

Environmentally friendly system for the degradation of multipesticide residues in aqueous media by the Fenton's reaction

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Received: 8 April 2013 / Accepted: 11 June 2013 / Published online: 30 June 2013
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Abstract A Fenton oxidation system employing zero-valent iron (whose source was swarf, a residue of metallurgical industries, in powder form) and hydrogen peroxide for the treatment of an aqueous solution with six pesticides was developed, and the effect of the iron metal content, pH, and hydrogen peroxide concentration was evaluated. The characterization of the aqueous solution resulted in: pH 5.6, 105 mg L⁻¹ of dissolved organic carbon, and 44.6 NTU turbidity. In addition, the characterization of the swarf by FAAS and ICP-MS showed 98.43±7.40 % of zero-valent iron. The removal was strongly affected by the content of iron metal, pH, and hydrogen peroxide concentration. The best degradation conditions were 2.0 g swarf, pH 2.0, and 5 mmol L⁻¹ H₂O₂. At the end of the treatment, the pesticide degradation ranged from 60 to 100 %, leading to 55 % mineralization. Besides, all hydrogen peroxide was consumed and the determination of total dissolved iron resulted in 2 mg L⁻¹. Thus, the advantages of this system are rapid degradation (up to 20 min), high-degradation rates, simple handling, and low cost.

Keywords Environmentally friendly system · Multipesticide degradation · Zero-valent iron · Fenton's reaction

Introduction

There has been a growing concern about the quality of water resources in the last decades. Economic growth, together with worldwide technological and agricultural development, has brought about environmental pollution (Oturán et al. 2011). In this context, pesticides represent a risk factor for the quality of water resources because these substances are generally toxic and non-biodegradable (Cabrera et al. 2010).

Some studies have recently reported the risk of water contamination by pesticides in the south of Brazil, as well as the detection of pesticides in groundwater, surface water, and drinking water (Cabrera et al. 2008; Caldas et al. 2010; Demoliner et al. 2010). Likewise, many researchers have shown the contamination of water resources all over the world (Fatta et al. 2006; 2007). Therefore, one of the most serious challenges, nowadays, is the protection of water resources by eliminating a significant part of the pollution caused by toxic and hazardous organic contaminants (Melo et al. 2009; Oturan et al. 2011). Classical biological oxidation has failed to eliminate toxic compounds or recalcitrant organic contaminants (Martín et al. 2010; Pérez et al. 2006). Moreover, physicochemical processes, such as adsorption on activated carbon, flocculation, and membrane filtration, only transfer the compounds from one phase to another without destroying them (Hermosilla et al. 2009; Martín et al. 2010; Oturan et al. 2011; Oller et al. 2011). Besides, the product that results from these processes must be considered a residue because it requires a supplementary technique to eliminate the total compound content (Arruda and Jardim 2007; Oturan et al.

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-013-1932-2) contains supplementary material, which is available to authorized users.

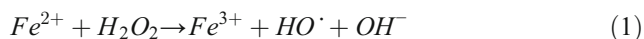
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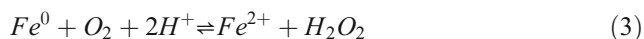
2011). Therefore, efficient oxidation technologies must be developed. Advanced oxidation processes (AOPs) can be considered promising alternative methods in the case of several pollutants and viable alternatives to conventional technologies (Hermosilla et al. 2009; Kallel et al. 2010; Masomboon et al. 2010; Gözmen et al. 2009; Zapata et al. 2009). Many researches on pesticide degradation by AOPs have recently been published (Arruda and Jardim 2007; Barreiro et al. 2007; Cabrera et al. 2010; Fan et al., 2011b; Kassinos et al. 2008; 2009; Pérez et al. 2006; Oturan et al. 2011).

AOPs are oxidation technologies based on the generation of hydroxyl radical which is a powerful (2.8 V redox standard potential vs. hydrogen electrode) unselect oxidant. AOPs are able to oxidize and mineralize a wide variety of organic compounds either by generating water, carbon dioxide, and inorganic ions (Klavarioti et al. 2011). Due to the high reactivity of hydroxyl radicals, the attack is non-selective and enables the treatment of wastewater containing different organic pollutants. The Fenton's process stands out among the AOPs because it is easy to handle and very efficient. Due to these characteristics, it has been used in several studies (Arruda and Jardim 2007; Barreiro et al. 2007; Hermosilla et al. 2009; Khan et al. 2009; Jiang et al. 2010; Martín et al. 2010; Fan et al. 2011a, b; Oller et al. 2011; Oturan et al. 2011).

The Fenton's reaction is based on the decomposition of hydrogen peroxide by Fe^{2+} to generate hydroxyl radicals, as described in Eq. (1) (Walling 1975).



