

Research Article

Degradation of Abamectin Using the Photo-Fenton Process

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The cultivation of strawberries generally requires substantial use of pesticides, and abamectin is the active principle of one of those most commonly employed. Conventional water treatment does not remove pesticides efficiently, so there is a need to investigate alternative procedures. The use of advanced oxidation processes (AOPs) can achieve good results in removal of toxic organic compounds present in aqueous solutions. The photo-Fenton process, one example of an AOP, was employed to study the degradation of abamectin. Results showed that when natural water samples contaminated with abamectin were treated using the photo-Fenton process, 70% of the initial amount of the compound was removed within 60 minutes of UV irradiation, and 60% mineralization was observed after 180 minutes of reaction.

1. Introduction

Biocides are one of the most important classes of compounds introduced into surface waters by human activities [1]. They are widely used in agriculture and can contaminate rivers and other water bodies due to transport from cultivated areas [2–5]. Although the pesticide industry has developed new compounds that are more effective, even at lower concentrations, and that present lower environmental impacts [6], the misuse of such pesticides can pose considerable toxicity risks to operators, consumers, and the wider environment [7].

The cultivation of strawberries uses large amounts of pesticides. One of the most commonly employed is Vertimec 18 EC, which contains 1.8% (w/v) of abamectin, the active principle. Abamectin belongs to the avermectin group and has the molecular formula $C_{48}H_{72}O_{14}$ (avermectin B1a) + $C_{47}H_{70}O_{14}$ (avermectin B1b). It is used primarily as a biocide. Abamectin is a toxic chemical and can be fatal if inhaled, ingested, or absorbed by the skin. It causes skin and eye irritation, and at high doses can cause damage to the central nervous system (CAS no., 71751-41-2). The substance is also highly toxic to fish and aquatic invertebrates. The maximum

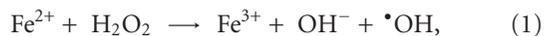
acceptable daily intake (ADI) is 0.01 mg kg^{-1} body weight, and the maximum residue limit is 0.02 mg kg^{-1} of the commercial product [8].

Effluents containing biocides cannot usually be treated efficiently using biological techniques, since the effluents are toxic to the microorganisms involved so that the biodegradation efficiency is reduced [9].

An alternative treatment that has been investigated is based on the use of advanced oxidation processes (AOPs), which are very efficient for the removal of potentially toxic organic compounds from water systems. In AOPs, hydroxyl radicals ($\cdot\text{OH}$) are formed as highly reactive intermediates, and can mineralize organic compounds to H_2O , CO_2 , and mineral acids [10–13].

The photo-Fenton process, an AOP, has attracted considerable interest due to its high efficiency in producing hydroxyl radicals during H_2O_2 decomposition catalysed by Fe^{2+} in acid solution under UV irradiation (1) and (2) [14]. Advantages of this process include the ability to use relatively low-cost reagents, and solar irradiation as the UV source. At the end of the process, the iron ions present can

be precipitated by increasing the pH, while the H_2O_2 is consumed during the reaction [15]:



The $\cdot\text{OH}$ generated can degrade organic pollutants present in aqueous solutions. Parameters such as pH and reagent concentration ratios must be controlled, in order to enhance the efficiency of the degradation process. The optimum pH range for the Fenton and photo-Fenton processes is 2.5–3.0 [16, 17]. The use of an excess amount of H_2O_2 can reduce the efficiency, since hydrogen peroxide can scavenge $\cdot\text{OH}$, generating $\cdot\text{HO}_2$ which has a lower reducing potential than the hydroxyl radical [18, 19].

Fenton and photo-Fenton processes have been successfully employed to treat a variety of effluents containing compounds such as dyes [20], antibiotics [21, 22], landfill leachates [23], and emerging contaminants [24].

The Federal University of Itajubá (Universidade Federal de Itajubá) is located in one of the major strawberry cultivation areas of Brazil. The objective of the present paper was to investigate the degradation efficiency of abamectin using the photo-Fenton process with UV irradiation.

