Fenton degradation of an alkaline saline solution containing phenol, 2,4-DCP and 2,4-D under sunlight in a

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*Corresponding author. Email: osvaldo@eq.ufrn.br falling-film reactor. In countries such as Brazil where sunlight is very abundant and herbicide industries represent an important economical activity, sun-based photochemical oxidation can be considered in order to treat in an efficient manner and at a low cost, herbicide-contaminated wastewater.

In this context, the aim of this work was to investigate the photo-Fenton degradation of an alkaline solution of phenol, 2,4-DCP and 2,4-dichlorophenoxyacetic (2,4-D) acid in medium of high salinity using a falling-film solar reactor. The influence of initial pH and concentrations of hydrogen peroxide and Fe^{2+} on the degradation process was investigated. The removal of dissolved organic carbon (DOC) content as well as concentrations of phenol, 2,4-DCP and 2,4-D were monitored and used for the process evaluation.

2. Experimental

2.1. *Materials*

All materials were used as received without further purification. Phenol (>99.5%), 2,4-DCP (98%) and 2,4-D (98%) were purchased from Sigma-Aldrich. H_2SO_4, NaOH and Hydrogen peroxide (H_2O_2, 30%) were all purchased from Merck. Distilled water was used throughout this study.

2.2. *Reactor*

Experiments of degradation of 2,4-D and precursors were performed in a falling-film solar reactor (Figure 1) that consisted of a stainless-steel plate surface, connected to a stirred tank of polypropylene (15 L). The plate surface was fitted with a 4-mm thick borosilicate glass cover, which served to avoid evaporation of the reaction medium during the experiments. The irradiated area was 0.437 m^2 with dimensions of 95 cm (length) and 46 cm (width). In Natal City, Brazil (latitude 5°47′7″S and longitude 35°11′13″W), the reactor was mounted on a fixed platform inclined 15° from ground and faced North. The additional 10° increment of the inclination above the latitude proved to be necessary to obtain an adequate draining of the film.[22] The reaction mixture was circulated through a centrifugal pump of 0.5 CV (trademark DANCOR) placed between the photochemical reactor and the stirred tank. The system was used to treat an alkaline synthetic effluent containing phenol (580 mg L^{-1}), 2,4-DCP (1000 mg L^{-1}) and 2,4-D (700 mg L^{-1}). This solution was prepared in alkaline pH, which is the natural pH found in real wastewater produced by herbicide industry.

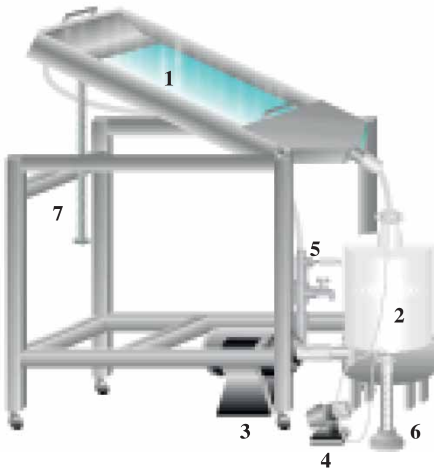

Figure 1. The photochemical system: (1) falling-film solar reactor, (2) stirred tank, (3) centrifuge pump 0.5 CV, (4) peristaltic pump, (5) system of sampling, (6) hydrogen peroxide vessel and (7) regulator screw of slope.

