



Electro-Fenton oxidation of imidacloprid by Fe alginate gel beads



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ABSTRACT

This study describes the removal of imidacloprid by a heterogeneous electro-Fenton system with iron alginate gel beads (EF-FeAB). The effects of the initial pH and initial concentration of alginate beads (FeAB) on the imidacloprid removal rate were studied. The removal efficiency was maintained with an increase in Fe dosage and decreased with an increase in the initial pH. The optimum dose of iron alginate gel beads (FeAB) was found to be 1.3 mM, and complete imidacloprid removal was observed within 120 min at an initial pH of 2. A kinetic analysis showed that the removal of imidacloprid by EF-FeAB followed a first-order kinetics model. Because complete mineralization was the primary goal, the main degradation routes of imidacloprid were proposed on the basis of LC-MS data. Finally, the process was implemented in continuous mode with FeAB in a stirred-tank reactor. High imidacloprid removals of 80% and 90% were achieved by operating for residence times of 2 and 4 h, respectively. The process ran continuously without operational problems, and the particle shapes were maintained throughout the oxidation process.

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1. Introduction

Pesticides are used for controlling, repelling, preventing or eradicating pests and include not only a wide range of chemical compounds but also antimicrobial or disinfectant agents. According to the active chemical groups, the main categories of pesticides are as follows: organochlorines, organophosphates, organosulfurs, carbamates, formamidines, dinitrophenols, pyrethroids, nicotinoids, spirocinas, phenylpyrazoles, pyrroles and pyrazoles, among others. Despite their positive effects in agriculture, their compositions often pose a threat to humans and the environment [1].

Pesticide production and application have progressively increased worldwide during recent decades. Among these compounds, imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitro-imidazolidin-2-ylideneamine] is a widely used insecticide introduced for agricultural use in the 1990s, and it is mainly used at the present to control sucking insects in crops (e.g., aphids, leafhoppers, thrips, whiteflies and termites) [2,3]. Imidacloprid belongs to the nicotinoid chemical family. Because of their molecular shape, size, and charge, nicotinoids fit into receptor molecules in the nervous system that normally receive the molecule acetylcholine. Imidacloprid and other nicotinoids irreversibly block acetylcholine receptors. Therefore, imidacloprid is toxic to some species of aquatic animals at extremely low concentrations [2]. In addition, according to the EPA, the high solubility of imidacloprid along with

its mobility and potential to leach into ground water are concerns during its transport to surface water in dissolved runoff [4].

More and more xenobiotics are being detected in the environment all the time, especially pesticides. To address the pollution of agricultural wastewater by pesticides, various treatment processes have been studied, namely physical treatments (lined evaporative beds and activated carbon adsorption), chemical treatments (photolysis, hydrolysis and chemical oxidation) and biological treatments (bacterial degradation) [5–7].

Different advanced oxidation processes (AOPs) have proven to be powerful oxidative techniques for treating several organic pollutants such as pesticides [8–12]. AOPs are based on the *in situ* generation of hydroxyl radicals ($\bullet\text{OH}$), a highly powerful oxidizing agent. Among these processes, Fenton and electro-Fenton techniques have attracted attention from investigators around the world. These processes are based on the oxidation of ferrous iron to ferric iron by hydrogen peroxide (Eq. (1)), releasing a hydroxyl radical with the capacity to oxidize contaminants.



The electro-Fenton process uses electric current for the *in situ* generation of H_2O_2 by O_2 reduction in the presence of dissolved Fe^{2+} . Furthermore, the overall process does not create secondary pollutants because there is a catalytic cycle with Fe^{3+} species in the medium that revert to Fe^{2+} by different reduction processes, which involve H_2O_2 or organic intermediate radicals, as well as the direct reduction of Fe^{3+} on the cathode. Therefore, the weight of the added ferrous iron (II) is much smaller than it is in the traditional Fenton method [13].

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Hence, the electro-Fenton process offers the advantage of avoiding the continuous addition of H_2O_2 , which is an unstable and potentially harmful compound. In addition, iron recycling reduces Fe precipitation at high pH values and the formation of Fe sludge [13]. Several studies have concluded that the electro-Fenton process is more economical, efficient and environmentally friendly for removing organic matter than other conventional processes [14–20]. In recent years, electro-Fenton processing has been shown to be an effective alternative for the removal of several substances such as refractory organic compounds from stabilized landfill leachate [21], photographic processing wastewater [22], cephalixin [23], atrazine [24] and flumequine [25]. In addition, pesticides were also treated with Fenton processes [26–29] to good effect. Zhao et al. [30] degraded the pesticide imidacloprid by employing a $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ /activated carbon aerogel cathode within a wide range of pHs, leading to 90% removal after 30 min of treatment.

The main drawbacks in Fenton or electro-Fenton processes are that the use of dissolved iron as a catalyst requires its subsequent removal from treated water, mostly as iron oxyhydroxide sludge. For this reason, significant efforts have been made in recent years in the field of heterogeneous catalysis to facilitate the reuse of iron [31–34]. Among the different catalysts used in heterogeneous Fenton reactions, iron alginate gel beads (FeAB) have shown high catalytic activities for the oxidation of organic compounds, with minimal iron leaching [35–38]. Their immobilization in biopolymer matrix beads is a simple, inexpensive and effective technique [37] that permits their operation within a wide range of pHs. Furthermore, FeAB can be continuously reused in batch or continuous mode for the treatment of synthetic dyes [36,37].