For an efficient reaction, a stoichiometric amount of ferrous ions and hydrogen peroxide is required. Benatti et al. have reported in their research work that the oxidative degradation of organic contaminants can be successfully accomplished by the Fenton's reaction. However, the concentration of certain inorganic constituents, such as sulfate, still remained extremely high for effluent discharge (Benatti et al. 2006, 2009). It usually means that huge quantities of these constituents need to be disposed of after the reaction is complete. However, when zero-valent iron is used in place of ferrous salts, the following reactions can occur



In an acid medium with no oxygen, the surface of the metal iron corrodes, thus giving rise to ferrous ions and hydrogen gas (Eq. (2)). The ferrous ions generated in Eq. (2) in the

presence of hydrogen peroxide react quickly via the conventional Fenton's reaction (Eq. (1)), producing hydroxyl radical and ferric ions (Namkung et al. 2008; Kallel et al. 2009). On the other hand, the metal iron can also decompose hydrogen peroxide in the presence of oxygen. In this case, dissolved oxygen is the main electron acceptor, resulting in rapid corrosion (Eq. (3)). Concurrently, the metal iron could cause the reduction of hydrogen peroxide to yield hydroxyl radical, as described in Eq. (4), and the ferrous ion can promote the subsequent decomposition of hydrogen peroxide as shown in Eq. (1) (Scherer et al. 2001; Gooddy et al. 2002; Satapanajaru et al. 2003).

The ferric ions can be reduced to ferrous ions by the metal iron surface according to Eq. (5) (Namkung et al. 2008; Kallel et al. 2009). This is the main advantage of the Fenton's system employing zero-valent iron.

However, small amounts of ferric species are formed, which is an inevitable fact. Nevertheless, this fact does not make the process unviable because this undesirable product will be able to start a new Fenton's reaction (Oturan et al. 2008; Jiang et al. 2010).

Therefore, this study aimed to develop and optimize an environmentally friendly and sustainable Fenton oxidation system employing zero-valent iron (a residue of the metallurgical industry) and hydrogen peroxide for the degradation of an aqueous solution with six different classes of pesticides and chemical groups, besides evaluating the effect of the following parameters: the amount of metal iron, pH, and the hydrogen peroxide concentration.

Materials and methods

Instrumentation

For the swarf characterization, the metal iron (Fe^0) measurements were carried out by a Model Vario 6 FL Flame Atomic Absorption Spectrometer (Analytik Jena AG, Germany), equipped with a deuterium background corrector and a hollow-cathode lamp for iron, operating at 8 mA (wavelength: 248.3 nm; spectral bandwidth: 0.2 nm). A conventional air/acetylene burner (10-cm slit) was used. Integrated absorbance with a 1-s integration time was used for signal evaluation.

An Inductively Coupled Plasma Mass Spectrometer (PerkinElmer SCIEX, Model Elan DRC II, Thornhill, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia), and a quartz torch with a quartz injector tube (2-mm i.d.) was used for Cr, Cu, Ni, Pb, Sn, and Sr determination. The nebulizer gas flow rate, the ion lens voltage, and the torch alignment were adjusted according to the manufacturer's instructions by using conventional nebulization. Monitored ions were ^{52}Cr , ^{63}Cu , ^{60}Ni , ^{208}Pb , ^{120}Sn , and ^{88}Sr . The plasma power and the

nebulizer gas flow rate were 1,300 W and 1.10 L min⁻¹, respectively.

During the optimization of the zero-valent iron system, high-performance liquid chromatography with diode array detector (HPLC-DAD) was employed. LC-DAD separation was performed by using an HPLC apparatus consisting of a column Thermo BDS Hypersil C18 particle size 5 µm (250×4.6 mm i.d.), from Thermo Scientific, a Waters 600 pump model, associated with a Waters 2996 Photodiode Array Detector and a Rheodyne 20-µL loop injector, connected to an Empower PDA software for data acquisition. The UV spectra were recorded in the 210–400 nm range.

For the determination by LC-DAD, the mobile phase composition was methanol (A) and ultrapure water pH 4.0 (B) acidified with phosphoric acid 1:1 (v/v). The gradient elution mode was: 0–6 min, 40 % A; 6–7 min, 40–75 % A; 7–25 min, 75 % A; 25–26 min, 75–40 % A; and 26–30 min, 40 % A. The flow rate was: 0–6 min, 0.8 mL min⁻¹; 6–7 min, 0.8–1.2 mL min⁻¹; 7–25 min 1.2 mL min⁻¹; 25–26 min, 1.2–0.8 mL min⁻¹; and 26–30 min, 0.8 mL min⁻¹, totalling to a 30-min running time. The mobile phases were degassed for 30 min in an ultrasonic bath before use.

The liquid chromatography coupled to electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) was used to confirm the pesticide degradation and evaluate the formation of carbofuran-3-hidroxy and 3,4 DCA, by-products of pesticides carbofuran and diuron, respectively. The LC-ESI-MS/MS was performed by a Waters Alliance 2695 Separations Module. The mass spectrometry was carried out by a Micromass Quattro Micro API with an ESI interface, connected to a Masslynx version 4.1, 2005 software for data acquisition. The liquid chromatography was performed by an XTerra analytical column 3.5 µm (50×3 mm, i.d.) (Waters, Milford, MA, USA). The determinations by LC-ESI-MS/MS were performed as previously described by Demoliner et al. (2010). The figure of merits of chromatography methodology can be seen at Table 1 in supplementary data.