2.3. *Procedure and analysis*

In order to perform each run, 10 L of the pollutant solution was poured into the system and then NaCl was dissolved in a concentration of 60 g L^{-1}. With the salt completely dissolved, ferric sulphate was added to get the desired initial concentration of Fe^{2+} (1, 1.75 or 2.5 mM). Immediately, the reactor was closed with the glass cap and covered with a dark bulkhead to prevent the action of the light before the desired moment. Sulphuric acid and sodium hydroxide were used to set the initial pH (5.0, 6.0 or 7.0). After the pH had been set, the first sample was withdrawn and then the bulkhead was taken off to irradiate the system. At the same time, 500 mL of hydrogen peroxide solution (225, 337 and 449 mM) was fed continuously to the stirred tank through the peristaltic pump (4.16 mL min^{-1}) during the first two hours of reaction. Since hydrogen peroxide was added to the system during 120 min of reaction time, the equivalent feeding rate ($F_{H_2O_2,\,in}$) was calculated to be 1.87, 2.80 and 3.74 mmol min^{-1} of H_2O_2. The concentrations of hydrogen peroxide used in this work were according to the reaction in stoichiometry, as described by Luna et al.[5] During the reaction, the pH was monitored and samples of 2 mL were withdrawn for DOC. In all DOC-samples was added 2 mL of a quenching solution containing equal quantities of $NaSO_3$, KI and NaOH. This solution is added to break the oxidation reaction and to precipitate the iron, and 3 mL of distilled water to complete a total volume of 7 mL. Then, the samples were filtered to separate the precipitated iron and sent to the DOC analysis. The photocatalytic experiments under sunlight were carried out in sunny days between 10:00 am and 13:30 pm during the month of April at Natal City, located in a Northeastern state in Brazil. January is the warmest month in Natal City, with temperature mean maxima of 31°C and minimum of 24°C, while July is mild with temperature mean maxima of 27°C and minimum of 22°C. The intensity of solar light was supplied by the Brazilian Institute of Space Research, and varied between 300 and 800 W m^{-2} during the experiments.

The DOC was determined using a Shimadzu Total Organic Carbon analyser (Shimadzu 5000A). Phenol, 2,4-D and 2,4-DCP were measured by high-performance liquid chromatography (Shimadzu model FCV-10AL VP).

Experimental data were statistically analysed and correlated by an empirical polynomial equation. The total degree of photochemical degradation was calculated based on the DOC per cent removal rate, according to the expression: $\%REM = (DOC_0 - DOC_t)/DOC_0$, where DOC_0 and DOC_t are the concentrations of the initial dissolved organic carbon and at reaction time t, respectively.

Table 1. Levels of variables in the experiments.

Levels	$[Fe^{2+}]_0$ (mM)	$F_{H_2O_2,\mathrm{in}}$ (mmol min^{-1})	pH_0
(−1)	1.00	1.87	5.0
Central point (0)	1.75	2.80	6.0
(+1)	2.50	3.74	7.0

2.4. *Experimental design*

A factorial design was proposed to evaluate the most relevant variables in order to obtain a model that can describe the removal percentage of DOC of the reaction under study. An experimental planning 2^3 was carried out, corresponding to eight experiments according to the limits established and three central points or repetitions. The levels of these variables are shown in Table 1.

3. Results and discussion

Preliminary experiments were performed to degrade the phenol/2,4-D/2,4-DCP mixture in saline medium in the photolysis, sunlight/H_2O_2 and sunlight/Fe^{2+} processes, at an initial pH ranging from 5 to 7. These processes resulted in a low consumption of organic matter with a carbon removal rate of about 10–15%, after 180 min of reaction. Blank experiments (Fenton reaction) were also carried out in the dark. The use of H_2O_2/Fe^{2+} in the absence of solar irradiation resulted in a maximum carbon removal of about 33%, after 180 min of reaction. A higher degradation of the phenol/2,4-D/2,4-DCP mixture as well as a higher removal of organic carbon were only observed with the simultaneous presence of sunlight/H_2O_2/Fe^{2+}, i.e. photo-Fenton process. The results of the phtoto-Fenton process are presented and discussed in more details in this section.