2. Experimental

2.1. Pesticide Solutions. Abamectin solutions were prepared from the commercially available pesticide, in distilled water at a concentration of 9 mg L^{-1} (400 mg L^{-1} TOC). This concentration is the same as that used by farmers during strawberry cultivation.

2.2. Photo-Fenton Process. Iron nitrate (0.5 mmol L^{-1}) was added to the abamectin solution, and the pH was adjusted to 2.5 using 1.0 mol L^{-1} H_2SO_4 . The photoreactor consisted of an UV lamp (Hg, 125 W, $\lambda_{\text{max}} = 365 \text{ nm}$), inserted into a double jacket whereby the system could be cooled by water recirculation, and was immersed in the reaction solution. 6.0 mmol L^{-1} of H_2O_2 was added to the abamectin solution, and the lamp was turned on to start the reaction (17 mW cm^{-2} , as measured by a Cole-Parmer radiometer, series 9811). Samples were withdrawn at predetermined intervals, over periods of 60 or 180 minutes. To halt the Fenton reaction, the pH was raised to pH 10 using 6.0 mol L^{-1} NaOH, in order to precipitate iron hydroxide. The supernatant was separated by centrifugation and used for the different chemical analyses. The choice of pH value and the H_2O_2 and Fe^{3+} concentrations was based on previous work that used the Fenton reaction to treat another herbicide [25–27].

Natural water samples from the José Pereira stream ($22^\circ 24' 50'' \text{ S}$ and $45^\circ 24' 02'' \text{ W}$, in WGS 84 datum) were also spiked with the same concentration of abamectin and irradiated under the conditions already described. The objective of these tests was to study the efficiency of the Fenton reaction under conditions more representative of those arising from agricultural contamination.

Experiments were also performed without irradiation (Fenton process), using the $\text{H}_2\text{O}_2/\text{UV}$ advanced oxidative process. Control experiments using UV alone (direct photolysis), H_2O_2 alone, and iron alone with UV were conducted in order to evaluate the influence of each parameter on the degradation process.

2.3. Abamectin Quantification. Abamectin was quantified by GC/FID using a Varian Model CP 3380 instrument equipped with an AB-5 column ($25 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). Aliquots ($1 \mu\text{L}$) of the eluted samples were injected into the GC. The operating conditions of the oven were an initial temperature of 50°C for 1 minute, a ramp to 200°C at $15^\circ\text{C min}^{-1}$, and a final hold at 200°C for 1 minute. The injector temperature was 240°C , and the FID detector temperature was 300°C . All samples were injected 4 times, and the results were calculated as averages. All experiments were performed in triplicate.

Analytical grade abamectin (Sigma-Aldrich) was used to generate the calibration curve. The detection limit (DL) and quantification limit (QL) were calculated using the ratio of the standard deviation (s) and the slope (S) of the calibration curve (3) and (4) [28]:

$$\text{DL} = 3.3 \times (s/S), \quad (3)$$

$$\text{QL} = 10 \times (s/S) \quad (4)$$

Since the abamectin solution used for the degradation experiments was prepared from a commercially available pesticide that contained other compounds, it was necessary to separate the abamectin from the aqueous solutions prior to the chromatographic analyses. This was achieved by solid phase extraction using Waters Sep-Pak C_{18} cartridges [29]. After the degradation process, the samples were centrifuged in order to separate out the iron precipitate. The supernatant (50 mL) was passed through the Sep-Pak cartridge at a flow rate of 1.66 mL min^{-1} , using a glass syringe. The abamectin retained in the cartridge was then eluted with an aqueous solution containing 85% methanol. This extract was used for abamectin quantification using GC.

2.4. Statistical Analysis. The statistical analysis employed R software and its complement Tinn-R [30] and considered the data to be randomly distributed. The residuals of the data were determined, together with the homogeneity of the variances. The multiple comparison analysis used the Tukey test (at a 5% significance level).

2.5. Hydrogen Peroxide Determination. The hydrogen peroxide concentration was monitored spectrophotometrically using the metavanadate method [31].

