Chlorpyrifos remediation in agriculture runoff with homogeneous solar photo-Fenton reaction at near neutral pH: phytotoxicity assessment

Kazem Naddafi, Susana Silva Martinez, Ramin Nabizadeh, Kamyar Yaghmaeian, Seyed Jamaledin Shahtaheri and Hoda Amiri

ABSTRACT

This study represents the first application of Fe–citrate-based photo-Fenton chemistry for the degradation of chlorpyrifos (CPF) spiked into agricultural runoff, and its phytotoxicity assessment. The effects of the initial CPF concentration, time and ratio of Fe–citrate/H₂O₂ on CPF removal during the photo-Fenton reaction were investigated and modeled with analysis of variance using R software by the response-surface methodology package. According to the stationary point in original units, the optimal condition for 70.00% CPF removal was as follows: CPF = 2.5 mg L⁻¹ (0.0), time = 48.0 min (0.585) and Fe–citrate/H₂O₂ = 0.075 (0.539). Beside running the system at near-neutral pH, another strength of this study is related to the treatment of agricultural runoff contaminated with CPF with a raceway pond reactor, which has the advantages of simplicity of the facilities and procedures, as well as the possibility of using sunlight more efficiently in the field of applications. Finally, untreated and treated agriculture runoffs were used as irrigation to determine their phytotoxic effects on seed germination of cress (Lepidium sativum). Solar photo-Fenton treatment greatly reduced phytotoxicity of agriculture runoff and showed the highest germination percentage (70%) compared to both raw agricultural runoff (60%) and untreated CPF-spiked runoff (35%).

Key words | chlorpyrifos, germination index, iron-citrate, organophosphorus pesticide, photo-Fenton

HIGHLIGHTS

- The study is the first application of Fe–citrate-based photo-Fenton chemistry for the degradation of chlorpyrifos spiked into agricultural runoff.
- Treatment of agricultural runoff contaminated with CPF with a solar raceway pond reactor is a promising application of this system in the field.
- The phytotoxicity result of the final effluent also showed a good potential for agriculture runoff reuse in irrigation.

INTRODUCTION

Chlorpyrifos (CPF) can be detected in water in a fairly wide range depending on the use of this pesticide in a given area: from 2.86 ng L⁻¹ in natural water to near its water solubility (2 mg L⁻¹) (Herrero-Hernández et al. 2013; Ccanccapa et al. 2016; Claver et al. 2006; Estevez et al. 2016). It appears to be a persistent pesticide that shows genotoxicity and mutagenicity according to several studies. These compounds are mainly those that are persistent with a half-life of more than 2 months in water, bioaccumulate, and have the potential for long-range environmental transport and adverse
effects on human health or the environment. The data on carcinogenicity are equivocal. There are a number of epidemiological studies that indicate that the Dursban CPF formulation can be carcinogenic in humans, the strongest association being for lung and rectum cancers (Watts 2012; EPA 2017). Pesticides are frequently found in influents and also in effluents of wastewater treatment plants that usually do not apply advanced chemical oxidation processes. To reduce the potential health risks, several treatment processes have been investigated to remove pesticides from aqueous matrices, including biological treatment (with low removal efficiency), photocatalysis, electrochemical degradation, Fenton oxidation, hydrogen peroxide oxidation, and plasma discharge, as well as physicochemical techniques that include adsorption, membrane technology, ozone, ozone/ultraviolet (UV) photolysis UV photolysis, and ultrasound (Bahena & Martínez 2006; Hoseini et al. 2016; Chavoshani et al. 2018; Fatima et al. 2019; Liu et al. 2019; Malakootian et al. 2019b; Patel et al. 2019; Malakootian et al. 2020).