The factorial design showed in Table 1 was carried out and the results of DOC removal and pH profile as function of time are presented in Figures 2 and 3. Figure 2(a) and 2(b) presents the results obtained in the experimental conditions developed at the lower level of hydrogen peroxide

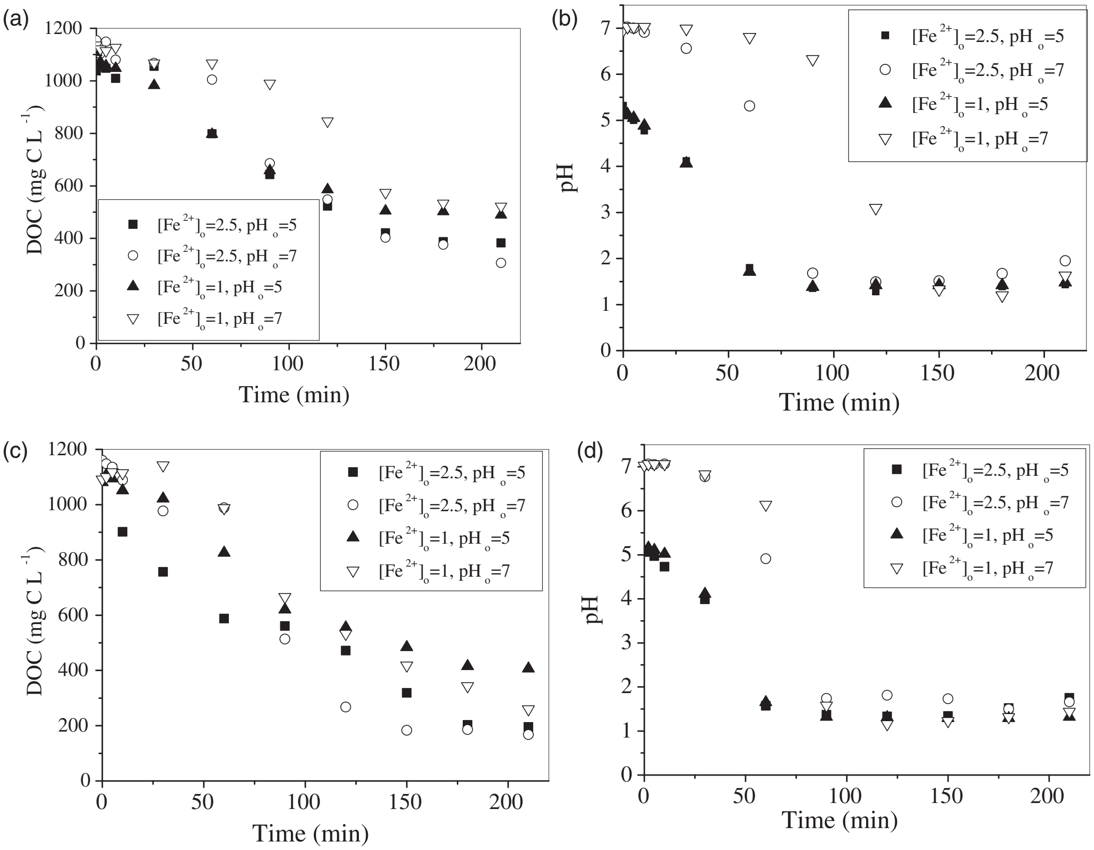

Figure 2. DOC-time and pH-time profiles for the photodegradation of phenol/2,4-D/2,4-DCP mixture carried out in the lower level of hydrogen peroxide flowrate ($F_{H_2O_2,\mathrm{in}} = 1.87$ mmol min^{-1}) (a and b); and higher level of hydrogen peroxide flowrate ($F_{H_2O_2,\mathrm{in}} = 3.74$ mmol min^{-1}) (c and d).