The ion chromatography (IC) with conductivity detector was used to confirm the mineralization of pesticides. Therefore, the determination of NH₄⁺, NO₂⁻, NO₃⁻, Cl⁻, PO₄²⁻, and SO₄²⁻ was carried out by an IC compact Pro 881 Metrohm equipped with autosampler, quaternary pump, column oven, chemical suppression system, and digital conductivity detector iDetector connected to MagIC Net™ software for data acquisition (Metrohm, Herisau, Suíça). The determination of ions was carried out by the method employed and established by Metrohm (ANC-135 and ANS-257, 2012).

The determination of the total dissolved iron (Fe²⁺) which remained at the end of the process was measured by a UV–vis Spectrophotometer (model UV 2550, Shimadzu, Japan) connected to UV-Probe software for data acquisition, according to norm NBR 13934, issued by the *Associação*

Brasileira de Normas Técnicas (Associação Brasileira de Normas Técnicas ABNT 2010). This determination was based on the reaction between ortho-phenanthroline and Fe²⁺, thus, giving rise to orange complexes at pH <5.0. Ferric ions can be reduced to ferrous ions by the addition of ascorbic acid.

The hydrogen peroxide residual content was measured by a UV–vis Spectrophotometer (model UV 2550, Shimadzu, Japan) connected to UV-Probe software for data acquisition, according to the colorimetric method developed by Eisenberg (Eisenberg 1975). This method was based on the reaction between hydrogen peroxide and titanium sulfate, which generates a yellow complex.

The Total Organic Carbon (TOC) content was measured by a TOC Analyzer (TOC, model TOC-V CPH, Shimadzu, Japan) and a non-purgeable organic carbon (NPOC) analysis was carried out. Turbidity was measured by a 2100 P Turbidimeter Hach (Hach Company, USA).

Materials and chemicals

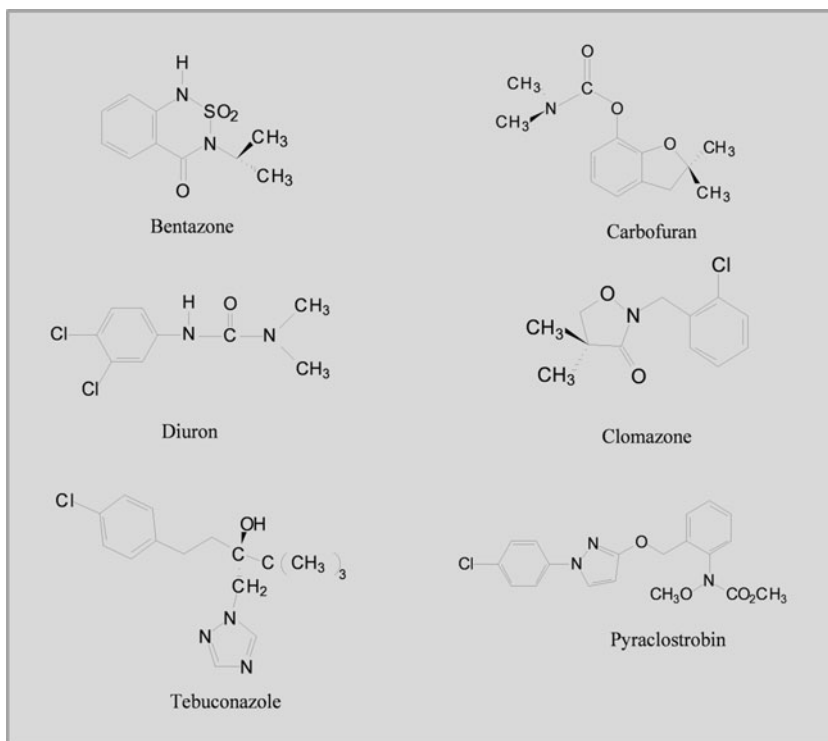
Hydrogen peroxide (29 %, w/w) and phosphoric acid (85 %, w/w) analytical grade were purchased from Synth (Brazil) and from Tedia (USA), respectively.

The aqueous solution used during the degradation experiments was prepared in the laboratory by adding 10 mg of each pesticide (Fig. 1) to 1-L distilled water. Some of the pesticides selected in this study had been detected in a previous research. In groundwater samples, carbofuran, clomazone, and tebuconazole were detected in concentrations ranging from 0.20 µg L⁻¹ to 10.40 µg L⁻¹ (Caldas et al. 2010). In drinking water and surface water, diuron and tebuconazole were detected in concentrations of 0.5 µg L⁻¹ (Demoliner et al. 2010).