Among them, the conventional Fenton process, which involves the production in situ of hydroxyl radicals (OH) by ferrous iron and hydrogen peroxide (H₂O₂), stands out for its high efficiency in the degradation of organic matter, operational simplicity, low cost and environmentally friendly process (Hashemi et al. 2018; Dutta et al. 2019; Heidari et al. 2019; Malakootian et al. 2019a; Malakootian & Heidari 2020). Despite its advantages, this process has not been widely used, due to the requirement for acidic conditions and the high and rapid consumption of H₂O₂ (which represents the main cost of the process) and iron (Zhang et al. 2019).

The first limitation can be solved by iron chelating agents such as ethylene-diamine-tetracetic acid, nitrotriacetic acid, oxalate, citrate and malonate. The resulting iron complexes maintain the solubility of Fe³⁺/Fe²⁺ over a wide pH range and exhibit high absorbance in the UV-vis region. The iron–citrate complex is a good alternative for the solubilization of iron in Fenton processes due to its low toxicity and global formation constant (log β = 14.29), and it being easily available and applicable to high pH values of up to 9.0. The electro-Fenton (EF) process, where H₂O₂ is generated directly at the cathode from the reduction of dissolved O₂ plus ferrous iron as a catalyst in low concentrations, has been reported as a suitable alternative to overcome the second disadvantage of conventional Fenton (Ou et al. 2008; Manenti et al. 2015; Ruales-Lonfat et al. 2016). The aim of this research is to study the CPF degradation capacity of the iron–citrate complex in Fenton and photo-Fenton treatments under simulated solar lighting, near-neutral pH in agricultural runoff under real conditions in a raceway pond reactor (RPR) as a powerful and inexpensive extensive photoreactor. When the treatment is directed to the oxidation of microcontaminants, the concentration of the contaminant is at least a thousand times less than that of the oxidation of macrocontaminants. Therefore, the process needs less oxidant species (mainly OH⁻ radicals) and, consequently, less irradiation (less photons) to achieve elimination. Until our study, no cases have been published for RPR photocatalyst applications that use sunlight which have been widely applied for microalgal mass culture and pesticide degradation and no study for CPF using the Fenton process. For this, a laboratory-scale RPR was designed as an alternative treatment technology to investigate the influence of the concentration of CPF and the ratio of Fe–citrate/H₂O₂ on the degradation of CPF at near-neutral pH (6.8 ± 0.3) under simulated sunlight.

MATERIALS AND METHODS

Chemicals

Chlorpyrifos (analytical grade) was purchased from Dr Ehrenstorfer (Germany, > 99% purity). Ferric-citrate (Fecitrate) was provided by Sigma-Aldrich. Acetonitrile (chromatography grade) was provided by Merck (Darmstadt, Germany). Acetonitrile was used for preparation of CPF stock solutions (1,000 mg L⁻¹). Several concentrations of CPF solutions (1–4 mg L⁻¹) were spiked into the agricultural effluent.

Runoff wastewater and experimental conditions

Several experiments were carried out in an RPR using real agricultural runoff from a farm land in Tehran, Iran. The characteristics of the agricultural runoff are shown in Table 1. The runoff was collected, acidified to pH 2.8 with sulfuric acid and used within 5 days. The small-scale RPR used to carry out the experiments has been reported in our previous work (Amiri et al. 2018), and is shown in the schematic representation (Figure 1). Briefly, the RPR consists of a fiberglass container (50 cm × 15 cm × 10 cm) separated by a central wall, forming two channels with a capacity of 7.5 L. It also has a motorized paddlewheel that uniformly maintains a mixed flow of a homogeneous system during the process and a halogen lamp (300 W, Osram, Munich, Germany, wavelength...
range: 400–800 nm) as visible light source for the photocatalytic reactions that take place in the solution exposed for up to 1 h. An illumination meter (LX-100S, KIMO, France) was used to measure the luminous intensity (lux), which was then converted to the irradiance unit (in W m\(^{-2}\)) using conversion factors (Thimijan & Heins 1985). An aqueous aliquot of 2.5 L of the agricultural effluent, spiked with CPF at near-neutral pH (6.8 ± 0.3), was placed in the RPR. The estimated light intensity was 697 ± 5.33 lux (7.5 \(\times\) 10\(^{-3}\) W m\(^{-2}\)), which is much lower than the global average solar irradiance (∼10 W m\(^{-2}\)) (Mendoza et al. 2017).

