



Fenton and Fenton-like oxidation of pesticide acetamiprid in water samples: Kinetic study of the degradation and optimization using response surface methodology



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HIGHLIGHTS

- Evaluation of acetamiprid degradation using Fenton.
- Investigation of the effect of different concentrations of H_2O_2 and Fe^{2+} .
- Evaluation of various initial pH and different iron salts as Fe^{2+} and Fe^{3+} sources.
- Application of response surface methodology in the evaluation of the process kinetics.
- Investigation of the use of zero valent iron as a constant source of ferrous ions.

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ABSTRACT

The aims of this study were (a) to evaluate the degradation of acetamiprid with the use of Fenton reaction, (b) to investigate the effect of different concentrations of H_2O_2 and Fe^{2+} , initial pH and various iron salts, on the degradation of acetamiprid and (c) to apply response surface methodology for the evaluation of degradation kinetics.

The kinetic study revealed a two-stage process, described by pseudo- first and second order kinetics.

Different $H_2O_2:Fe^{2+}$ molar ratios were examined for their effect on acetamiprid degradation kinetics. The ratio of $3\text{ mg L}^{-1} Fe^{2+}: 40\text{ mg L}^{-1} H_2O_2$ was found to completely remove acetamiprid at less than 10 min. Degradation rate was faster at lower pH, with the optimal value at pH 2.9, while Mohr salt appeared to degrade acetamiprid faster.

A central composite design was selected in order to observe the effects of Fe^{2+} and H_2O_2 initial concentration on acetamiprid degradation kinetics. A quadratic model fitted the experimental data, with satisfactory regression and fit. The most significant effect on the degradation of acetamiprid, was induced by ferrous iron concentration followed by H_2O_2 . Optimization, aiming to minimize the applied ferrous concentration and the process time, proposed a ratio of $7.76\text{ mg L}^{-1} Fe(II): 19.78\text{ mg L}^{-1} H_2O_2$. DOC is reduced much more slowly and requires more than 6 h of processing for 50% degradation. The use to zero valent iron, demonstrated fast kinetic rates with acetamiprid degradation occurring in 10 min and effective DOC removal.

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1. Introduction

Pesticides represent one of the most important classes of organic pollutants mainly due to their widespread use and increased toxicity. They pose a threat to environmental recipients, since they can exhibit increased persistence, bioaccumulation and be easily transported over long distances from their deposition sources (Gavrilescu, 2005; Loewy et al., 2011).

Neonicotinoids comprise a fairly new and widely used category of organic compounds, which could pose a threat to the aquatic

and terrestrial environment. They represent the fastest-growing class of commercialized insecticides for the past two decades, covering 17% of global pesticide market (Jeschke, 2008). Their active compounds and basic by-products, exhibit high water solubility and polarity, increased photo-stability as well as persistence in water and soil matrices, thus enabling their transference in water, both surface and groundwater (Dujaković, 2010).

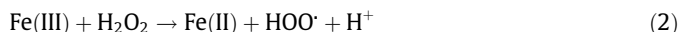
Acetamiprid is a widely applied third generation insecticide of this group. It can be used in a variety of crops, for example vegetables, melons, fruit trees, wheat, tobacco, cotton. It is soluble in most organic solvents and shows increased solubility in water (25 g L^{-1}) (Kagabu, 1997; Matsuda, 2001). It absorbs to less than $\lambda_{\text{max}} 290\text{ nm}$ and therefore is stable to the influence of solar

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radiation (Kagabu, 1995). Despite the extended use of acetamiprid (Fig. 1), its degradation has been less frequently investigated.

The Fenton reaction is an advanced oxidation process (AOP) that underlines generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$) and is considered a viable alternative for the oxidative degradation of organic pollutants. Its advantages are the applicability to room temperature, low cost, simplicity and environmental friendliness, while the disadvantages include the need to regulate pH to acidic conditions, the possible coexistence of different interferences and the inevitable production of iron sludge, representing an extra step in the final process, which is to coagulate and collect iron sludge using filtration. Both ferric and ferrous ions can react with peroxide, although the reaction of Fe (II) with H_2O_2 , has been established as Fenton reaction (Eq. (1)) while in literature the reaction of Fe (III) with H_2O_2 is referred to as Fenton-like reaction (Eq. (2)). Reaction with ferric ions (Eq. (2)) is much slower than with ferrous ions (Eq. (1)) and therefore represents kinetically the decisive stage (Fenton, 1984).



Zero valent iron (ZVI or Fe^0) has been studied as an alternative source of iron for Fenton-like reaction, as it is the most commonly used active tool for the in situ treatment of contaminated groundwater and it is able to process a wide range of organic pollutants (Ghauch, 2001; Bergendahl, 2004; Ghauch, 2008; Zhou, 2008; Pignatello et al., 2006).

Response surface methodology is a statistical approach that has become a useful tool for optimizing analytical data, providing reduced number of experiments, low cost and possibilities to evaluate interactions among variables. It is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behavior of a data set with the objective of making statistical previsions. These techniques also enable the selection of optimal experimental conditions, helping to avoid trivial mistakes during optimization (Ramirez, 2005; Bezerra, 2008).

