



## Evaluation of different parameters on the acetamiprid degradation by bimetallic Fe/Ni nanoparticles



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### ABSTRACT

This work investigates the effect of different variables on acetamiprid degradation in aqueous systems by Fe/Ni nanoparticles. The variables studied were pH (2.0–5.0), temperature (283–313 K), and nanoparticles dosage (0.200 to 0.500 g L<sup>-1</sup>). The reactions monitoring was made by HPLC. The degradation was greater than 90% in only 5 reaction minutes. The results showed that occurs the formation of hydroxyl radicals in the system because in the presence of *tert*-butyl alcohol, used as scavenger of these radicals, there was a significant reduction in the degradation rate of approximately 100–10%. Kinetic studies were performed and the results showed that the reaction kinetics followed a pseudo-first order. The degradation rate ( $k_{obs}$ ) was increased when dosage of the nanoparticles and temperature were increased. Regarding pH, the degradation rate increased with decreasing pH of the medium. Finally, the reuse of the nanoparticles was evaluated yielding a 70% of efficiency in acetamiprid degradation.

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## 1. Introduction

Neonicotinoids are among the most effective insecticides for the control of sucking insect pests such as aphids, whiteflies, and leaf-and plant hoppers [1]. According to Jeschke and co-workers the discovery of neonicotinoid insecticides can be considered as a milestone in agrochemical research over the past three decades [2]. These compounds, which include imidacloprid, acetamiprid, clothianidin, thiamethoxam, thiacloprid, dinotefuran and nitenpyram, are an important group of neurotoxins specifically acting as antagonists of the insect nicotinic acetylcholine receptors (nAChR) [3]. However, the improper use of these compounds can lead to environmental contamination. Studies have reported the presence of these contaminants in low concentrations (ng or  $\mu\text{g L}^{-1}$ ), the reason for being called micropollutants [4,5]. Even though their concentration is low, they may pose a threat to the environment through accumulation [4]. Due to the persistence of these compounds in the environment, numerous strategies have been studied to provide their effective degradation.

In this context, different chemical degradation methods, such as advanced oxidation processes [5–7], photocatalytic [8], bioremediation [9] and zero-valent metals [10] have been reported for the

removal of neonicotinoids from aqueous solutions. Nanoscale zero valent iron (nZVI) particles have been proposed extensively as an environmental remediation material, especially for the treatment of halogenated hydrocarbons [11].

Fenton-like oxidation of organic contaminants as the heterogeneous catalyst since nZVI acted not only reduction, but also oxidation. When these processes occur under aerobic conditions, the oxidation of Fe<sup>0</sup> to Fe<sup>2+</sup> is accompanied by the production of H<sub>2</sub>O<sub>2</sub> from the reduction of O<sub>2</sub>. The resulting combination of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> (otherwise known as “Fenton’s reagent”) possesses strong oxidizing capability toward a variety of organic compounds as a result of the production of hydroxyl radicals upon the oxidation of ferrous iron by H<sub>2</sub>O<sub>2</sub> [12]. However, the formation of iron oxide or hydroxide on the ZVI surface usually decreases its reactivity. In order to solve this problem, a second catalytic metal, such as Ni, Cu or Pd, has been incorporated to the ZVI to form nano bimetallic particles [13]. The combination of nZVI with a noble metal is referred to as a bimetallic nanometal [14].

The incorporation of a catalytic metal into nanoscale iron is, therefore, a reasonable approach to facilitate the production of hydrogen gas and enhance degradation efficiency of nanoscale iron [15]. Furthermore, due to its extremely small size and high surface energy, nZVI particles are vulnerable to aggregation via Van der Waals and magnetic attraction forces, hence diminishing their reaction effectiveness. Thus, to prevent the aggregation of

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nanoparticles, researchers have found that loading nZVI particles with a second metal catalyst such as Ni can greatly speed up the reaction rate [16]. Bimetallic nanoparticles can have a combination or enhancement of the properties associated with their single counterparts, but also many interesting and surprising new properties with a combination of multiple functions and broadened application fields, which is explained by synergistic effects of both metals [17]. In these materials, Fe with a negative redox potential ( $E^0 = -0.44$  V) is usually active and acts as an electron donor to reduce the pollutants, whereas another metal, such as Ni, with a positive redox potential is often inactive ( $E^0 = -0.25$ ) and acts as a catalyst to improve the reactivity of Fe [18]. Several compounds can be degraded by this process, especially by Fe/Ni nanoparticles, such as decabromodiphenyl ether [13], DDT [19] and aroclor 1242 [20].

Thus, this work aims to evaluate the effect of different parameters on acetamiprid degradation in aqueous systems by reductive processes mediated by Fe/Ni nanoparticles.

## 2. Experimental

### 2.1. Chemicals

All aqueous solutions were made with purified water from a Milli-Q system and were stored at 4 °C. Acetamiprid (minimum 98.0%), sodium borohydride (minimum 98.0%), *tert*-butyl alcohol and methanol (minimum 99.9 wt%) were purchased from Sigma-Aldrich. Ferrous sulfate heptahydrate, nickel chloride hexahydrate, ethanol, sulfuric acid and sodium sulfate were purchased from VETEC.