Experimental procedure

The system was based on the spontaneous corrosion of metal iron on the swarf surface in the presence of hydrogen peroxide and in acidic conditions. It produces ferrous ions, which react with hydrogen peroxide in the Fenton's reaction, resulting in hydroxyl radicals (Kallel et al. 2009). All experiments were carried out in a special system designed for the degradation of an aqueous solution, as shown in Fig. 2. The system consists of a 1-L separation funnel, a 1-L beaker, and a PVC gutter (1-m long) whose magnetic boards hold the swarf. One liter of aqueous solution (containing 10 mg L⁻¹ of each pesticide), previously acidified with phosphoric acid, was introduced into the separation funnel, followed by the addition of hydrogen peroxide (ranging from 1 to 10 mmol L⁻¹). The solution percolated the gutter for 20 min at room temperature (25 °C) with neither natural nor artificial light. For sample characterization and degradation checking under different pH conditions, aliquots were collected before (with and without pH adjustment and with

Fig. 1 Chemical structures of the selected pesticides



H₂O₂ addition) and during the experiment. All aqueous samples were withdrawn and filtered by a PTFE 0.45-μm, Millipore, Millex® before the analysis by HPLC-DAD, LC-MS/MS, and IC. Samples were mixed with methanol, and stored and cooled at -18 °C in order to stop the Fenton’s reaction. However, for the TOC content analysis, samples were mixed with Na₂S₂O₃. If methanol had been used in the TOC content analysis, this content would have been affected. On the other hand, the use of Na₂S₂O₃ should be avoided in the chromatographic analysis, mainly for LC-MS/MS, because it may precipitate during the analysis and clog up the chromatograph.

For the swarf characterization by flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS), about 1-g swarf was digested with 5-mL concentrated HCl and stirred for 5 min in a vortex. Afterwards, it was kept at 140 °C for 2 h in a hot plate.

Statistical calculations

All statistical calculations were performed by GraphPad InStat (GraphPad InStat Software Inc, Version 3.00, 1997) software. A 95 % significance level was adopted for all comparisons.

Results and discussion

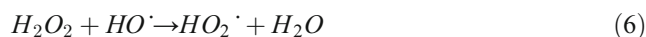
Characterization of swarf and aqueous solution

The characterization of the aqueous solution resulted in pH 5.6, TOC 105 mg L⁻¹ carbon, and 44.6 NTU turbidity. In

addition, the characterization of the swarf by FAAS and ICP-MS revealed 98.43±7.40 % of zero-valent iron, whereas Cr, Cu, Ni, Pb, Sn, and Sr were detected in the following concentrations: 0.45±0.02 mg g⁻¹; 0.57±0.05 mg g⁻¹; 0.16±0.01 mg g⁻¹; 0.344±0.015 mg g⁻¹; 0.0265±0.0003 mg g⁻¹; and 0.0155±0.0015 mg g⁻¹, respectively.

Effect of H₂O₂ concentration on the pesticide degradation efficiency during oxidation

Equation (6) shows that the Fenton’s reaction depends on a stoichiometric amount of hydrogen peroxide (Walling 1975). When excessive hydrogen peroxide is employed, it can react with the hydroxyl radical and inhibit the Fenton’s reaction. Likewise, in the presence of large amounts of hydrogen peroxide, the oxidation of organic substrates is inhibited (Tang and Tassos 1997; Gulkaya et al. 2006). It occurs because the hydroxyl radical reacts with the excess of hydrogen peroxide to produce a hydroperoxyl radical, which is less reactive than the hydroxyl one, according to Eq. (6) (Walling 1975).



In addition, the excess of H₂O₂ can also affect the concentration of ferrous ions in the oxidation reaction because ferric ions react with hydrogen peroxide yielding Fe(III)-hydroperoxy complexes (Laat and Gallard 1999). Thus, ferric ions cannot be reduced to ferrous ions by the metal iron surface, as suggested by Eq. (5).

