Photo-Fenton degradation of the insecticide esfenvalerate in aqueous medium using a recirculation flow-through UV photoreactor

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ABSTRACT

The aim of the study was to evaluate the efficiencies of photo-Fenton (Fe^{2+}) and (Fe^{3+}) processes in the degradation of high-concentrations of esfenvalerate (in the form of aqueous emulsion of a commercial formulation) using a recirculation flow-through photoreactor irradiated with UV light from a 15 W lamp (254 nm emission peak). The results obtained using a basic photo-Fenton (Fe^{2+}) reaction (esfenvalerate 17 mg L^{-1}; ferrous sulphate 1 mM; hydrogen peroxide 25 mM; pH 2.5) were compared with those acquired when ferrioxalate (1, 3 or 5 mM) served as the iron source. Degradation of the active component of the commercial formulation was significantly greater, and the rate of oxidation more rapid, using a photo-Fenton (Fe^{3+}) process compared with its Fe^{2+} counterpart. The most efficient degradation of the insecticide (75% in 180 min) was achieved with a reaction mixture containing 5 mM ferrioxalate. However, under the same experimental conditions, degradation of pure esfenvalerate preceded much faster (99% in 60 min) and was 100% complete within 180 min reaction time.

1. Introduction

The pyrethroids comprise a class of synthetic compounds whose structures are based on those of the naturally occurring pyrethrin insecticides. Pyrethroids are widely employed in urban areas for the control of pests in residential premises and on industrial sites (both interior and exterior locations), and in rural regions to protect a variety of agricultural crops [1]. The application of synthetic pyrethroid insecticides has increased substantially over the last few decades, concomitant with the decline in use of organophosphate pesticides that are far more toxic to birds and mammals [2,3].

Esfenvalerate [(S)-α-cyano-3-phenoxybenzyl-(S)-2-(4-chlorophenyl)-3-methylbutyrate] is a synthetic pyrethroid that is used against a wide range of pests including flies, moths and beetles. Because of its lipophilic nature, esfenvalerate is considered to be relatively immobile in the soil, showing only a small tendency to leach and, consequently, a low potential to pollute ground water. However, esfenvalerate can bind to particulate matter (clay, soil and sediment) and organic material that may be present in surface water in the form of a suspension [3]. Indeed, the levels of esfenvalerate that have recently been detected in water and sediment samples [4,5] suggest that the insecticide may represent a significant toxic hazard [6]. Furthermore, esfenvalerate has received considerable attention because of its adverse effects on animal and human reproductive health [7–9]. In this context, esfenvalerate is considered a potential endocrine disruptor and may be capable of interfering with the proper functioning of estrogen, androgen and thyroid hormones in humans and animals [10]. Moreover, the pyrethroid insecticide has been included in the initial list of 58 pesticides to be screened under the Endocrine Disruptor Screening Program (EDSP) organised by the Environmental Protection Agency (EPA) [11]. The "Final Work Plan" adopted by the EPA in 2010 has also called for a detailed evaluation of esfenvalerate with respect to its potential ecological and human health risks.

There is clearly an urgent need to elaborate efficient technologies for the removal of insecticides from water, sediments and soils. Promising results have been achieved through the application of advanced oxidation processes (AOPs) based on the production of hydroxyl radicals that successively attack organic material in a non-selective manner [12]. Hydroxyl radicals may be generated under atmospheric or subcritical conditions of temperature and pressure using a variety of reacting systems involving homogeneous or heterogeneous phases and in the presence or absence of catalysts and/or reactive energy (electrochemical, UV–vis or ultrasound).

The Fenton reaction is based on the complex redox interaction between Fe^{2+} and hydrogen peroxide to generate hydroxyl radicals, and it is believed that the Fe^{2+}/Fe^{3+} complexes so-formed play important catalytic roles in the further degradative processes. The efficiency of the interaction is improved under UV–vis irradiation [12], and the so-called photo-Fenton reaction has become one of the most widely used of AOPs in that it represents an

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environmentally friendly application of solar energy with commercial potential in the degradation of contaminants in effluents. While various photo-Fenton processes have been proposed recently for the degradation of toxic and non-biodegradable pollutants present in both low and high-concentrations [13–16], no publications have focussed on the degradation of esfenvalerate by AOPs. The aim of the present study was, therefore, to investigate the suitability and efficiency of photo-Fenton processes in the degradation of high-concentrations of esfenvalerate in aqueous emulsion using a recirculation flow-through UV photoreactor.