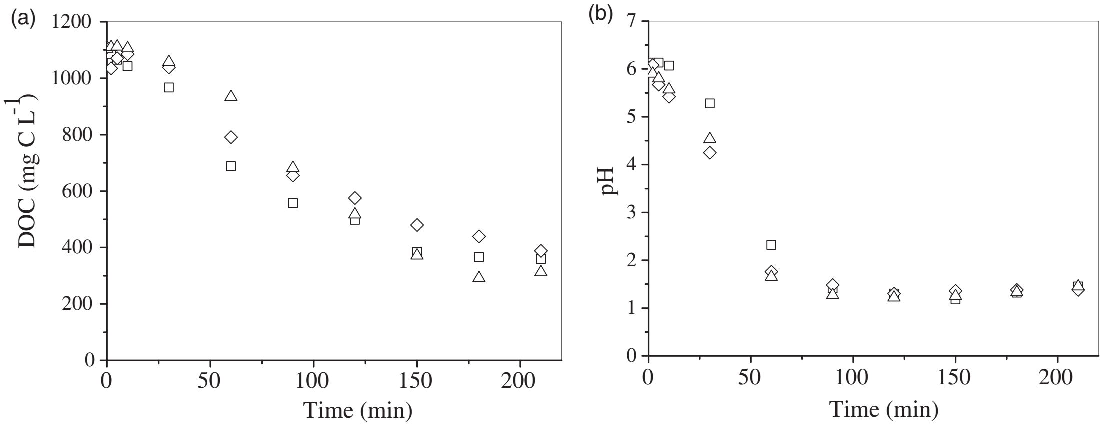

Figure 3. DOC-time (a) and pH-time (b) profiles for the photodegradation of phenol/2,4-D/2,4-DCP mixture for the three repetitions of the central point; $[Fe^{2+}] = 1.75$ mM, $F_{H_2O_2,\,in} = 2.80$ mmol min^{-1} and $pH_0 = 6$.

flowrate ($F_{H_2O_2,\,in} = 1.87$ mmol min^{-1}), while Figure 2(b) and 2(c) shows the behaviour at the highest level of hydrogen peroxide flowrate ($F_{H_2O_2,\,in} = 3.74$ mmol min^{-1}). In all experimental conditions, a significant removal of DOC, with values ranging from 53% to 85%, in 180 min of reaction was observed. It was observed that after 180,min of reaction, the removal of DOC decreased slightly with respect to time. It can be seen that the greatest reductions of DOC occurred with the highest level of ferrous concentration, i.e. $[Fe^{2+}] = 2.5$ mM. In these conditions, about 60–67% of DOC removal with the lowest level of hydrogen peroxide concentration ($F_{H_2O_2,\,in} = 1.87$ mmol min^{-1}) was obtained (Figure 2(a)), and about 85% of removal with the highest level of hydrogen peroxide concentration ($F_{H_2O_2,\,in} = 3.7$ mmol min^{-1}) (Figure 2(c)). In Figure 2(b) and 2(d), a significant decay of pH values as function of time, followed by a stable behaviour can be observed. The final values of pH were between 1 and 2.5. Similar behaviour was also observed by Luna et al.,[5] from photochemical oxidation of phenol/2,4-D/2,4-DCP mixture, treated by the photo-Fenton process in a system composed of an annular reactor with a medium-pressure Mercury lamp (450 W). This reduction in pH occurs possibly due to the formation of organic intermediates acids.[8] It is known that the photo-Fenton process occurs only at acid pH, around 3.[23,24] The initial pH conditions studied in this work were 5–7. However, it was observed that the removal of DOC occurred at values of pH even before 3. This occurred probably by thermal effect on the direct reaction between the hydrogen peroxide and the organic compounds. In conditions of higher concentration of ferrous ions ($[Fe^{2+}] = 2.5$ mM) and initial pH of 5, the pH profile presented a decay more pronounced in comparison with the other experimental conditions studied, stabilizing after a much faster time. The presence of higher amounts of ferrous ions in the solution promotes the formation of more reactive species HO, which are desirable to degrade the phenol/2,4-D/2,4-DCP mixture.

Table 2. Results of carbon removal (% REM 120) from the 2^3 full factorial experimental design.