### 2.2. Nanoparticles preparation and characterization

The nanoparticles preparation was conducted using a slight modification of the method reported by Weng et al. [21] and Shi et al. [22]. Initially, a solution of ethanol-water (4:1, v/v) was added to a mixture of iron ferrous sulfate heptahydrate (9.8500 g), nickel chloride hexahydrate salts (0.8129 g) and the system was stirred for 10 min. Then sodium borohydride solution ( $1.08 \text{ mol L}^{-1}$ ) was added drop wise to the mixture at a rate of 1–2 drops per second with constant stirring. After metal reduction, the bimetallic nanoparticles were filtered, washed with water and ethanol and then stored in ethanol. The characterization of the bimetallic nanoparticles was performed using a Transmission Electron Microscope (TEM) (Tecnai G2-20 - SuperTwin FEI, Hillsboro, OR, USA) equipped with a microanalysis system for X-ray Energy Dispersive Spectroscopy (EDS) and a flame-atomic absorption spectrophotometer (Shimadzu, AA-6701F).

### 2.3. Acetamiprid degradation and sample analysis

The batch acetamiprid degradation experiments were carried out in a cylindrical reactor with a double jacket for circulation of external thermostatic water to regulate the solution temperature. In all the experiments, an appropriate mass of Fe/Ni nanoparticles was added to 100 mL of acetamiprid solution ( $8.98 \times 10^{-5} \text{ mol L}^{-1}$ ) under constant temperature. The pH was kept constant with the addition of a  $\text{H}_2\text{SO}_4$  solution ( $0.3 \text{ mol L}^{-1}$ ). To verify whether the analyte would undergo hydrolysis, control experiments were performed under the same experimental conditions but without the addition of Fe/Ni nanoparticles. For each time interval, small aliquots (for HPLC analysis) were filtered by membrane filter (cellulose, pore size of  $0.45 \mu\text{m}$ ) for further analysis. Kinetic studies were performed at different reaction conditions (temperature,

mass nanoparticles, pH and the presence of the electrolyte sodium sulfate).

Similar experiments were carried out in the presence of hydrogen peroxide ( $5 \text{ mmol L}^{-1}$ ).

### 2.4. Identification of the species responsible for the degradation

*tert*-Butyl alcohol (TBA) was usually used as a scavenger of  $\cdot\text{OH}$ , to identify the major reactive radical species generated in the heterogeneous Fenton-like systems [23]. The experiment was performed according to the above procedure, keeping the pH constant at 3, using a dosage of  $0.500 \text{ g L}^{-1}$ . TBA were added at the system in the zero reaction time ( $C = 1 \text{ mmol L}^{-1}$ ). Aliquots were taken at different time intervals for HPLC analysis.

### 2.5. Kinetic studies

(1) pH study: The pHs monitored were 2.0, 3.0, 4.0 and 5.0. The pH of the reaction system was adjusted and kept constant with  $\text{H}_2\text{SO}_4$  solution ( $0.3 \text{ mol L}^{-1}$ ). The dosage of Fe/Ni nanoparticles was  $0.500 \text{ g L}^{-1}$  and the temperature was 298 K. All assays were performed in duplicate. (2) Dosage of nanoparticles study: The bimetallic nanoparticles dosage monitored were 0.200, 0.300, 0.400 and  $0.500 \text{ g L}^{-1}$ . The temperature was 298 K and the pH was 3.0. All assays were performed in duplicate. (3) Temperature study: The temperatures monitored in this study were 283, 293, 303 and 313 K. The dosage of Fe/Ni nanoparticles was  $0.500 \text{ g L}^{-1}$  and the pH was 3.0. All assays were performed in duplicate.

### 2.6. Influence of electrolyte in the acetamiprid degradation process

The effect of  $\text{Na}_2\text{SO}_4$  concentration in the system was evaluated and the concentrations monitored were 5; 10; 30 and  $50 \text{ mmol L}^{-1}$ . The dosage of Fe/Ni nanoparticles, temperature and pH were, respectively,  $0.500 \text{ g L}^{-1}$ , 298 K and pH 3.0. All assays were performed in replicate.

### 2.7. Analytical methods

The acetamiprid degradation was monitored by High-Performance Liquid Chromatography (HPLC-UV) (Shimadzu - LC 20AT) with a UV-vis detector (Shimadzu SPD 20A) using a C18 column ( $4.6 \times 150 \text{ mm}$ ,  $5.0 \mu\text{m}$ ). The following operating conditions were employed: an isocratic elution of  $\text{MeOH}:\text{H}_2\text{O}$  (55:45, v/v), a flow rate of  $1.0 \text{ mL min}^{-1}$ , an injection volume of  $20 \mu\text{L}$ , and the UV-vis detector set at a 255 nm wavelength. The remaining acetamiprid was identified by comparing the retention times of the standard with the samples, and the concentrations were estimated using the analytical curves.

### 2.8. Total Organic Carbon (TOC) analysis

Total Organic Carbon (TOC) experiments were carried out on a TOC 5000A (Shimadzu, Kyoto, Japan) instrument at 680 °C using platinum as catalyst.

## 3. Results

### 3.1. Characterization of Fe/Ni nanoparticles

According to Wang and Li, the nanoparticle production process by chemical reduction involving  $\text{NaBH}_4$  is widespread [24]. Compared with physical methods, chemical methods for the preparation of bimetallic nanoparticles are more widely used because they are easy to perform and the nanoparticles can have

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