2. Experimental

2.1. Chemicals

Esfenvalerate (analytical standard; purity 97%) was obtained from Sigma–Aldrich (St. Louis, MO, USA; product number 46277), while a commercial formulation (Sumidan 25 EC®) containing $25\,g\,L^{-1}$ esfenvalerate was purchased from an agricultural store. All other reagents were of analytical grade unless otherwise stated. Methanol, acetonitrile and sulphuric acid were obtained from Mallinckrodt (Xalostoc, Edomex., Mexico), formic acid (reagent grade), sodium sulphite and ammonium molybdate were from Merck (Darmstadt, Germany), sodium oxalate and a 30% (w/w) solution of hydrogen peroxide (reagent grade) were from Ecibra (São Paulo, SP, Brazil), ferric nitrate nonahydrate was from Químis (Diadema, SP, Brazil), and ferrous sulphate heptahydrate was from Synthy (Diadema, SP, Brazil). Purified water (resistivity $18.2\,M\Omega\,cm$) was prepared using a Millipore (Eschborn, Germany) Milli-Q water purification system.

2.2. Photodegradation procedure

Hydrolysis and photodegradation experiments were carried out on the laboratory scale using a recirculation flow-through UV photoreactor, the cell of which was maintained in a Nova Ética (São Paulo, SP, Brazil) thermostatically controlled bath and irradiated using a Philips (Amsterdam, The Netherlands) 15 W UVC lamp (254 nm emission peak). In each experiment, the reactor was filled with 2 L of test solution and operated at a flow rate of $150\,L\,h^{-1}$ [determined using an Applitech (São Paulo, SP, Brazil) model AP300SS rotameter].

Preliminary experiments were performed in order to establish the kinetics of hydrolytic and photolytic degradation of the esfenvalerate-based commercial formulation. Hydrolysis was carried out in the absence of hydrogen peroxide, ferrous ions and light, and was performed using esfenvalerate emulsion ($17\,mg\,L^{-1}$) at its original pH of 6.3, and after adjustment to pH 2.5 by the addition of sulphuric acid. Photolysis was performed in the absence of hydrogen peroxide and ferrous ions, using an esfenvalerate emulsion ($17\,mg\,L^{-1}$; pH adjusted to 2.5) irradiated with UV light (254 nm). The kinetics of both the hydrolytic and photolytic reactions were established by determining the amounts of esfenvalerate remaining in sample aliquots of the reaction mixture that had been collected at appropriate reaction times within a 180 min reaction period.

In order to evaluate the behaviour of the esfenvalerate formulation during the photo-Fenton (Fe^{2+}) procedure, an initial experiment was conducted using an esfenvalerate emulsion ($17\,mg\,L^{-1}$) containing 1 mM ferrous sulphate with pH adjusted to 2.5 by the addition of sulphuric acid. The reaction was performed by gradually adding hydrogen peroxide solution ($30\,mg\,mL^{-1}$) at a flow rate of $1.0\,mL\,min^{-1}$ over a period of 62 min to give a final peroxide concentration of 25 mM. The total reaction time was 180 min, being the period determined in equilibrium experiments for the observation of a significant decrease in hydrogen peroxide concentration. In kinetic experiments, sample aliquots of the reaction mixture were taken at appropriate reaction times. Sodium sulphite (0.1 g) was added immediately to each sample in order to quench the peroxide and stop the Fenton reaction. The quenched sample was subsequently diluted with methanol, filtered through a $0.45\,\mu m$ cartridge and immediately analyzed in order to evaluate the levels of esfenvalerate, total organic carbon (TOC) and hydrogen peroxide present.

For comparison purposes, photo-Fenton (Fe^{3+}) experiments were performed in the presence of 1, 3 or 5 mM ferrioxalate (prepared by mixing appropriate amounts of ferric nitrate and sodium oxalate) with the pH of the reaction mixtures being adjusted to 2.5 by the addition of sulphuric acid.