Experiment	Levels of normalized variables			REM 120 (%) 120 min
	$[Fe^{2+}]_0$	$F_{H_2O_2,\,in}$	pH_0	
1	1	–1	–1	49.57
2	1	1	–1	64.29
3	1	–1	1	52.50
4	1	1	1	76.93
5	–1	–1	–1	47.05
6	–1	1	–1	48.62
7	–1	–1	1	45.43
8	–1	1	1	51.17
9	0	0	0	49.20
10	0	0	0	53.48
11	0	0	0	55.25

Figure 3 presents the profiles of DOC removal and pH as function of time for the three repetitions of the central point, $[Fe^{2+}]_0 = 1.15$, $F_{H_2O_2,\,in} = 2.80$ and $pH_0 = 6.0$. Under these experimental conditions were also observed a significant DOC removal and a decay of pH as function of time. From Figure 4, it can be seen that there was good reproducibility of experimental runs, with similar behaviour for the DOC removal and pH decay for the three repetitions. The maximum standard deviation observed for the DOC removal was about 10%, calculated according to the values for three repetitions of the central point as shown in Table 2.

Table 2 shows the results of organic carbon removal for the reaction time of 120 min from the 2^3 full factorial experimental design.

The effect of each variable was calculated and presented in a Pareto chart in order to evaluate the effects and interactions on 120 min of reaction (Figure 4(a)). From Figure 4(a), it can be seen that Fe^{2+} and hydrogen peroxide concentrations showed the most significant effects. In the present study, initial pH shows no effect on the carbon removal. The interaction effect $[Fe^{2+}]_0 \times pH_0$, $F_{H_2O_2,\,in} \times pH_0$ and

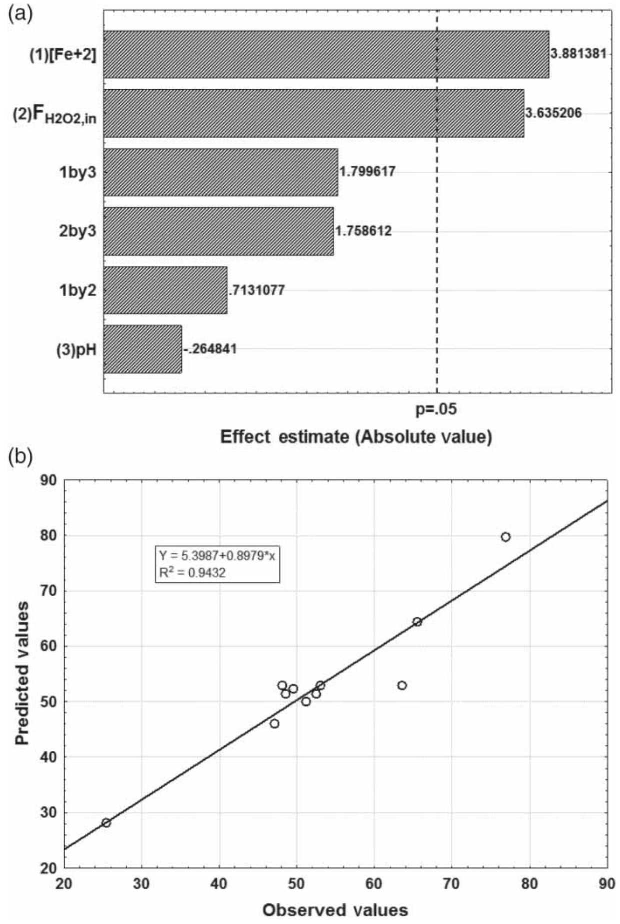

Figure 4. (a) Pareto chart obtained by factorial design 2^3, for carbon removal at 120 min in photo-Fenton process under sunlight and (b) experimental versus predicted (model) values of REM 120 (%).

$[Fe^{2+}]_0 \times F_{H_2O_2,\,in}$ also showed no statistical significance and were therefore considered negligible.