2.6. Total Organic Carbon (TOC). The mineralization of organic material in the solution during the photodegradation was monitored by quantifying total organic carbon (TOC) using a carbon analyser (TOC 5000A, Shimadzu). These analyses were performed in the laboratory of the LAPOA

group, at the Institute of Chemistry, UNESP (Araraquara, São Paulo, Brazil).

3. Results and Discussion

Determination of abamectin is usually performed by liquid chromatography [32–35]. At present there are no reports in the literature concerning analysis of the compound by gas chromatography, so that a new method therefore needed to be developed. Injection of a methanolic solution of abamectin showed that it eluted at a retention time of 5.7 minutes. Validation of an analytical method involving a separation technique (such as GC) requires determination of parameters including the linearity of the analytical curve, the DL, and the QL [28]. The calibration curve obtained here showed good linearity, with a high correlation coefficient (0.9988). The calculated detection and quantification limits were 0.0168 mg L^{-1} and 0.0511 mg L^{-1} , respectively, which are low compared to the initial pesticide concentration. Repeatable quantification of abamectin was achieved after separation using Sep-Pak cartridges, showing that the method was also selective. These results demonstrated that the technique used to quantify abamectin met the requirements of the present paper, which were to identify abamectin and monitor its concentration with precision during the photo-Fenton treatment process.

3.1. Control Experiments. In order to understand the influence of the different experimental variables on the degradation of abamectin, experiments were performed using each variable individually. Combinations of variables (such as iron and UV) were also employed. Figure 1 shows the comparative results obtained for these tests.

Abamectin was destroyed by direct photolysis, with 39% removal after 1 hour of irradiation (Figure 1). This result indicates that the pesticide could be photodegraded if present in surface water within the photic zone. Mushtaq et al. [36] showed that avermectin, the chemical group to which abamectin belongs, was also degraded by direct photolysis in natural water after 22 days of solar irradiation. Nevertheless, direct photolysis will not occur in the natural environment when the compound is absorbed in the sediment, or when it is present below the photic zone.

Kamel et al. [37] studied the degradation of abamectin in Saudi Arabian soil. Removal rates of 66% and 88% were observed after 7 and 14 days of solar irradiation, respectively. However, the residual concentration remained higher than that permitted by legislation.

When iron was used alone, together with UV, there was 45% abamectin removal after 60 minutes of irradiation. This probably indicates that photoactive complexes formed between iron and other compounds present in the original pesticide sample, and/or their intermediates, were generated during the degradation process [25, 38]. Similar behaviour was observed by Park et al. [39] using the dye Acid Orange 7, by Silva et al. [25] during photo-Fenton degradation of the herbicide tebuthiuron using solar irradiation, and by Sun

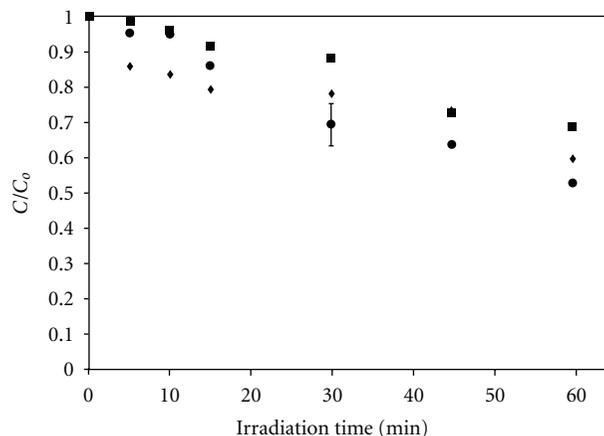


FIGURE 1: Comparison of the efficiency of degradation of abamectin using different treatments: —◆— direct photolysis; —■— H_2O_2 ; —●— $\text{Fe} + \text{UV}$. Initial conditions: $[\text{H}_2\text{O}_2] = 6.0 \text{ mmol L}^{-1}$; $[\text{Fe}^{3+}] = 0.5 \text{ mmol L}^{-1}$; abamectin = 9.0 mg L^{-1} , $\lambda = 365 \text{ nm}$; $\text{pH} = 2.5$.

and Pignatello [40], who attributed the second stage of 2,4-D degradation to iron complex photolysis in the presence of pesticide degradation intermediates. The relatively high degradation efficiency obtained here is interesting since there was no use of H_2O_2 , which could reduce the costs of treatment.