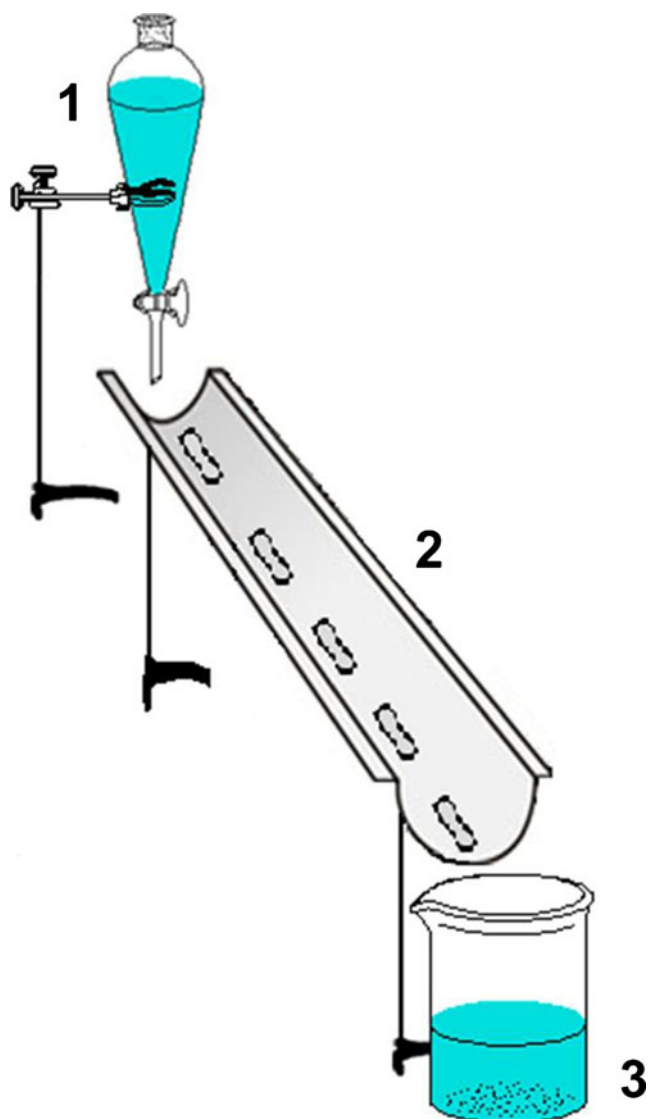


Fig. 2 Illustration of the system designed for the degradation of pesticides (1 1-L separation funnel containing synthetic wastewater previously acidified and with hydrogen peroxide; 2 PVC gutter whose magnetic boards hold the swarf; 3 1-L beaker containing wastewater after percolated by PVC gutter)

Therefore, to determine the effect of the hydrogen peroxide concentration on the degradation of the pesticides in the synthetic wastewater, the amount of swarf and the pH value were fixed, while the hydrogen peroxide concentration ranged from 1 to 10 mmol L⁻¹. Results of these experiments have been reported in Fig. 3. As shown in Fig. 3, degradation rates increase gradually, up to 5 mmol L⁻¹ H₂O₂. Hydrogen peroxide concentration above 5 mmol L⁻¹ reduces the degradation rates of all pesticides.

Finally, a *t* test was carried out to compare the results obtained for degradation in ten experiments. The Tukey's multiple comparison test was used to indicate significant differences among the main degradation with 95 % significance level adopted for all comparisons. No significant

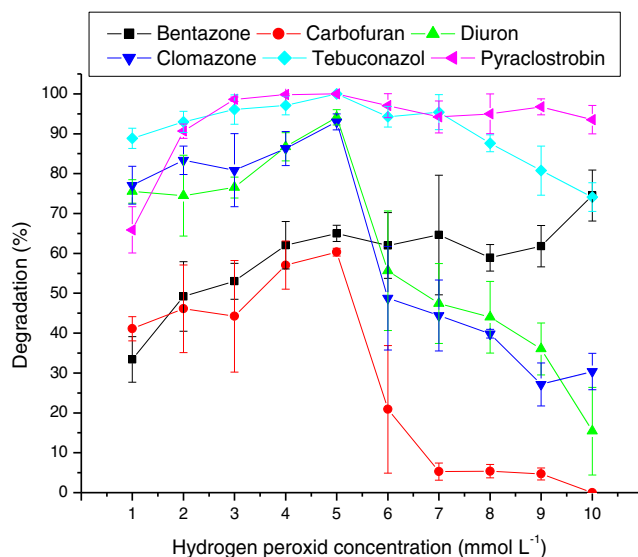


Fig. 3 Effect of different H₂O₂ concentrations on the pesticide degradation by Fenton's oxidation, obtained after 20 min (experimental conditions: pH 2.0; 2.0-g iron metal). Bars indicate the RSD percentage values

difference (*t* test, $P > 0.05$) was found from 2 to 5 mmol L⁻¹. However, it is important to mention that when 5 mmol L⁻¹ hydrogen peroxide was used, the standard deviation was lower. Thus, this concentration was used for further experiments.

Effect of pH

In the absence of a substrate, the hydroxyl radical generated in Eq. (1) can oxidize the second ferrous ion. It shows that the Fenton's reaction is extremely dependent on the pH. In this sense, only in acid conditions, the hydroxyl radical is predominantly oxidant, because ferric ions can catalytically

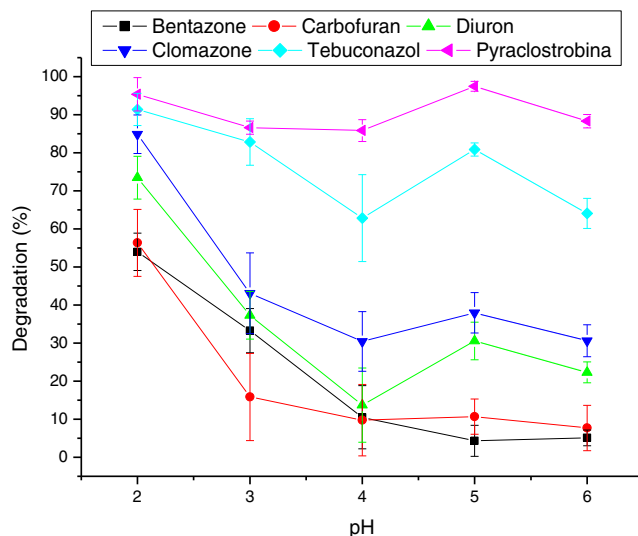


Fig. 4 Effect of different pH values on the pesticide degradation efficiency by Fenton's oxidation (experimental conditions: 5 mmol L⁻¹ H₂O₂; 2.0-g iron metal). Bars indicate the RSD percentage values