### Analytical determinations

The CPF concentration of each sample was analyzed using a Varian chrome pack CP–3800 gas chromatograph as reported previously (Amiri et al. 2018). Total nitrogen and total phosphorus were measured using a Hach test kit (Germany). Total iron concentration (unfiltered and filtered with a 0.45 μm diameter polytetrafluoroethylene syringe-driven filter) was measured using the method of 1,10-phenanthroline following ISO 6332 (ISO 1988); H\(_2\)O\(_2\) was measured using ammonium metavanadate following Pupo Nogueira and co-workers’ method (Nogueira et al. 2005).

### Experimental design

The experimental variables that influence the degradation of CPF were determined by half fractional factorial design. A central composite design (CCD) was then executed for three independent variables to design the experiments. A five level, three variables central composite rotatable design was employed for the optimization with respect to three important reaction variables: CPF concentration (\(X_1\)), time (\(X_2\)) and Fe–citrate/H\(_2\)O\(_2\) (\(X_3\)). Design generation and statistical analysis were performed using the R software by the response-surface methodology (RSM) package. RSM comprises a set of methods to explore the optimal operating conditions through experimental methods (Lenth 2009; Amiri et al. 2018).

According to Equation (1), the actual value of an independent variable converts to its coded form (\(X_1–X_3\)) by calculating the statistical value:

\[
X \sim \frac{(X_i - M)}{R}
\]

(1)

where \(X_i\), \(M\) and \(R\) are the coded value of the \(i\)th independent variable, actual value, mean of actual value ((\(\text{min} + \text{max})/2\)) and range of actual value ((\(\text{max} – \text{min})/2\)), respectively. According to the Montgomery method (Amiri et al. 2018).
the total number of experiments carried out was 23, as shown in Table 2. The empirical second-order polynomial model was used to create a prediction model by the experimental data (Naddafi et al. 2018).

Phytotoxicity assessment

This experiment was performed following the methodology described by Jaafarzadeh et al. (2017). Briefly, 10 mL of treated and untreated CPF spiked into agricultural runoff, or control solutions (ultrapure water and raw agricultural runoff), was added to Petri dishes with one layer of filter paper. Then, 30 cress (Lepidium sativum) seeds, disinfected with sodium hypochlorite followed by washing 10 times with de-ionized water, were added to each Petri dish and incubated in the dark at 24°C (± 2°C) for 72 h. The germination index (GI) (%) was calculated according to the following equation

\[
\text{GI}(\%) = 100 \times \frac{\text{seed germination} \times \text{root length of the sample}}{\text{seed germination} \times \text{root length of the control}}
\]

Statistical analysis

Using R software (3.0.3), multiple regression was chosen to the generalized minimum square to find the relationship between independent and dependent variables. Moreover, the stationary point in original units was used, as a result of the analysis of the variance table in the R software, to estimate an optimal condition for the removal of CPF.

<table>
<thead>
<tr>
<th>Run order</th>
<th>Actual and coded values of independent variables used for the experimental design (CCD)</th>
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<tr>
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RESULTS AND DISCUSSION

Model fitting and statistical analysis

Box and Wilson developed the CCD, which corresponds to one of the most popular response-surface designs (Lenth 2009). It is a first-order (2N) design augmented by additional center and axial points to allow the estimation of the tuning parameters of a second-order model. According to the design created, 23 experiments were performed for the Fenton solar treatment process.

Table 2 presents the independent variables and experimental and predicted results for CPF degradation. A quadratic model was chosen among several verified models as the best for CPF oxidation percentage. According to Table 3, the model coefficient for the response was estimated using the multiple regression analysis technique included in the RSM. Also from the analysis of variance (ANOVA), it is clear that the linear coefficients (X1, X2, X3), second-order (two-way interaction (X1:X3, X2:X3)) and pure quadratic terms (X2², X3²) contribute significantly to the model, so the canonical analysis is relevant.

