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Comprehensive solution for acetamiprid degradation: Combined electro-Fenton and adsorption process

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ABSTRACT

In recent times, electro-Fenton treatment has become a very interesting approach in which the powerful oxidants, hydroxyl radicals, are generated by the combination of Fenton's reaction and electrochemical process. However, in several cases, total removal of pollutants such as acetamiprid from effluents after advanced oxidation processes was not completely reduced because of the presence of inorganic ions. In this work, the development of heterogeneous catalyst was performed by the manufacture of iron-base-hydrogel catalysts. The catalytic activity and physical resistance of the different iron-base-hydrogels were assessed at different operational conditions and the catalyst which provided the best performance was a mixture of polyvinyl alcohol-alginate-goethite. After electro-Fenton treatment of acetamiprid, the presence of inorganic pollutants, Cl^- , NO_3^- and NH_4^+ , was detected and a combined electro-Fenton and adsorption process was developed for a total remediation. Under optimal conditions, the simulation of the continuous operation in an electro-Fenton reactor and the subsequent treatment of the water stream generated by fixed-bed adsorption filter containing activated carbon were performed. The obtained results permit to conclude that a combined treatment of electro-Fenton and adsorption process can be an appropriate approach for the comprehensive remediation of water streams.

1. Introduction

Because of the anthropogenic development, the presence of synthetic organic compounds in the environment has become a serious problem. These pollutants can be released to the atmosphere, waters and soils; however, the main source of pollution is related to effluents generated in the industrial activities and agro-productive process.

Several types of synthetic organic compounds have emerged over last years and they have been classified as emerging pollutants. However, the nature of these compounds is very different and pharmaceuticals, personal care products, pesticides, ionic liquids and surfactants are included under this classification [1]. At the present time, in addition to determine and regulate the concentration of these substances in the environment, it has highlighted the need to minimize their release and to find treatment technologies appropriated for their removal.

The wide variety of pesticides belongs to the group of emerging pollutants and their massive application in the crops to eradicate plagues, have influenced to consider their presence as environmental concern [2]. From a few years ago the use of neonicotinoid pesticides has been recommended as substitutes for organophosphate and carba-

mate pesticides as a result of their efficacy and selective nervous system attacking mechanism [3]. Acetamiprid belongs to this class and is widely used for controlling sucking type insects [4]. This pesticide presents a significant leaching potential because of high solubility in water which may thwarted removal percentage by conventional technologies used for the purification of wastewater [5].

In recent times, the use of Advanced Oxidation Processes (AOPs) has attracted the attention of the scientific community owing to their efficacy for treatment of wastewater containing synthetic organic compounds [6,7]. Among the different AOPs, electro-Fenton has become a very interesting approach in which the powerful oxidants, hydroxyl radicals, are generated by the combination of Fenton's reaction and electrochemical process. In this technique, the Fenton's reagents, H_2O_2 and iron, are continuously generated and regenerated, respectively, in an electrochemical reactor. Recently, several investigations have carried out to optimize the operational parameters and design an electrochemical reactor able to achieve the mineralization of organic compounds by electro-Fenton process [8,9]. Furthermore, continuous mode operation on wastewater treatment plants has successfully promoted the development of heterogeneous processes in which the catalyst is easily retained in the electrochemical reactor

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[10–12].

Although organic pollutants may be removed by this technology, in several cases, the presence of inorganic ions may hinder the total pollutant removal from effluents after electro-Fenton process. Thus, Meijide et al. [8] determined the high nitrate ions concentration throughout thiamethoxan treatment showing significant conversion rate of initial nitrogen. In fact, the conversion of initial nitrogen was around 99% (19% of NH_4^+ and 80% NO_3^-) after 8 h treatment when more than 92% TOC removal was achieved. Similarly, Bocos et al. [13] detected the generation of Cl^- , NO_3^- and NH_4^+ when the TOC reduction was near to 90% after 2 h of electro-Fenton treatment of 1-butyl-3-methylimidazolium triflate.

According to the literature, the presence of these inorganic ions generates an environmental problem. Thus, nitrate concentrations in freshwater range are typically in the range 0.1 to 4 mg/L $\text{NO}_3\text{-N}$ and more specifically, unpolluted waters generally have nitrate levels below 1 mg/L $\text{NO}_3\text{-N}$. On the contrary, the effluent of some sewage treatment plant or industries may have levels above 10 mg/L $\text{NO}_3\text{-N}$, which involves health problems [14]. On the other hand, chlorides are not usually harmful to people and public drinking water standards require chloride concentration below 250 mg/L [15]. Ammonium levels in unpolluted groundwater are usually below 0.2 mg/L, however, this inorganic ion represents negligible relevance to human health and therefore, no standard levels have been set. The suggested threshold for ammonium cation concentration regarding odour and taste in drinking water is around 1.5 mg/L and 35 mg/L, respectively [16].

Thus, the presence of these ions after electro-Fenton process requests a complementary treatment to achieve the total remediation of water streams. Therefore, in this study, novel heterogeneous catalysts were developed for electro-Fenton degradation of prepared acetamiprid solutions. After the optimization of the treatment using the new catalysts, the role of the different forms of inorganic nitrogen and chlorine was investigated and their removal evaluated by the simulation of the adsorption onto activated carbon using Fixed-bed Adsorption Simulation Tool (FAST) v2.1 software.