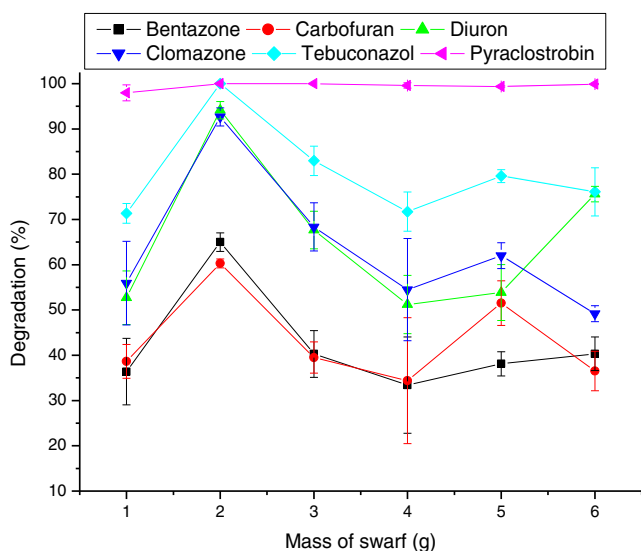


Fig. 5 Effect of different iron metal mass on the pesticide degradation efficiency by Fenton's oxidation (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0). Bars indicate the RSD percentage values

decompose hydrogen peroxide to H₂O and O₂ (Walling 1975; Laet and Gallard 1999).

The effect of acidic medium conditions on the degradation was studied with pH ranging from 2.0 to 6.0. Figure 4 shows the values of degradation rates at different pH. The pH effect on the degradation rates was carried out by fixing the swarf mass and hydrogen peroxide concentration. Percolating time was 20 min at laboratory temperature (25 °C). The highest degradation rates for all pesticides were obtained at pH 2.0. When pH ≥ 3.0, the Fenton's reactions showed lower degradation efficiencies than the value obtained at pH 2.0 for all pesticides, except for pyraclostrobin and tebuconazole. On the other hand, when pH=2, the hydroxyl radical can add to the aromatic ring and may also abstract a hydrogen atom and lead up to a radical chain oxidation (Walling 1975; Casero et al. 1996; Neyens and Baeyens 2003). Lu et al. have shown that

the oxidation of carbofuran occurs when the radical hydroxyl attacks the furan ring (Lu et al. 2011). These facts show that the pH of the medium also plays an important role in the degradation of these pesticides in this study. In addition, previous researches reported that pH=2 are usually the best for the Fenton's reaction employing zero-valent iron (Kallel et al. 2009; Khan et al. 2009). Thus, pH=2.0 was selected for further experiments.

Effect of the amount of swarf

For the determination of the optimum amount of swarf mass for the degradation rates of six pesticides, experiments were carried out with pH 2.0 and 5 mmol L⁻¹ hydrogen peroxide. The effect of the swarf mass was studied from 1.0 to 6.0 g. The results of these experiments are shown in Fig. 5. The swarf mass improved the degradation efficiency up to 2.0 g. On the other hand, its excess may inhibit the process efficiency due to the production of aqueous complexes, such as Fe(III)-hydroperoxy. Thus, 2.0-g swarf was chosen because this amount could promote better degradation rates of all pesticides, except for pyraclostrobin, since it presented high-degradation rates in all experiments.

Degradation efficiency and mineralization employing optimized conditions

When the best degradation conditions (5 mmol L⁻¹ H₂O₂, pH 2.0, and 2.0-g swarf) were applied to the synthetic wastewater containing 10 mg L⁻¹ of each pesticide, the highest degradation efficiency of these organic compounds was observed. Figure 6 shows the chromatographic profile for the synthetic wastewater before and after treatment by zero-valent iron and hydrogen peroxide.

Afterwards, an experiment was carried out to evaluate the degradation efficiency of the system at different reaction

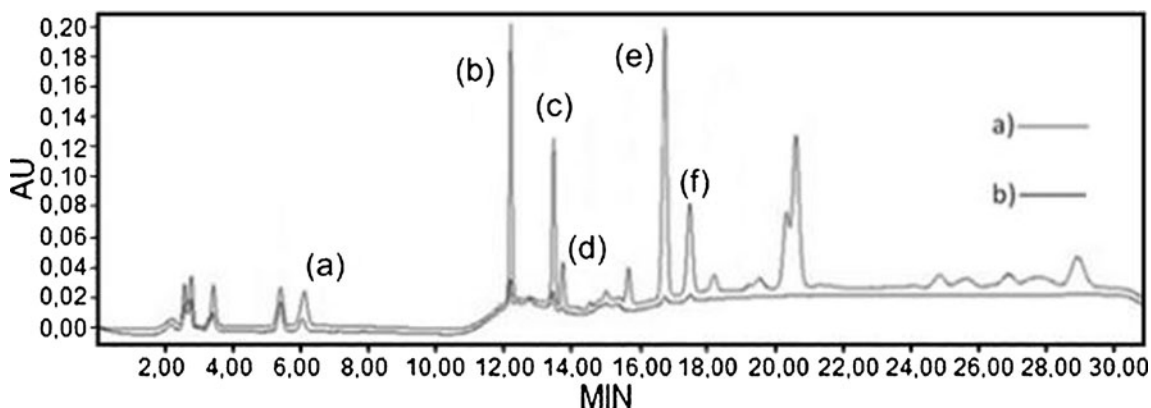


Fig. 6 Chromatograms of synthetic wastewater before (a) and after (b) treatment by valent-zero iron and hydrogen peroxide (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0; and 2.0-g iron metal). Where:

bentazone t_r of 5.9 min (a), carbofuran t_r of 12.1 min (b), diuron t_r of 13.4 min (c), clomazone t_r of 13.7 min (d), tebuconazole t_r of 17.1 min (e), and pyraclostrobin t_r of 17.8 min (f)