The quadratic model thus obtained is given by Equation (2)

\[
Y = 40.1190 - 7.5298X_1 + 25.4978X_2 + 24.8431X_3 - 3.5266X_1X_2 + 14.2927X_1X_3 + 18.3277X_2X_3 + 2.6838X_1^2 - 6.9079X_2^2 - 11.8408X_3^2
\]

(2)

R² and p-value for lack of fit are two important parameters to investigate the fitness of the model. Table 4 presents the ANOVA result of the model for CPF degradation. It is clear that the predicted model (R²) satisfactorily explains 97.5% of the total variations. In addition, R²-adjusted value of 0.984 indicates the high degree of correlation between the observed and predicted values for the efficiency of CPF removal in the model. With regard to the lack of fit, as a critical parameter of the validation of the model, the fitness of the model is confirmed without significant differences between the observed and predicted model data (p-value of lack of fit > 0.05). A very high F-value (F-statistic = 56.53, much higher than unity) and a very low probability value (p-value = 5.835 × 10⁻⁹) indicate that the model obtained was highly significant.

Removal of CPF by photo-Fenton process

The CPF degradation efficiency can be greatly reduced by excess or deficiency of hydrogen peroxide and iron in the Fenton process. In addition, the use of appropriate reagent concentrations will affect both economic and aesthetic aspects by preventing additional operating costs due to the excessive use of reagents and will moderate the difficulties encountered in removing excess iron to achieve effluent standards. Although H₂O₂ is an essential parameter for the creation of OH⁻ radicals, its high concentration acts as a radical scavenger and performs a self-decomposition to O₂ and H₂O that causes a reduction in efficiency. Thus, the use of adequate concentrations of hydrogen peroxide and iron in the Fenton process is important. The water matrix used in the experiments contained 1.8 ± 0.16 mg L⁻¹ and 0.34 ± 0.1 mg L⁻¹ of total nitrogen and total phosphorus respectively with a conductivity of 420 ± 0.8 μS cm⁻¹. Therefore, some of the hydroxyl radicals generated during the treatment were expected to
react with organic molecules other than the target compounds. Consequently, the presence of all these species and compounds in the runoff should be taken into account, as they generally slow down the reaction rate compared to water containing less organic matter and inorganic constituents (Naddafi et al. 2018).

**Fe–citrate concentration**

The effect of Fe–citrate concentration on the degradation efficiency of CPF (2.5 mg L\(^{-1}\)) was conducted in the presence of 0.2, 0.5, 0.8 and 1.0 mg L\(^{-1}\) of \(\text{Fe}^{2+}\) with 10 mg L\(^{-1}\) of \(\text{H}_2\text{O}_2\). It was observed that the degradation percentage improved with increasing reagent and time, until the Fe–citrate/\(\text{H}_2\text{O}_2\) ratio increased to more than 0.08, as shown in Figure 2. The 3D response-surface and 2D contour plots in Figure 3 visualize the relationship between CPF removal as response and experimental levels of variables (CPF, time, Fe–citrate/\(\text{H}_2\text{O}_2\)) and their interactions. The response-surface plots show that at low and high levels of Fe–citrate/\(\text{H}_2\text{O}_2\) ratios, CPF oxidation was minimal. The literature confirms that the Fe/\(\text{H}_2\text{O}_2\) ratio higher than 0.10 may decrease the efficiency of contaminant removal due to the scavenging of hydroxyl radicals (Mirzaei et al. 2017).