For more than 30 years, the use of H_2O_2 , a strong oxidant, has been commonplace in treatments involving oxidation of organic and inorganic pollutants [41, 42]. In the present paper, use of H_2O_2 alone (in the absence of irradiation) resulted in 30% removal of abamectin after 60 minutes (Figure 1).

3.2. Degradation Studies. Considering that in the control experiments abamectin removal was in the region of only 30% to 45%, the efficiency of degradation of the compound was also investigated using three different AOPs. Figure 2 shows the results of abamectin degradation using Fenton and photo-Fenton reactions, and the $\text{H}_2\text{O}_2/\text{UV}$ system.

In the experiments using the Fenton reaction, there was 40% abamectin removal after 1 hour of irradiation. Similar degradation efficiency was observed after the same time interval using $\text{H}_2\text{O}_2/\text{UV}$. Due to the radiation source used, which had a wavelength limit of $\lambda_{\text{max}} = 365 \text{ nm}$, the UV radiation was not able to cause H_2O_2 decomposition, which requires a wavelength near 254 nm [43]. In the present study, the UV radiation probably only acted to remove abamectin by direct photolysis.

Use of the photo-Fenton system improved abamectin degradation, with up to 55% removal after 30 minutes of reaction, and 80% removal after 60 minutes of irradiation. Similar results were obtained by Pignatello [16], who showed that the photo-Fenton process was more efficient than the Fenton process for degradation of 2,4-dichlorophenoxyacetic acid, since photo-reduction of Fe^{3+} ions to Fe^{2+} increased the catalytic effect. The Fe^{2+} ions can react again with H_2O_2 , and continue the Fenton reaction. The results obtained in

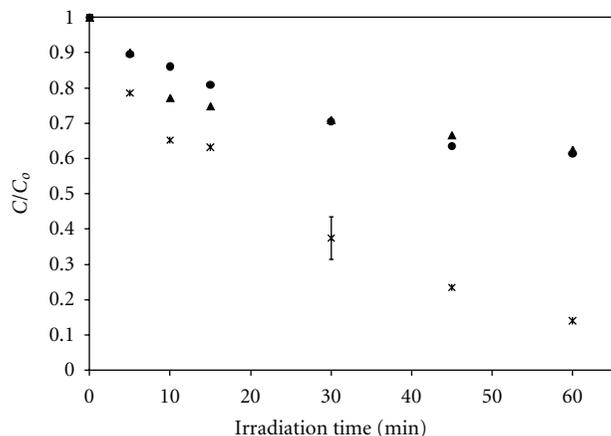


FIGURE 2: Comparison of degradation efficiency of abamectin using different AOPs: —▲— H₂O₂/UV; —●— Fenton reaction; —×— photo-Fenton reaction. Initial conditions: [H₂O₂] = 6.0 mmol L⁻¹; [Fe³⁺] = 5.0 mmol L⁻¹; abamectin = 9.0 mg L⁻¹, λ = 365 nm; pH = 2.5.

the present paper indicate that the photo-Fenton process is effective for the treatment of water and effluents contaminated with abamectin, with a high removal rate within a short irradiation period of up to 60 minutes.

The hydrogen peroxide concentration is an important parameter influencing Fenton and photo-Fenton processes. At high concentrations it can be detrimental to the degradation of organic compounds in water, since excess H₂O₂ can act as radical scavenger [44]. On the other hand, a lack of H₂O₂ interrupts the Fenton reaction, because its absence can halt hydroxyl radical production and, consequently, destruction of organic compounds. Therefore, monitoring the H₂O₂ concentration can help in adjustment of its initial concentration, and identify any need for further addition during the Fenton process.

Monitoring H₂O₂ levels showed that after 60 minutes there was a residual concentration of at least 10% of the initial concentration, and that there was therefore no need to add more H₂O₂ during the period of irradiation.