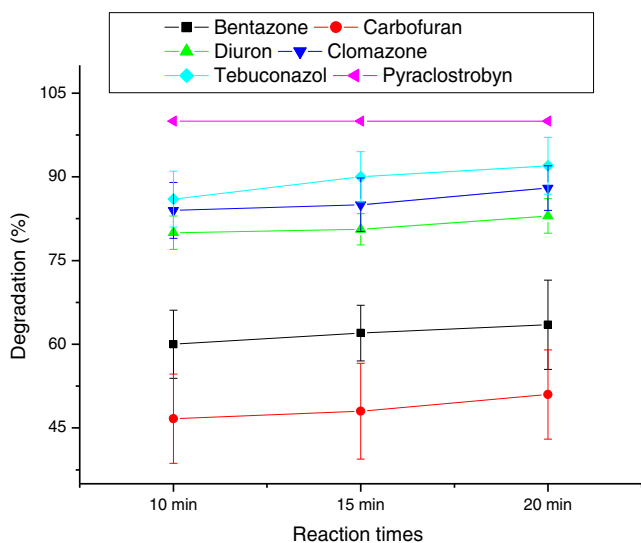


Fig. 7 Degradation efficiency of the system at different reaction times (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0; and 2.0-g iron metal). Bars indicated the RSD percentage values

times. Figure 7 shows that, after a 10-min reaction time, the system showed degradation rates between 47 and 100 %. The higher the reaction time, the more the degradation rate increased, e.g., after 20 min, the degradation rates were between 60 and 100 %.

In addition, a *t* test was carried out to compare the results obtained for these experiments. ANOVA was applied to evaluate the statistical similarity among three degradation rates under study. The Tukey's multiple comparison test was used to indicate significant differences among the main degradation rates, with 95 % significance level adopted for all comparisons. Results showed that the degradation rates at different reaction times were not significantly different (*t* test, $P > 0.05$).

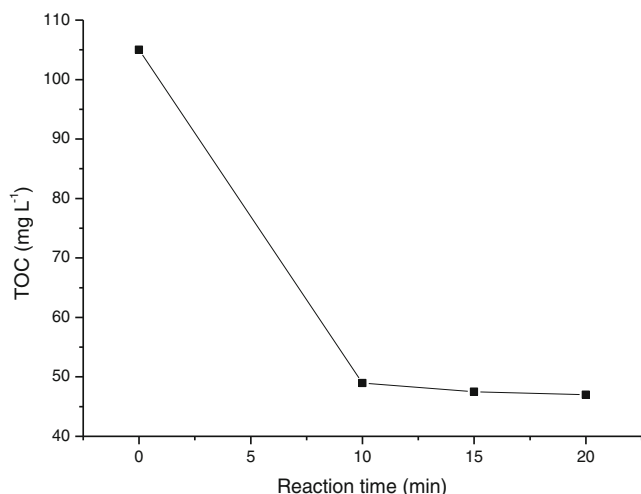


Fig. 8 Total organic carbon concentration during treatment (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0; and 2.0-g swarf)

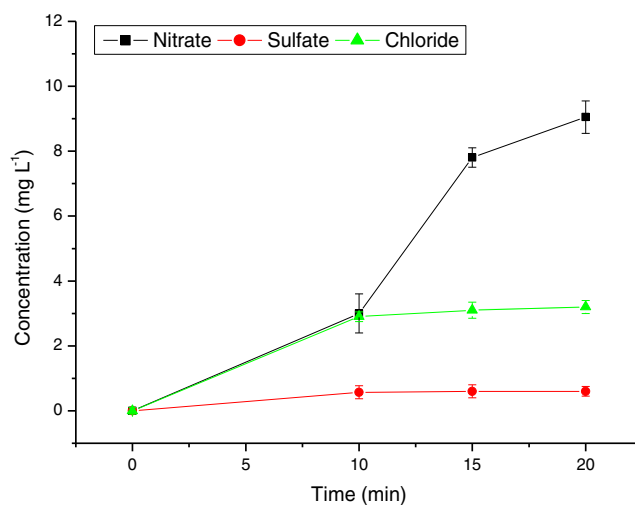


Fig. 9 Evaluated formation of NO₃⁻, Cl⁻, and SO₄²⁻ by ionic analysis (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0). Bars indicate the RSD % values

Figure 8 shows that the system under development also resulted in an excellent degree of aqueous solution mineralization, with 55 % mineralization after 20 min. The NPOC value was reduced from 105 to 47 mg L⁻¹. Furthermore, the ionic analysis by IC was used to confirm the mineralization of the aqueous solution. Results of this analysis (Figs. 9 and 10) revealed the formation of NO₃⁻, Cl⁻, PO₄²⁻, and SO₄²⁻, which were detected in the following concentrations: 9.05; 3.2; 1,809.7; and 0.6 mg L⁻¹, respectively; it complies with Brazilian laws regarding effluent disposal (National Environmental 2005).