2.3. Analytical procedures

Esfenvalerate was determined quantitatively by HPLC using a Shimadzu (Kyoto, Japan) Prominence LC 20 AT modular system comprising two CBM-20 A pumps, a CTO-10AS oven, a SIL 20A autosampler, an SPD-20A variable wavelength detector and an LC-10 Workstation Class data processor. Separations were carried out on a Supelco (Bellefonte, PA, USA) Supelcosil C-18 column ($250\,mm \times 4.6\,mm$ i.d.; $5\,\mu m$), protected by a Supelcosil C-18 column guard column ($20\,mm \times 4.6\,mm$ i.d.; $5\,\mu m$), eluted with mixtures of 0.5% formic acid in water (solvent A) and 0.5% formic acid in acetonitrile (solvent B) according to the program: 0–10 min, 60% B (isocratic); 10–11 min, 60–90% B (linear gradient); 11–30 min, 90% B (isocratic). The chromatographic conditions were: oven temperature 25 °C; flow rate $1.0\,mL\,min^{-1}$; injection volume $20\,\mu L$ (Rheodyne loop); and UV detection at 277 nm.

Mineralization of esfenvalerate in the commercial formulation (emulsion) and in the analytical standard (suspension) was evaluated through TOC analysis using a Shimadzu model TOC-V_{CPN} analyzer. The TOC concentration included the carbon content of the target compound, the by-products generated during the experiment and (where appropriate) that of the ferrioxalate present in the reaction mixture. The TOC value ($mg\,L^{-1}$) in the emulsion/suspension analyzed immediately after the addition of hydrogen peroxide (0 min) was set at 100%, and the percentage of mineralization was calculated from the level of residual TOC determined in an aliquot of the reaction mixture collected at final reaction time (180 min).

The amount of hydrogen peroxide consumed was estimated by measuring absorption at 350 nm (Cary-50 Scan UV-VIS spectrophotometer; Varian Inc., Lake Forest, USA) following the addition of ammonium molybdate to a sample of the reaction mixture [17].

3. Results and discussion

3.1. Preliminary investigation

Since the aim of the study was to evaluate the efficiency of the photo-Fenton degradation of esfenvalerate at high-concentrations, the initial amount of commercial formulation employed was always greater than its maximum solubility ($0.002\,mg\,L^{-1}$) in water at room temperature. Although the reaction mixture was in the form of an emulsion, constant circulation through the photoreactor maintained homogeneity and allowed reaction kinetics to be evaluated and compared under different experimental conditions.

No previous information was available concerning the behaviour of esfenvalerate during photo-Fenton (Fe^{2+}) treatment and, hence, an initial study was carried out in which the concentrations of reagents (ferrous sulphate 1 mM; hydrogen peroxide 25 mM) were chosen arbitrarily. The detection limit of
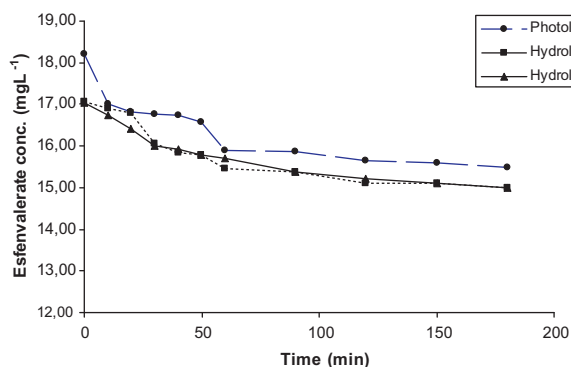
Fig. 1. Decrease in esfenvalerate concentration during the degradation of an esfenvalerate-based commercial formulation by hydrolysis at pH 6.3 and 2.5, and by photolysis at pH 2.5 [reaction mixture: esfenvalerate 17 mg L^{-1}; absence of ferrous ion and hydrogen peroxide].

Fig. 3. Level of residual hydrogen peroxide evaluated during the degradation of an esfenvalerate-based commercial formulation by a photo-Fenton (Fe^{2+}) process [reaction mixture: esfenvalerate 17 mg L^{-1}; ferrous sulphate 1 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].

the HPLC method (0.018 mg L^{-1}) governed the amount of esfenvalerate (17 mg L^{-1}) required in the reaction mixture in order to obtain optimal kinetic evaluations.

The pH value (2.5) of the reaction mixture was determined according to a literature report [13] that claimed pH 3–4 as the optimum range to promote the formation of hydroxyl radicals in Fenton processes.