Figure 3 shows the outcome of the multiple comparison tests (Tukey's test at 5% level of significance) applied to the results of the degradation experiments. The photo-Fenton reaction (a) presented higher abamectin degradation efficiency than the other treatments. The Fe/UV treatment (b) showed better degradation efficiency compared to the H₂O₂ and H₂O₂/UV treatments (c). The results using UV alone and the Fenton process were statistically similar to the results obtained for Fe/UV, H₂O₂ alone, and H₂O₂/UV. These results indicated that each individual process could degrade abamectin to some extent; however, the best results were obtained using the photo-Fenton process.

3.3. Photo-Fenton Degradation of Abamectin in Natural Aquatic Samples. Abamectin removal by the photo-Fenton process reached 80% using solutions prepared in distilled water. In order to investigate removal of the pesticide under more natural conditions, the influences of the different

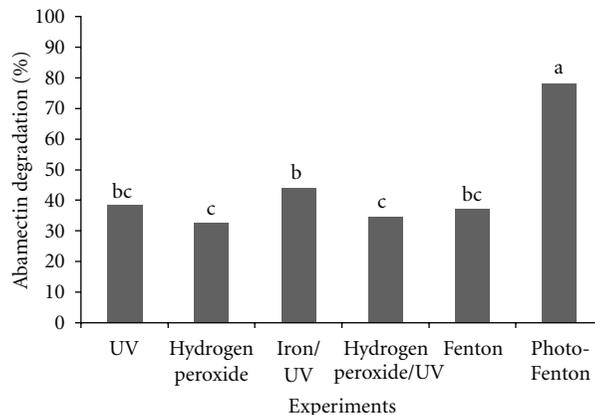


FIGURE 3: Multiple comparison tests for the different processes applied to abamectin removal. The same letters above the means for the different procedures indicates that statistically there were no differences between the procedures, using Tukey's test at a 5% level of significance. Conditions: [H₂O₂] = 6.0 mmol L⁻¹; [Fe³⁺] = 0.5 mmol L⁻¹; abamectin = 9.0 mg L⁻¹; λ = 365 nm; initial pH = 2.5.

physical and chemical parameters were investigated using water samples collected from the José Pereira stream, which were spiked with abamectin. Samples were collected on rainy and dry days. The water collected on a dry day showed values of 120 mg L⁻¹ of total solids and 2 mg L⁻¹ of BOD, while the sample collected during precipitation showed values of 307 mg L⁻¹ of total solids and 4 mg L⁻¹ of BOD. A comparison of abamectin degradation using either distilled water or the natural water samples is shown in Figure 4. It has been reported that organic compound degradation decreases in the presence of natural organic matter and solids, due to reduced penetration of UV radiation. The organic material can compete with the target compound for hydroxyl radicals and/or form complexes with iron, which reduces the efficiency of Fenton degradation [45]. However, even given the possible interferences, abamectin degradation under these conditions reached 70% after 60 minutes of reaction. No difference was observed between degradation of the pesticide in natural water samples collected on rainy or dry days.

3.4. TOC Analysis. Although the results showed that abamectin could be degraded, there was no significant difference in the TOC values after 60 minutes of irradiation. This suggests that abamectin was not mineralised, but that intermediates were generated during the reaction. In a similar study, Fallmann et al. [46] used the photo-Fenton process to treat an aqueous solution containing 100 ppm (TOC) of Vertimec, and observed 20% mineralization after 50 minutes of irradiation, achieving 90% after 150 minutes. However, the authors used a smaller quantity of initial TOC compared to the amount used in the present work (400 ppm). In another study, Bauer et al. [43] used the photo-Fenton reaction to treat a liquid effluent containing a mixture of 10 different pesticides, including Vertimec. The authors used an initial TOC concentration of 10 ppm of each