2. Material and methods

2.1. Reagents

Acetamiprid analytical standard (Pestanal® grade) was used for the electro-Fenton assays. Iron (II) sulphate heptahydrate (catalyst, 99%), goethite (catalyst, 30–63% Fe) and anhydrous sodium sulphate (supporting electrolyte, 99%) were supplied by Sigma-Aldrich. For the analytical determinations HPLC grade organic solvents were provided by Fisher Chemicals. The standards for the determination of carboxylic acids: oxalic, malonic, succinic, glycolic, formic, acetic and oxamic acids were provided from Sigma-Aldrich.

2.2. Experimental procedure

The experiments were carried out in an undivided cylindrical cell (250 mL 60 i.d. and 90 mm) with a two-electrode system using as cathode graphite-felt (19.0 × 6.0 × 0.6 cm Mersen, RVG 2000) and as anode BDD (3.5 × 2.0 × 0.2 cm Neocoat®). The cathode was placed on the inner wall of the glass cell whereas the anode was located on the centre of the reactor. The reactor was filled with 150 mL of 60 mg/L acetamiprid solution at pH 3 using 10 mM Na_2SO_4 as supporting electrolyte. Magnetic stirring was used in order to avoid concentration gradients. In the electro-Fenton assays, different iron-base catalysts were evaluated and atmospheric-pressure air was continuously bubbled at 1 L/min in order to saturate the aqueous solution for the *in situ* electrogeneration of H_2O_2 by oxygen reduction on the cathode.

2.3. Development of heterogeneous catalyst

Two different heterogeneous Fenton catalysts were prepared using polyvinyl-alcohol alginate (PVA-A) as matrix support. The manufacturing process was performed as follow:

- Fe-PVA-A catalyst. PVA-A beads (\varnothing 3–4 mm) were prepared by dropping a solution of 40 g/L of sodium alginate and 60 g/L of polyvinyl alcohol into a 0.17 M CaCl_2 solution. After that, the iron (II) was adsorbed by putting in contact during 15 h the beads with a solution of 500 mg/L of iron (II) in a ratio 0.06 g/mL. The iron content of the beads (0.36 mg/g) was calculated by the iron remained in the solution after the absorption measure by ICP.
- G-PVA-A catalyst. The beads (\varnothing 3–4 mm) were prepared by dropping a solution of 40 g/L of sodium alginate, 30 g/L goethite and 60 g/L of polyvinyl alcohol into a 0.17 M CaCl_2 solution. The iron content (22.37 mg/g) of the beads was determined by ICP after the acid digestion of the beads.

2.4. Analytical methods

2.4.1. Acetamiprid concentration

The degradation of pesticide was monitored by HPLC (Agilent 1100) equipped with an XDB-C8 reverse-phase column (150 × 4.6 mm i.d. 5 μm). The mobile phase composed of water:acetonitrile (90:10 v/v) was pumped by linear gradient elution (from 10% to 50% acetonitrile after 12 min and then, the re-equilibration) at 1 mL/min for 16 min. Prior to chromatographic analysis; all samples were filtered through 0.45 μm PVDF filters. The separation was carried out at room temperature and the column effluent was monitored spectrophotometrically at a wavelength of 246 nm.

2.4.2. Identification of degradation products

The main intermediate products formed in the electro-Fenton process were identified by gas chromatography mass coupled (GC–MS), high-performance liquid chromatography (HPLC) and ion chromatography (IC) and Berthelot method. The analytical procedures are following detailed.

2.4.2.1. GC–MS. After treatment, the aqueous samples were extracted three times with chloroform, dried over anhydrous sodium sulphate and concentrated to dryness by vacuum evaporation. The concentrated extract was analyzed in a GC–MS system (Agilent Technologies) equipped with a HP5-MS capillary column (30 m × 250 μm × 0.25 mm) using hydrogen carrier gas. The injector temperature was 280 °C whereas the temperature of the column oven was initially set at 50 °C for 5 min, further increasing at 5 °C/min up to 280 °C where it was held for 5 min.

2.4.2.2. HPLC. Generated short-chain carboxylic acids were determined by HPLC (Agilent 1100) equipped with ion-exclusion Rezex™ ROA–Organic Acid H+ (8%) column (300 × 7.8 mm; Phenomenex) at 55 °C. The mobile phase was a solution of 0.025 M H_2SO_4 solution at a flow rate of 0.5 mL/min.

2.4.2.3. IC. The concentration of nitrate and chloride released during the treatments were measured by IC (Dionex ICS-3000 equipped with a conductivity detector) using an anionic exchanger column, Metrosep A Supp 5250/4.0 mm (Metrohm) (C.A.C.T.I. University of Vigo). The volume of injection was 20 μL . A solution of 3.2 mM sodium carbonate and 1.0 mM sodium hydrogen carbonate solution at 0.7 mL/min was used as mobile phase.

2.4.2.4. Berthelot method. On the other hand, ammonium concentration was detected by automated segmented flow analyzer (Bran & Luebbe AA3 Autoanalyzer) according to Berthelot reaction

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