Preliminary experiments revealed that esfenvalerate was not substantially degraded by hydrolysis or photolysis carried out in the absence of hydrogen peroxide and ferrous ions. Thus, after 180 min of reaction, the degradation of esfenvalerate in the commercial formulation stabilized at 12% following hydrolysis at pH 6.3 or 2.5, and at 15% following photolysis (Fig. 1). Oxidation of esfenvalerate during the photo-Fenton (Fe^{2+}) reaction proceeded very slowly (Fig. 2). The concentration of esfenvalerate started to show a significant reduction (of 11%) only after 120 min of reaction, and degradation of the commercial formulation stabilized at 39% after 150 min. Additionally, the removal of TOC (initial value
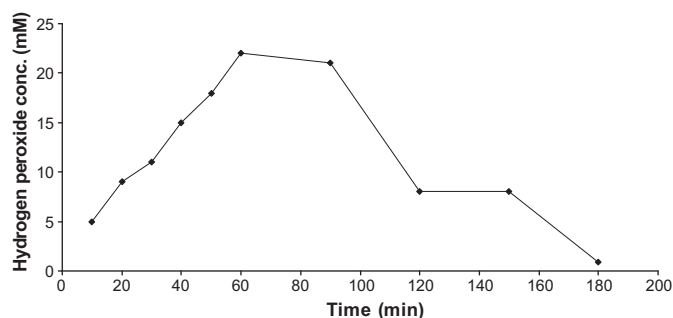
392.9 mg L^{-1}) was extremely inefficient with a reduction of just 2.8% after the total reaction time of 180 min. On the other hand, hydrogen peroxide was consumed throughout the reaction period (Fig. 3), with the highest consumption occurring between *ca.* 90 and 120 min of reaction time. HPLC analysis of the initial emulsion of the commercial formulation (Fig. 2) revealed the presence of an unidentified component, with retention time around 13 min, together with esfenvalerate (retention time 18 min). The HPLC peak associated with this compound was almost entirely eliminated after 120 min of reaction (Fig. 2), and the timing of this degradative process appeared to coincide with the highest rate of consumption of hydrogen peroxide. The low efficiency of degradation of esfenvalerate observed with the commercial formulation could be linked to the presence of this unidentified organic compound, which was probably more reactive than esfenvalerate. It is apparent from the HPLC profile of the reaction mixture determined at 180 min of reaction time (Fig. 2) that degradation of esfenvalerate commences only after complete oxidation of this unidentified component has been completed.
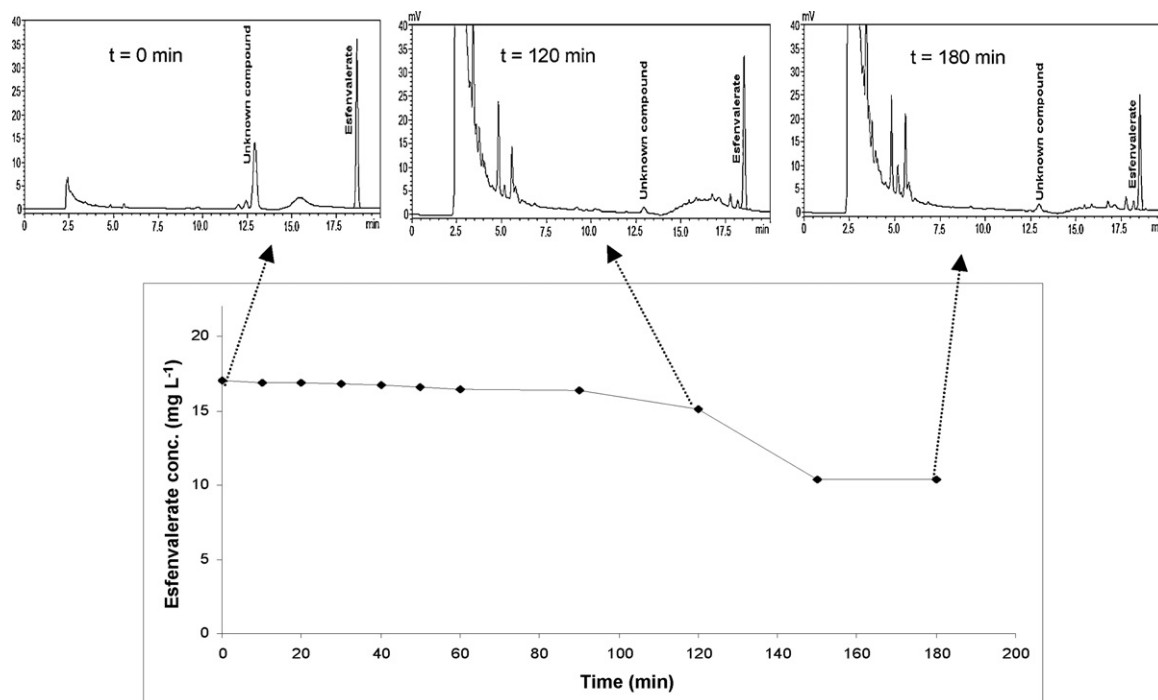
Fig. 2. Decrease in esfenvalerate concentration and HPLC-UV profiles during the degradation of an esfenvalerate-based commercial formulation by a photo-Fenton (Fe^{2+}) process [reaction mixture: esfenvalerate 17 mg L^{-1}; ferrous sulphate 1 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].