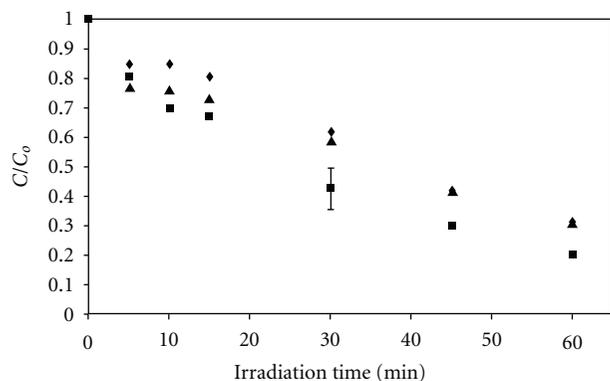


FIGURE 4: Comparison of abamectin degradation using the photo-Fenton process for: —▲— natural water; —◆— natural water (rainy day); —■— distilled water. Conditions: $[H_2O_2] = 6.0 \text{ mmol L}^{-1}$; $[Fe^{3+}] = 0.5 \text{ mmol L}^{-1}$; abamectin = 9.0 mg L^{-1} ; $\lambda = 365 \text{ nm}$; initial pH = 2.5.

pesticide in distilled water, which was treated in a solar UV reactor (300–400 nm). For the photo-Fenton process they used a concentration of $10^{-3} \text{ mmol L}^{-1} \text{ FeSO}_4 \cdot 7H_2O$ and 33 wt % of H_2O_2 , which was added in five portions. TOC removal was in excess of 80% after 3 hours of irradiation using the solar photo-Fenton process. The results of these two earlier studies suggest that in the present work, where the Vertimec solution contained an initial 400 ppm of TOC, the irradiation time and the amount of H_2O_2 were probably not sufficient to achieve pesticide mineralization.

Additional experiments were therefore performed in order to try to improve removal of TOC. In an attempt to reproduce the results obtained by Fallmann et al. [46], the initial concentration of TOC was decreased from 400 ppm to 100 ppm of Vertimec, the H_2O_2 concentration was raised to 20 mmol L^{-1} , with an iron concentration of 0.5 mmol L^{-1} . The exposure time was increased to 180 minutes, in line with that employed by Fallmann et al. [46]. The results of these studies, with a ratio Fe/H_2O_2 of 0.0833, showed that 60% of TOC was removed after 180 minutes. This result is very similar to those reported by Bauer et al. [43] and Fallmann et al. [46].

The possibility of reducing treatment costs was studied by decreasing the Fe/H_2O_2 ratio used for mineralization of 400 ppm (TOC) of Vertimec. Using iron and H_2O_2 concentrations of 1.0 mmol L^{-1} and 80 mmol L^{-1} , respectively (Fe/H_2O_2 ratio of 0.0125), there was 60% TOC removal after 180 minutes of irradiation. A further experiment was performed employing 0.5 mmol L^{-1} of iron and 80 mmol L^{-1} of H_2O_2 (Fe/H_2O_2 ratio of 0.00625); however, there was no observable removal of TOC. These results showed that there was a limiting amount of reagents required to achieve TOC removal. Abamectin could be degraded using Fe/H_2O_2 ratios smaller than 0.0125; however, there was no change in the TOC value, indicating that both the original organic compound and TOC should be monitored in order to ensure detoxification of the solution.

Studies of the toxicity and biodegradability of the possible reaction intermediates will be essential in order to

establish the optimum concentrations of the photo-Fenton reagents. Future investigations should provide information that addresses the need to effectively mineralize the pesticide, or at least degrade it to a nontoxic intermediate. Additional work is also needed to investigate the possibility of combining a biological process with the photo-Fenton treatment described in the present work.

4. Conclusions

Determination of abamectin by gas chromatography was successfully used to assess the efficiency of degradation of the pesticide by the photo-Fenton process.

The photo-Fenton process was shown to be an effective treatment for water and effluents contaminated with abamectin, achieving a high removal rate of 70% of the chemical after 60 minutes of UV irradiation. Increasing the concentrations of Fe^{2+} and H_2O_2 enabled attainment of at least 60% pesticide mineralization after 180 minutes of irradiation.

Acknowledgments

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