**Assessment of CPF concentration with time**

In this study, we tried to simulate the real condition of agricultural runoff contaminated with CPF on a pilot plant scale. The CPF degradation is visualized through the contour plot and the 3D view of response-surface plots (Figure 3). The plots were represented based on two factors: CPF and Fe–citrate/\(\text{H}_2\text{O}_2\) ratio, with the time kept at a fixed level (37.78 min); and CPF and time, holding Fe–citrate/\(\text{H}_2\text{O}_2\) ratios at a fixed level (0.05). As can be seen in this figure, the efficiency of CPF degradation was reduced by increasing its concentration, while time has a positive effect on the solar photo-Fenton process. This occurs because high concentrations of CPF require higher concentrations of oxidant species (hydroxyl radicals, ferryl complexes, etc.) for effective removal. Therefore, at a constant level of other operating parameters, the generated oxidant species do not meet the demand for additional contaminant input concentration. In addition, in the Fenton reaction, when the concentration of CPF increases, the number of active sites, where radical reactions take place, is limited, which reduces the absorption of light by hydrogen peroxide in the Fenton photocatalytic reaction. However, the generation of \(\text{OH}^–\) radicals and other oxidant species is retained and as a consequence the removal efficiency decreases.

**Mechanism of CPF removal in the system**

The equilibrium Fe(III) speciation within the pH range of 4.6–8.0 is FeCit\(^{\text{2+}}\) (Hamm et al. 1954; Zepp et al. 1992; Faust & Zepp 1993; Hug et al. 2001; Ou et al. 2008). The mechanism of the homogeneous solar photo-Fenton degradation of CPF in the presence of Fe(III)-citrate species
(Fe(OH)Cit) involves several reaction processes, such as the following.

(a) Photochemical redox reactions of Fe(OH)Cit produce Fe(II) and the citrate radical Cit− (HO-CR2-COO− with R = -CH2COO−) (Hug et al. 2001) followed by decarboxylation to the carbon centered 5-hydroxoglutarate radical, 5-HGA2− (HO−CR2), which reacts with O2 to form various oxidants such as OH−, O2−, HO2, and H2O2 (Faust & Zepp 1993; Anfossi et al. 2006) eliminating the CPF from the aqueous system. Other competing reactions can also take place with the citrate radical such as back-reaction with Fe(II) to re-form Fe(III) or the reduction of Fe(OH)Cit− species (Faust & Zepp 1993).

(b) The reaction of Fe(II) species, photochemically produced, with H2O2 at neutral pH might not result in OH− radical formation (Rush et al. 1990) but in the formation of Fe(IV) species (Koppenol & Liebman 1984). There is evidence that many Fe(II) and Fe(III) chelates (such as citrate, L) react thermally with H2O2 to form ferryl complexes, (L)Fe(IV) = O, or one electron ligand-oxidized ferryl complexes, (L−)Fe(IV) = O. These species, like OH− radicals, can be strong and nonselective oxidizing agents (Leising et al. 1991; Sun & Pignatello 1993).

Figure 3 | Design-expert plot: response-surface contour (left) and 3D (right) plots near the stationary point for CPF removal (%) at pH = 6.8 ± 0.3. a: Initial CPF concentration (mg L−1), b: Fe-citrate/H2O2 ratio, c: removal efficiency (%) and d: time (min).
(c) Direct photolysis of $\text{H}_2\text{O}_2$ produces $\text{OH}^\cdot$; however, this production process is comparatively slow because $\text{H}_2\text{O}_2$ weakly absorbs solar irradiation.

Thus, it is expected that $\text{OH}^\cdot$ and ferryl complexes are responsible for the homogeneous solar photo-Fenton degradation of CPF.

Validation of the model

The optimal oxidation conditions ($X_1 = 2.5 \text{ mg L}^{-1} (0.0)$, $X_2 = 48.0 \text{ min} (0.585)$ and $X_3 = 0.075 (0.539)$) for CPF removal were suggested by the variance analysis table of the R software. The theoretical CPF removal that was predicted under the above conditions was 70.00%. This set of conditions was determined as optimal by the RSM optimization approach and was used to experimentally validate and predict the values of the responses using the model equation. The mean removal efficiency for CPF was $65 \pm 1.03\%$ ($n = 3$), which corresponds well to the predicted value of the model equation, confirming that the response model was adequate for optimization.