Fig. 4. Decrease in esfenvalerate concentration during the degradation of an esfenvalerate-based commercial formulation by photo-Fenton (Fe^{3+}) processes [reaction mixtures: esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 1, 3 or 5 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].
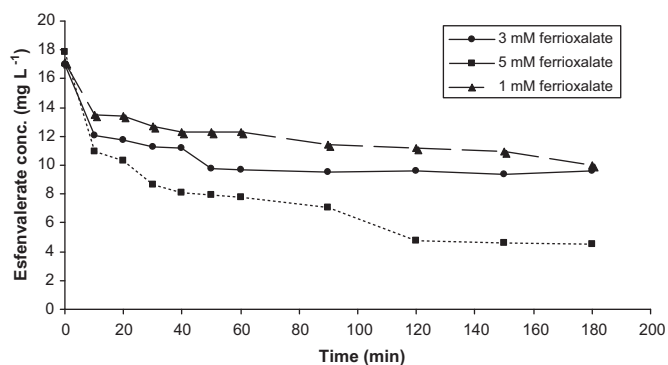
Fig. 5. Level of residual hydrogen peroxide evaluated during the degradation of an esfenvalerate-based commercial formulation by photo-Fenton (Fe^{3+}) processes [reaction mixtures: esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 1, 3 or 5 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].

3.2. Influence of iron source on the photo-Fenton reaction

It is known that complexes of Fe^{3+} in acidic medium absorb strongly in the wavelength range applicable to photolysis, i.e. from 250 to 480 nm, and their presence improves the efficiency of the photo-Fenton degradation of hazardous materials [18]. In this context, potassium ferrioxalate has been employed extensively as a chemical actinometer in the measurement of light intensity [12,19,20]. The intermediates and products formed in heterogeneous photo-Fenton systems in which ferrioxalate surface and solution complexes were subjected to photolysis have been reported [12,21]. In the present study, degradation of esfenvalerate (in the form of a commercial formulation) by photo-Fenton (Fe^{2+}) reaction was compared with that affected by a photo-Fenton process employing a Fe^{3+} oxalate complex. Additionally, the effect of iron concentration on esfenvalerate degradation conducted under different experimental conditions was determined.

In order to evaluate the efficiency of the Fe^{3+} complex, the conditions of the preliminary photo-Fenton (Fe^{2+}) experiment were repeated but with ferrioxalate 1 mM replacing the ferrous sulphate. As shown in Fig. 4, oxidation of the commercial formulation in the presence of Fe^{3+} complex was very efficient with the concentration of esfenvalerate being reduced by 21% within 10 min of reaction and by 42% at the termination of the reaction (180 min). Moreover, at the end of the photo-Fenton (Fe^{3+}) experiment, TOC removal had attained 11.6%, a value that is more than 4-fold greater than that obtained with photo-Fenton (Fe^{2+}).

The concentration of hydrogen peroxide in the reaction mixture containing 1 mM ferrioxalate stabilized at around 12.1 mM after 120 min of reaction, representing a consumption of 48% of the reagent supplied during the experiment (Fig. 5). This means that, although around 50% of the peroxide added was still present in the reaction mixture, its availability did not hinder the scavenging action of the hydroxyl radicals. Thus, despite the different degradation rates observed, hydrogen peroxide was still being use efficiently throughout the experiment.