The LC-ESI-MS/MS was used to evaluate the formation of carbofuran-3-hydroxy and 3,4 DCA by-products of pesticides carbofuran and diuron. This analysis revealed that these compounds were also removed during treatment of

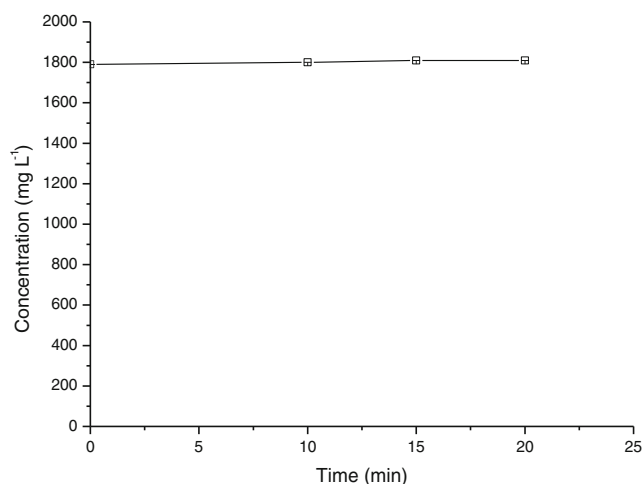


Fig. 10 Evaluated formation of PO₄²⁻ by ionic analysis (experimental conditions: 5 mmol L⁻¹ H₂O₂; pH 2.0). Bars indicate the RSD percentage values

synthetic wastewater. These by-products were detected in lower concentrations ($18 \mu\text{g L}^{-1}$ of 3,4 DCA and $39 \mu\text{g L}^{-1}$ of carbofuran-3-hidroxy) at the end of the treatment.

Considerations on tebuconazole and pyraclostrobin

As shown in Fig. 4, tebuconazole has the highest degradation rates for all pH values, a fact that can be explained by the hydrolysis and oxidation of tebuconazole in aqueous medium, due to the activity catalytic of the metals in the solution (Mann 2003; Calza et al. 2002). In addition, the high-degradation rates of the pesticide tebuconazole may be also explained by the extensive cleavage of the aromatic ring, producing degradates that lead to the mineralization (Calza et al. 2002).

The pesticide pyraclostrobin has low persistence in the environment. Hydrolysis was not observed in any value of pH. In environmental conditions, hydrolysis will not be expected (APVMA, 2003). However, pyraclostrobin showed high-degradation efficiency for all hydrogen peroxide concentrations, pH, and metal iron mass. It may occur due to the extensive cleavage and hydroxylation-type degradates that are formed together with the mineralization of the chlorophenyl side ring (APVMA, 2003).

Determination of total dissolved iron

At the end of the treatment, the determination of total dissolved iron using colorimetric determination by spectrophotometry (Associação Brasileira de Normas Técnicas ABNT 2010) resulted in $2 \text{ mg L}^{-1} \text{ Fe}^{2+}$, which is in accordance with the Brazilian laws regarding effluent disposal (CONAMA, 2005).

Determination of hydrogen peroxide residual

The determination of hydrogen peroxide residual content employing the colorimetric method by spectrophotometry (Eisenberg 1975) revealed that all hydrogen peroxide was consumed at the end of the Fenton's process.

Conclusions

The system that was developed, based on Fenton oxidation with zero-valent iron and hydrogen peroxide for the degradation of six different classes of pesticides and chemical groups, proved to be efficient. The degradation efficiency was strongly affected by the pH, the metal iron mass, and the hydrogen peroxide concentration. The best degradation conditions were pH 2.0, $5 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$, and 2.0-g swarf. At the end of the treatment, total organic carbon was reduced

(55 % mineralization) and the degradation rates ranged from 60 to 100 %.

The advantages of this system are rapid degradation (up to 20 min), high-degradation rates, simple handling, and low cost. In addition, it is an environmentally friendly and sustainable method because the source of the metal iron was swarf, a residue of a metallurgical activity. Besides, the aqueous complexes of ferric ions generated by this oxidation process during the treatment can start a new Fenton's reaction.

Acknowledgments The authors acknowledge the financial support and fellowships granted by the Brazilian agencies CAPES, FINEP, PETROBRAS, CORSAN and FURG. Part of this study was supported by a grant from the Brazilian Agency FAPERGS/CNPq (process number 010/0022-0), CNPq/CAPES (process number 552318/2011-6), CNPq (process number 477083/2011-00), FAPERGS (process number 11/0816-3), FAPERGS/PROCOREDES (process n°0905342), CAPES/PNPD (process number 23038.028239/2009-69). E.G. Primel received a productivity research fellowship from the Brazilian Agency CNPq (DT 310517/2012-5)

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