Based on these results, an empirical model was developed to predict the removal percentage of organic carbon in 120 min of reaction time (REM 120) in the photo-Fenton process using the falling-film solar reactor. The correlation was applied at 120 min due to the fact that it was the last time that hydrogen peroxide was added into the reaction medium. The empirical model, Equation (1), was obtained with the experimental data shown in Table 2. The experimental data and the predicted values obtained from Equation (1) are given in Figure 4(b). The obtained correlation coefficient was 0.9432, indicating a good agreement between the experimental and predicted data of organic carbon removal. Furthermore, Equation (1) was also used to build response surface plot presented in Figure 5.

$$\begin{aligned}(\%)\,\text{REM }120 = 47.38 \pm 1.98 + (2.56 \pm 2.32)[Fe^{2+}]_0 \\ + (1.99 \pm 2.32)F_{H_2O_2,\,in}.\end{aligned} \tag{1}$$

The effect of each significant variable of the photodegradation process can be observed in Figure 5. The carbon removal increases proportionally with the concentrations of Fe^{2+} and hydrogen peroxide. This indicates that the highest percentage of organic carbon removal can be obtained at 2.5 mM of $[Fe^{2+}]_0$ and 3.74 mmol min^{-1} of $F_{H_2O_2,\,in}$.

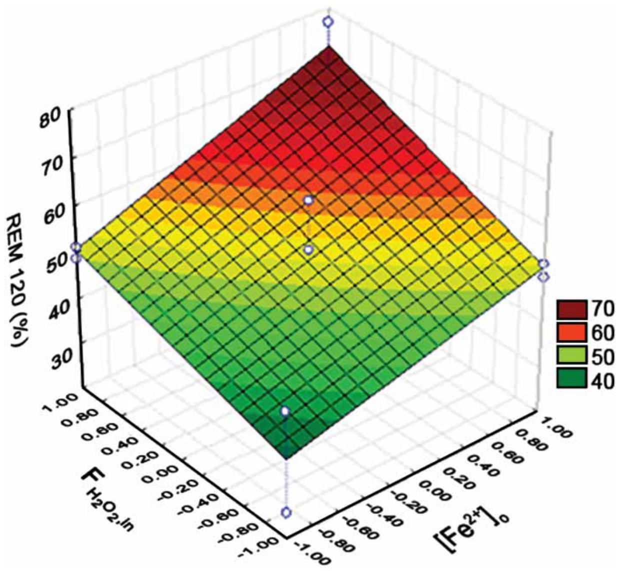

Figure 5. Response surface of empirical model for carbon removal at 120 min of reaction in photo-Fenton process under sunlight.

The analysis of the pollutant concentration for the individual species phenol, 2,4-DCP and 2,4-D was also expressed in terms of residual carbon, and allowed its comparison with profiles of DOC for each experimental condition of reaction. Figure 6 shows the profiles of DOC and pollutants' removal corresponding to experiments performed in the limits –1 and 1. Figure 7 shows the results for the three repetitions in central point. DOC values shown in Figures 6 and 7 are the same as those shown in Figures 2 and 3. It can be seen that in all experimental conditions studied in this work, all three pollutants phenol, 2,4-DCP and 2,4-D are completely degraded, while some extents of DOC remain in the solution after 240 min of reaction. Therefore, at 240 min of reaction yet there is no complete conversion of the organic matter to water, carbon dioxide and other inorganic species. It is known that the rate of organic carbon reduction is remarkably slower than that of the organic pollutant molecules.[25–27] In all experimental conditions tested in this work, it was observed that pollutants phenol, 2,4-DCF and 2,4-D were completely degraded in reaction times over 90 min, except for the conditions shown in Figure 6(h), where complete degradation of these pollutants occurred in about 30 min. Thus, the most favourable conditions for the complete degradation of the three pollutants investigated in this work were: $[Fe^{2+}] = 2.5$ mM, $F_{H_2O_2,\,in} = 3.74$ mmol min^{-1} and pH = 5. From Figure 7, it is observed that the removal behaviour of the three pollutants is similar for the three repetitions in central point. It can also be observed that complete removal of the three