The results presented here indicate that, along with the organic compounds present in the insecticide emulsion, esfenvalerate is more efficiently oxidized when ferrioxalate rather than ferrous sulphate is used as iron source. It has previously been suggested that the high quantum yield of Fe^{2+} generated by the ferrioxalate complex represents one of the main reasons for the high efficiency of ferrioxalate in the photo-Fenton (Fe^{3+}) compared with that based on the use of Fe^{2+} salts [20].
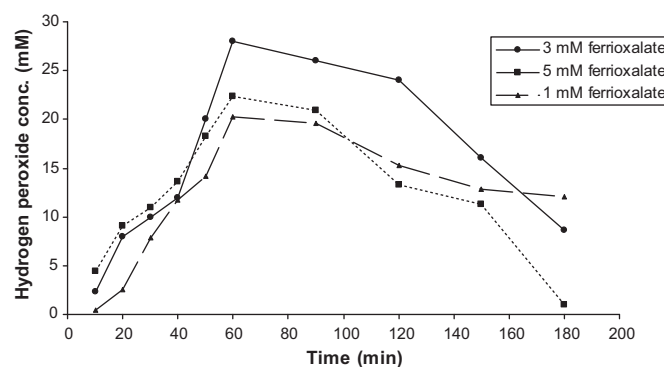
3.3. Influence of ferrioxalate concentration on the photo-Fenton reaction

In order to determine the effect of Fe^{3+} complex concentration on the efficiency of the photo-Fenton degradation of esfenvalerate, reactions were carried out using 3 and 5 mM ferrioxalate while maintaining the concentrations of commercial formulation and of hydrogen peroxide at the levels employed in the earlier experiments (Fig. 4). The most efficient elimination of insecticide was achieved in the presence of 5 mM ferrioxalate with 75% of the esfenvalerate having been removed after 180 min reaction time in comparison with the 42 and 53% degradation observed with 1 mM and 3 mM ferrioxalate, respectively. Additionally, TOC removal in the presence of 5 mM ferrioxalate attained 46% (initial value $523.1\,mg\,L^{-1}$) at the end of the reaction against values of 11.6 (initial value $226.8\,mg\,L^{-1}$) and 15.2% (initial value $379.6\,mg\,L^{-1}$) achieved with 1 and 3 mM ferrioxalate, respectively.

While there were no significant differences in the amount of hydrogen peroxide required to bring about the degradation of esfenvalerate in the presence of 1 or 3 mM ferrioxalate (Fig. 5), the peroxide was almost totally consumed (0.26 mM residual) after 180 min reaction time with 5 mM ferrioxalate. It is well know that when the hydrogen peroxide concentration is too high, simultaneous reactions can occur that consume peroxide in the matrix thus reducing the efficiency of hydroxyl radical generation [15,22]. In the present study, peroxide was gradually consumed during the reaction period, and even after stabilization of esfenvalerate degradation (i.e. after 120 min reaction), which implies that the reagent was utilised efficiently in each of the experiments.