Phytotoxicity evaluation

The toxicity tests following by treatment process are critical in the evaluation of effluent quality. Hence, both untreated and treated agricultural runoff were assessed for their phytotoxicity. The result for cress seed germination inhibition upon exposure to different concentration of CPF in runoff is given in Figure 4. Treated agricultural runoff showed highest germination percentage (70%) compared to both raw agricultural runoff (60%) and untreated CPF-spiked runoff CPF spiking (35%). This result can be attributed to the formation of non-toxic oxidation intermediates, which were not toxic to *Lepidium sativum*. In addition, iron ions (nutrients) present in the iron-citrate complex might have contributed to the germination. Regarding the results of cress seed germination, as the most sensitive plant (*Jaafarzadeh et al. 2017*), the final effluent has a good potential for water reuse in irrigation.

Critical comparison of Fenton reaction for CPF degradation

Previous works reported the influence of Fenton reagent on CPF degradation. For instance, Affam and collaborators (*Affam et al. 2012*) investigated the effect of the Fenton process on the degradation of an effluent containing a mixture of three pesticides: of chlorpyrifos (initial concentration (Co) = 100 mg L$^{-1}$), cypermethrin (Co = 50 mg L$^{-1}$) and chlorothalonil (Co = 250 mg L$^{-1}$), and reported a chemical oxygen demand (COD) and total organic carbon (TOC) removal of 69.03 and 55.61%, respectively, in 60 min reaction. In addition, these authors (*Affam et al. 2014*) examined the effect of UV Fenton pretreatment operating conditions combined with the aerobic sequencing batch reactor (SBR) on degradation and biodegradability (bio-chemical oxygen demand/COD ratio) improvement of chlorpyrifos (Co = 805.56 ± 10.0 mg L$^{-1}$), cypermethrin (Co = 105.75 ± 10.0 mg L$^{-1}$) and chlorothalonil (Co = 692.08 ± 10.0 mg L$^{-1}$) pesticide wastewater under optimal condition (as shown in Table 5); a higher COD and TOC removal was reported for the UV Fenton-SBR treatment. *Saini & Kumar (2016)* used the Fenton oxidation process for the degradation of 30 mg L$^{-1}$ of CPF, reporting an efficiency removal of CPF of 94% with a COD decrease of 83.51% in 60 min of reaction time. In addition, *Augustine et al. 2016* examined solar irradiation to enhance Fenton treatment of CPF pesticide wastewater with an initial concentration of 200 mg L$^{-1}$ finding a COD decrease of 89.20% in 60 min of reaction time. It is important to mention that the solubility of CPF in water is 2 mg L$^{-1}$. Therefore, CPF concentrations higher than 4 mg L$^{-1}$ create a milky solution that interferes with both the treatment process and the measurement method using high-performance liquid chromatography or gas chromatography by reducing the repeatability and accuracy of the experiments. The documents mentioned (Table 5) that have examined the degradation of initial CPF concentrations above 4 mg L$^{-1}$ appear to be far from the natural condition and should be considered more in relation to their results. This present study reports the
first application of Fe–citrate-based photo-Fenton chemistry for the degradation of 4 mg L\(^{-1}\) of CPF at pH = 6.8 with a CPF removal efficiency of 65 ± 1.03% in 48 min of reaction time using agricultural runoff polluted with CPF. Our results compete with those reported in the literature, showing an important advantage in the almost neutral pH (6.8) used compared to the common pH = 3 used in Fenton processes.