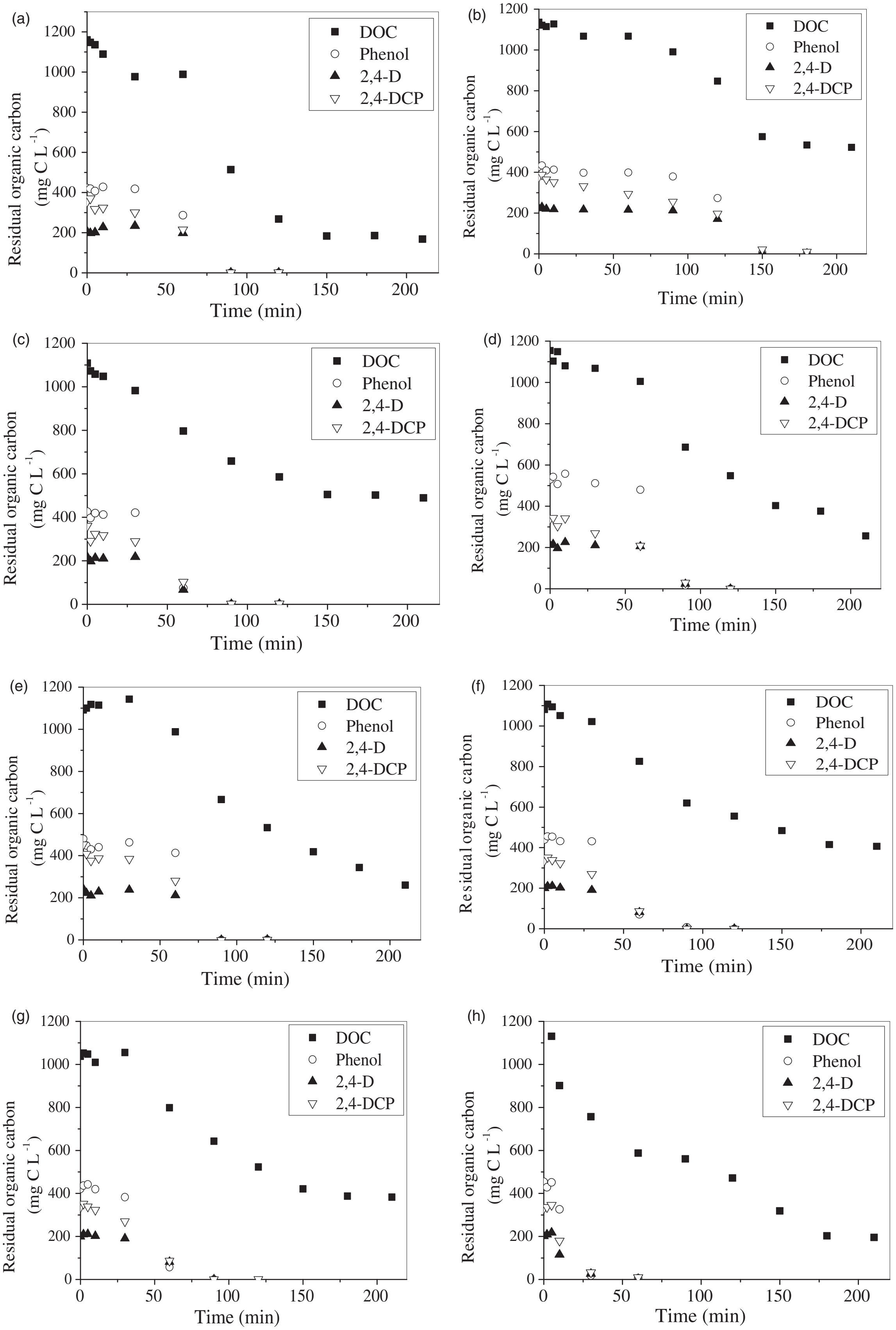

Figure 6. DOC and phenol, 2,4-D and 2,4-DCP concentration–time profiles from the experiments corresponding to the limits –1 and 1 of the 2^3 factorial design, considering the following sequence of values of the variables $[Fe^{2+}]_0$ (mM), $F_{H_2O_2,\,in}$ (mmol min^{-1}) and pH_0: (a) 2.5, 4.74, 7; (b) 1, 1.87, 7; (c) 1, 1.87, 5; (d) 2.5, 1.87, 7; (e) 1, 3.74, 7; (f) 1, 3.74, 5; (g) 2.5, 1.87, 5 and (h) 2.5, 3.74, 5.