3.4. Influence of esfenvalerate matrix on the photo-Fenton reaction

It has been demonstrated that some organic compounds potentially present in commercial formulations can seriously affect the efficiency of the degradation process. In order to investigate this aspect further, degradation experiments were performed using pure esfenvalerate (analytical standard). For this purpose, an appropriate amount of the standard was dissolved in methanol and the resulting solution diluted with water (in the proportion of 1:400, v/v). The experiment was performed using the reaction conditions that had previously provided the most efficient degradation of the commercial formulation (i.e. esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 5 mM; hydrogen peroxide 25 mM; pH 2.5). As shown in Fig. 6, the degradation of pure esfenvalerate was rapid (94% degradation in 60 min) and the standard had been completely eliminated after 180 min. Similarly, in comparison with commercial formulation,
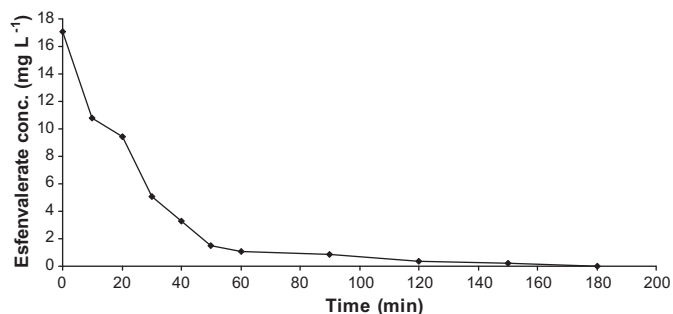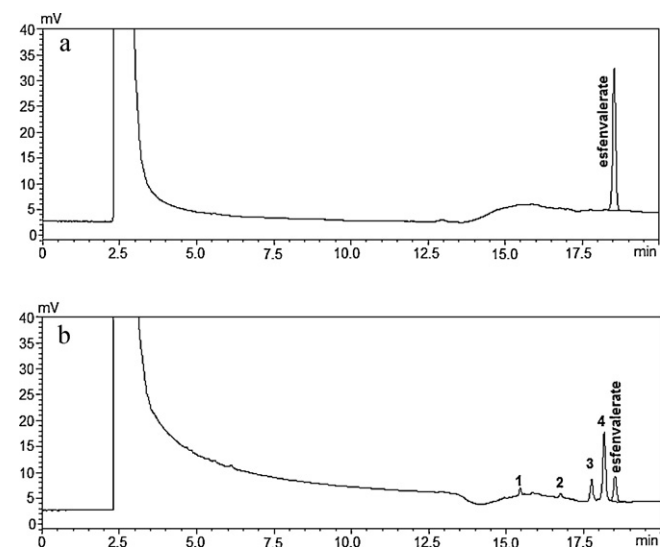
Fig. 6. Decrease in esfenvalerate concentration during the degradation of pure esfenvalerate by a photo-Fenton (Fe^{3+}) process [reaction mixture: standard esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 5 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].
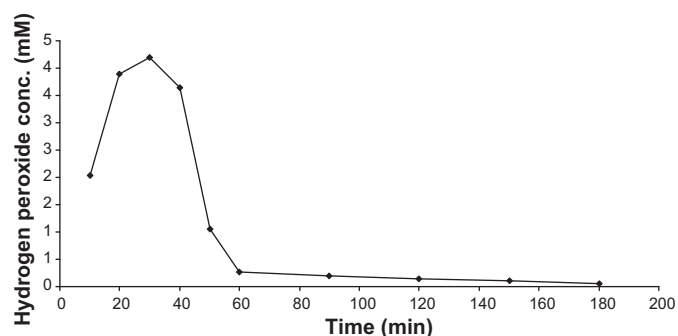
Fig. 7. Level of residual hydrogen peroxide evaluated during the degradation of pure esfenvalerate by a photo-Fenton (Fe^{3+}) process [reaction mixture: standard esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 5 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].

Fig. 8. HPLC-UV profiles of an esfenvalerate-containing reaction mixture after (a) 0 min and (b) 60 min of degradation by a photo-Fenton (Fe^{3+}) process [reaction mixture: esfenvalerate $17\,mg\,L^{-1}$; ferrioxalate 5 mM; hydrogen peroxide 25 mM (attained by gradual addition); pH 2.5].

the consumption of hydrogen peroxide occurred far more rapidly in the presence of pure esfenvalerate with 99% of the reagent having been used up during the first 60 min of reaction and 100% consumed at 180 min (Fig. 7). However, TOC removal attained only 36% (initial value $705.3\,mg\,L^{-1}$) at the termination of the reaction owing to the generation of carbon-containing by-products that can be observed in the HPLC profiles presented in Fig. 8.

4. Conclusion

Esfenvalerate, present in aqueous emulsions of a commercial formulation, could be degraded in a recirculation flow-through UV photoreactor using variations of the photo-Fenton process. Hydrolysis and photolysis of esfenvalerate in the absence of hydrogen peroxide and ferrous ions led to the degradation of just 12 and 15%, respectively, of the active component of the commercial formulation following 180 min of reaction. Photo-Fenton processes carried out under diverse experimental conditions, including different types and amounts of iron sources, revealed that the most efficient degradation (75% in 180 min) of esfenvalerate in the commercial preparation could be achieved with a reaction mixture containing 5 mM ferrioxalate and 25 mM hydrogen peroxide at pH 2.5. Under the same experimental conditions, however, degradation of pure esfenvalerate proceeded much more rapidly (99% in 60 min) and was complete within 180 min reaction time. The observed variation in the efficiency of degradation of the two forms of esfenvalerate was caused by the presence of an organic compound in the commercial formulation that was more reactive than active principle itself. Although the degradative efficiency of the photo-Fenton (Fe^{3+}) reaction was enhanced by an increase in ferrioxalate concentration, TOC removal (mineralization) was not complete owing to the formation of organic by-products.

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