**CONCLUSIONS**

The solar photo-Fenton process with iron–citrate showed promising results for CPF remediation at near-neutral pH conditions, with the use of a low iron concentration (Fe–citrate concentration: 0.75 mg L\(^{-1}\) relative to the Fe content) and avoiding precipitation of ferric hydroxides. This study reports the first application of photo-Fenton chemistry based on Fe–citrate for CPF degradation. Photo-degradability of CPF (2.5 mg L\(^{-1}\)) increased from zero to 80% in 60 min by increasing reagent ratio from 0 to 0.1. Under the optimum operating conditions (CPF = 2.5 mg L\(^{-1}\), and Fe–citrate/H\(_{2}O_{2}\) = 0.075), 70.00% degradation of the CPF occurred in 48 min.

Another promising application of this system is related to the treatment of agricultural runoff contaminated with CPF in an RPR, because of the simplicity of the facilities and procedures, as well as the possibility of using sunlight more efficiently in field applications. The phytotoxicity result of the final effluent also showed a good potential for agriculture runoff reuse in irrigation section.

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**Table 5** | Comparison between Fenton treatment technologies related to chlorpyrifos degradation

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Initial concentration</th>
<th>Fenton features</th>
<th>Removal efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>CPF = 4 mg L(^{-1}) Salinity = 0.22 ± 0.02 mg L(^{-1}) TDS = 210 ± 0.94 mg L(^{-1}) Total nitrogen = 1.8 ± 0.16 mg L(^{-1}) Total phosphorus = 0.34 ± 0.01 mg L(^{-1})</td>
<td>pH = 6.8 ± 0.3 H(<em>{2}O</em>{2}):Fe–citrate 10:0.75</td>
<td>Reaction time = 48 min; CPF = 65 ± 1.03%</td>
<td>Present study</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>COD = 1,330 mg L(^{-1})</td>
<td>pH = 3, H(<em>{2}O</em>{2}) dosing rate 120 mg min(^{-1}), [Fe(^{2+})] = 5.0 mM.</td>
<td>Reaction time = 70 min; COD = 77.00%</td>
<td>Samet et al. (2012)</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>CPF = 100 mg L(^{-1}), cypermethrin = 50 mg L(^{-1}), chlorothalonil = 250 mg L(^{-1}).</td>
<td>pH = 3 H(<em>{2}O</em>{2}):COD 3:1 H(<em>{2}O</em>{2}):Fe(^{2+}) 10:1</td>
<td>UV Fenton (60 min) COD = 69.03% TOC = 55.61%</td>
<td>Affam et al. (2012)</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>CPF = 805.56 ± 10.0 mg L(^{-1}), cypermethrin = 105.75 ± 10.0 mg L(^{-1}), chlorothalonil = 692.08 ± 10.0 mg L(^{-1}), COD = 3,350.0 ± 100 mg L(^{-1}), TOC = 2,960.0 ± 100 mg L(^{-1})</td>
<td>pH = 3 H(<em>{2}O</em>{2}):COD 2:1 H(<em>{2}O</em>{2}):Fe(^{2+}) 25:1</td>
<td>UV Fenton (60 min)COD = 64.8% TOC = 45.9% UV Fenton-SBR (40 d operation at 12 h hydraulic retention time COD = 96.2% TOC = 97.4%)</td>
<td>Affam et al. (2014)</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>CPF = 30 mg L(^{-1}), COD = 385 mg L(^{-1}).</td>
<td>pH = 3, H(<em>{2}O</em>{2}) = 0.571 mol L(^{-1}), Fe(^{2+}) = 3 g L(^{-1})</td>
<td>Reaction time = 60 min; CPF = 94% COD = 83.51%</td>
<td>Saini &amp; Kumar (2016)</td>
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<td>Chlorpyrifos</td>
<td>CPF = 200 mg L(^{-1}).</td>
<td>pH = 3 H(<em>{2}O</em>{2}):COD 2.5:1 H(<em>{2}O</em>{2}):Fe(^{2+}) 10:1</td>
<td>Reaction time = 60 min; TOC = 89.20%</td>
<td>Augustine et al. (2016)</td>
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ACKNOWLEDGEMENTS

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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