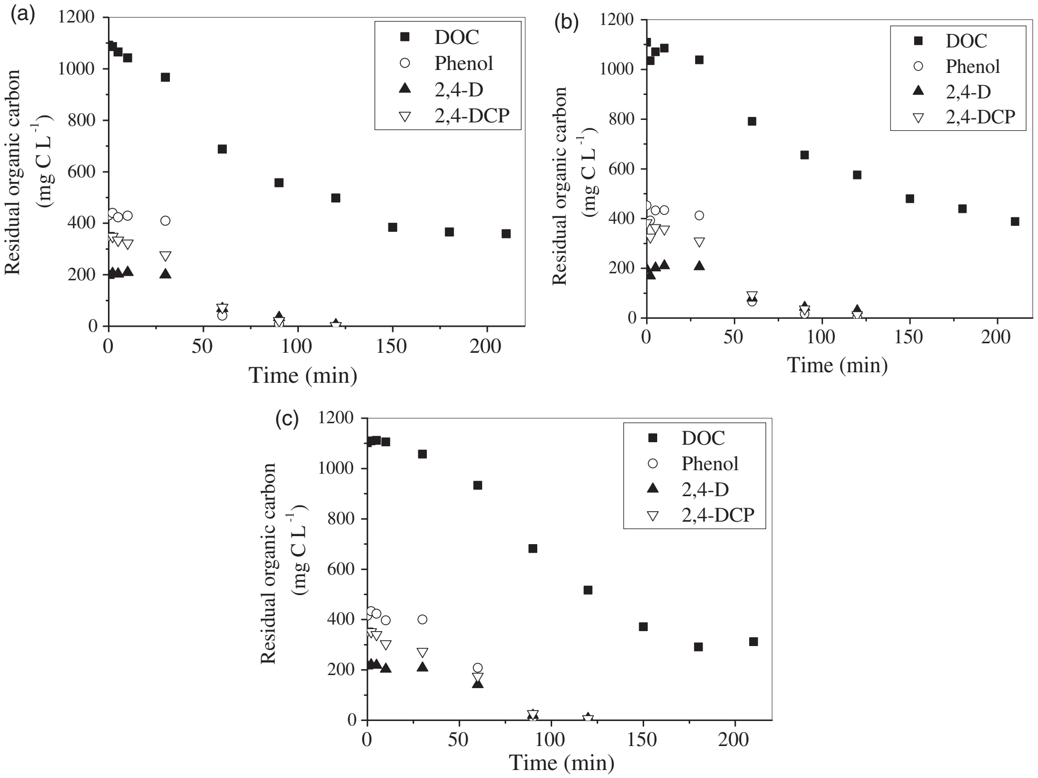

Figure 7. DOC and phenol, 2,4-D and 2,4-DCP concentration–time profiles from the experiments corresponding to three repetitions in central point of the 2^3 factorial design; $[Fe^{2+}]_0 = 1.75$ mM; $F_{H_2O_2,\text{in}} = 2.80$ mmol min^{-1}; and $pH_0 = 6$.

pollutants occurs in approximately 90 min, which is another indication of experimental reproducibility of this study.

4. Conclusions

A highly saline-containing aqueous solution of phenol, 2,4-DCP and 2,4-D was efficiently degraded in the presence of ions ferrous and H_2O_2 starting with initial pH of 5 to 7. Despite the runs started at initial pH higher than 3, there was an efficient degradation of organic carbon over the reaction time, causing a slower removal at the beginning of the reaction and significantly increasing from the time when the pH reached its optimal value, approximately 3, when photo-Fenton reaction occurs. Falling-film solar reactor demonstrates to be effective in the degradation of aromatic pollutants in saline medium. The phenol/2,4-D/2,4-DCP mixture was completely degraded at the first 30 min of $[Fe^{2+}]/[H_2O_2]$/sunlight process, whereas about 85% of DOC was removed at 180 min, under the most adequate experimental conditions used in this work.

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