The aims of this study were (i) to assess the degradation of the insecticide acetamiprid through Fenton and Fenton-Like reactions, using various ferrous iron sources, (ii) to investigate the effect of different concentrations of H_2O_2 and Fe^{2+} , initial pH and iron salts on the degradation on the selected pesticide and (iii) to apply response surface methodology for the kinetic study.

2. Materials and methods

2.1. Reagents

Insecticide acetamiprid (CAS number 135410-20-7) was used in solid crystalline form, purity 99.9% (Fluka Pestanal). Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was prepared in situ using Millipore Direct-Q 3 UV System device. For the buffer solutions of the hydrolysis experiments monohydrate citric acid purity 99.9% (Fluka), Na_2HPO_4 , NaH_2PO_4 , NaHCO_3 and Na_2CO_3 (99.9% Fluka) were used. H_2SO_4 (>99.5% trace analysis) from Sigma–Aldrich was used. For the kinetics experiments, hydroxyl peroxide (30% w/v solution) from Panreac was used, and in order to check the effectiveness of

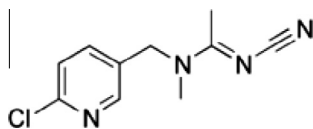


Fig. 1. Structure of selected neonicotinoid pesticide acetamiprid ((E)-N-[(6-chloro-3-pyridinyl)methyl]-N-cyano-N-methylethanimidamide).

iron salts, solid crystalline substances $\text{Fe}_2(\text{SO}_4)_3$ (heptahydrate) from Panreac, FeCl_2 (exahydrate) from Merck and ammonium ferrous sulfate – Salt of Mohr (exahydrate) from Panreac, were used. For the analysis of ferrous ions, Phenanthroline 1–10 solid was obtained from Panreac (99.7%). CH_3COOH and CH_3COONa were obtained as solids (99.9% purity) from Sigma–Aldrich. For the chromatographic analysis methanol (LC–MS purity) and formic acid (99.5%) were obtained from Merck. Zero-valent iron (powder 75–150 μm) was obtained by Sigma Aldrich. NH_4VO_3 solid for H_2O_2 concentration measurement was purchased by Sigma Aldrich.

2.2. Chromatographic determination of acetamiprid

The concentration of the active substance acetamiprid was determined using a Waters Acquity Ultra-pressure Liquid Chromatography with a C18 chromatography column (1.7 μm , $2.1 \times 50 \text{ mm}$) coupled with photodiode array detector (monitoring wavelengths 254 nm, 220 nm and 280 nm). The gradient elution was achieved with solvent A: ultrapure water:methanol (98:2) with 0.1% formic acid and B: methanol with 0.1% formic acid (organic phase) at a flow-rate of 0.45 mL min^{-1} , with sample volume of 20 μL . The analysis time was 6 min. A gradient elution was applied starting at A:B ratio of 95:5 and staying stable until 0.5 min. Then, eluent A decreased to 10% in 1.3 min and stayed isocratic 3 more minutes. Eluent A increased again to 95% and stayed stable for 1.2 min to prepare next sample. Empower software was used for the analysis of the chromatographic data. R_t of fluoxetine was 2.40 min. Under these conditions the limit of detection was calculated at 0.05 mg L^{-1} .

2.3. Hydrolysis and Fenton degradation experiments

Aqueous standard solutions were prepared mainly due to the increased acetamiprid water solubility. Hydrolysis of the selected pesticide was studied in four baseline pH levels at an initial concentration of acetamiprid 5 mg L^{-1} ($0.023 \text{ mmol L}^{-1}$). To adjust pH, three buffers were used (pH = 3.7, 6.9 and 10.0) to cover three ranges of pH (acidic, neutral and basic) to a final volume of 1 L. Buffer pH 3.7 was prepared as follows: in a 250 mL flask, 20.014 g monohydrate citric acid were dissolved in ultrapure water. 5.610 g KOH were added and the solution was warmed to 50°C for 30 min. After cooling to room temperature, the solution was diluted with ultrapure water to a final volume of 1 L. Buffer pH 6.9 included 1.375 g KH_2PO_4 and 1.419 g Na_2HPO_4 in 1 L of ultrapure water. For the basic buffer pH 10, 2.121 g NaHCO_3 και 2.676 g Na_2CO_3 were diluted with ultrapure water in 1 L. Hydrolysis was also realized at pH 2.9 using 0.1 M H_2SO_4 which is considered to exhibit the most effective degradation results at a Fenton reaction (Zepp et al., 1992).

For Fenton experiments, various solutions of the active substance were added in dark bottles (250 mL) at different initial concentrations after appropriate dilution of the concentrated standard stock solution of the compound and they were agitated. The pH adjustment was realized by adding sulfuric acid 0.1 M at various levels. For the study of the effect of hydrogen peroxide concentration and ferrous or ferric ion concentration, to the degradation rates of acetamiprid, different initial amounts of reagents were added to the reactor. Samples were obtained at frequent time periods and analyzed for acetamiprid concentration, DOC content, ferrous ion concentration and hydrogen peroxide concentration.

Ferrous ions were determined photometrically as follows: 4 mL sample were added to 0.4 mL phenanthroline 0.1% w/v in 0.8 mL acetic ammonium buffer (pH = 4). After 10 min, the developed color is measured at 510 nm (Wittbrodt and Palmer, 1996).

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