This study focuses on the applicability of FeAB as a heterogeneous electro-Fenton catalyst in the degradation of imidacloprid. The efficiency of the electro-Fenton method with iron alginate gel beads (EF-FeAB) was studied through the reduction of imidacloprid and the characterization of imidacloprid transformation products by LC–MS. Finally, the reusability of this catalyst was shown in continuous mode experiments under ideal operational conditions.

2. Experimental

2.1. Imidacloprid solution

Imidacloprid solution (100 mg L^{-1}) was prepared using an imidacloprid-grade Pestanal analytical standard provided by Sigma–Aldrich (Barcelona, Spain).

2.2. Iron alginate gel beads (FeAB)

A 2.0% (w/v) sodium alginate solution was purchased from Sigma–Aldrich (Barcelona, Spain) and dropped through a syringe into hardening solution composed of 0.05 M Fe^{3+} (Fe_2SO_3 , Sigma–Aldrich (Barcelona, Spain)) to create spherical alginate beads loaded with Fe [37]. These particles were cured at 4°C for 2 h in the gelling solution, then filtered and washed repeatedly with distilled water. Finally, they were stored at 4°C in distilled water for the degradation study.

2.3. Batch electrochemical reactor set-up

Several batch experiments were completed in an electrochemical cell with a working volume of 0.15 L. The cathode was formed from a graphite sheet (Carbon Lorraine, France) and a Boron-Doped Diamond (BDD) (DiaChem, Germany) electrode was used as an anode. Both portions were connected to a direct current power supply (HP model 3662). The electrodes (surface 11 cm^2) were placed in opposition to each other with an electrode gap of 6 cm. A constant

potential drop of 5 V was applied with a power supply (HP model 3662). This value was shown to be optimal by Iglesias et al. [35]. The process was monitored with a multimeter (Fluke 175). The reactor was filled with imidacloprid solution at the desired pH. The solution was agitated with a magnetic stirrer to avoid concentration gradients.

During the electro-Fenton process (Fig. 1A), a continuous bubbling (1 L min^{-1}) of air at atmospheric pressure was maintained in the reactor around the cathode; this flow started 10 min before the electro-Fenton process to reach a stationary O_2 concentration. This bubbling was carried out for the *in situ* generation of H_2O_2 by the electrochemical reduction of oxygen [39]. Under this configuration, different experiments were carried out using free and immobilized Fe ion (FeAB) systems according to the selected concentration of Fe.

2.4. Sample preparation and preservation

For all experiments, 1 mL samples were taken periodically from the reactor to be analyzed for pH, pesticide concentration and degradation product identification. The samples were saved in hermetically sealed glass vials and protected from light. Vials were stored at 4°C until the analysis.

2.5. Imidacloprid analysis

The sample imidacloprid concentrations were determined by HPLC (Agilent 1100) equipment with an XDF-C8 reverse-phase column ($150\text{ mm} \times 4.6\text{ mm i.d.}$, $5\ \mu\text{m}$). Prior to injection, the samples were filtered through a $0.45\ \mu\text{m}$ Teflon filter. The injection volume was set at $20\ \mu\text{L}$, and an isocratic eluent (50:50 acetonitrile/water) was pumped at a rate of 1 mL min^{-1} for 5 min. Detection was performed with a diode array detector at 270 nm, and the column temperature was maintained at room temperature.

To identify the transformation products obtained in the imidacloprid degradation, several samples were analyzed with HPLC–MS (Agilent 1100) equipment with an LC column Luna $5\ \mu\text{C}18\ 100\text{A}$. The samples were filtered through a $0.45\ \mu\text{m}$ Teflon filter before injection. In this case, the isocratic eluent was 98% (1 nM aqueous sodium formate and 0.1% formic acid) and 2% (acetonitrile and 0.1% of formic acid) that was pumped at a rate of 0.4 mL min^{-1} for 40 min. Detection was carried out with a diode array detector at 220 nm and the column temperature was maintained at 35°C . The coupled mass spectrometer was a Hewlett-Packard 5989B with a detection range from 10 to 2000 Da.

2.6. Kinetic studies

Kinetic studies were conducted to model the EF-FeAB behavior. The imidacloprid concentration profiles were fitted by using a suitable kinetic equation and the rate constants were calculated by using SigmaPlot 4.00 (1997) software. The SigmaPlot curve fitter uses an iterative procedure, based on the Marquardt–Levenberg algorithm, which seeks the values of the parameters that minimize the sum of the squared differences between the observed and predicted values of the dependent variable.

2.7. Continuous reactor of EF-FeAB process set-up

An electrochemical cell with the same characteristics as the one used for the batch experiments was employed (Fig. 1B). The electro-Fenton reactor had a working volume of 0.15 L with 4.27 g of FeAB and a working pH value of 2. The H_2O_2 was produced electrochemically by bubbling compressed air near the cathode at approximately 1 L min^{-1} . The pesticide solution was homogenized by a magnetic stirrer. A dual-headed peristaltic pump was used to maintain a

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