



## Application of green zero-valent iron nanoparticles to the remediation of soils contaminated with ibuprofen



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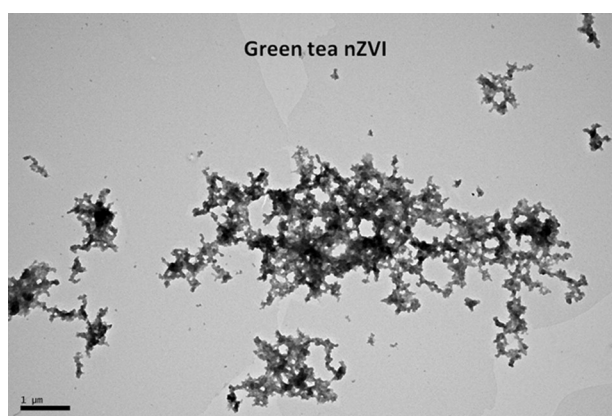
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### HIGHLIGHTS

- Green zero-valent iron nanoparticles (nZVI) were produced using natural extracts.
- The green nanoparticles degraded ibuprofen in aqueous solutions and in soils.
- The remediation process is enhanced when complemented with nZVI catalyzed Fenton reaction.
- The use of nZVI is extremely competitive when compared with common oxidants.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Zero-valent iron nanoparticles (nZVIs) are often used in environmental remediation. Their high surface area that is associated with their high reactivity makes them an excellent agent capable of transforming/degrading contaminants in soils and waters. Due to the recent development of green methods for the production of nZVIs, the use of this material became even more attractive. However, the knowledge of its capacity to degrade distinct types of contaminants is still scarce.

The present work describes the study of the application of green nZVIs to the remediation of soils contaminated with a common anti-inflammatory drug, ibuprofen. The main objectives of this work were to produce nZVIs using extracts of grape marc, black tea and vine leaves, to verify the degradation of ibuprofen in aqueous solutions by the nZVIs, to study the remediation process of a sandy soil contaminated with ibuprofen using the nZVIs, and to compare the experiments with other common chemical oxidants.

The produced nZVIs had nanometric sizes and were able to degrade ibuprofen (54 to 66% of the initial amount) in aqueous solutions. Similar remediation efficiencies were obtained in sandy soils. In this case the remediation could be enhanced (achieving degradation efficiencies above 95%) through the complementation of the process with a catalyzed nZVI Fenton-like reaction. These results indicate that this remediation technology represents a good alternative to traditional and more aggressive technologies.

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## 1. Introduction

Zero-valent iron (ZVI) is a well known remediation agent because of its use in permeable reactive barriers. These barriers are commonly and efficiently used in the treatment of soil and groundwater which have been contaminated with distinct contaminants, such as halogenated hydrocarbons (e.g. trichloroethylene or perchloroethylene) or heavy metals (e.g. arsenic or chromium) (Thiruverikatachari et al., 2008). In the last fifteen years ZVI gained attention of the scientific community because of its utilization as a nanomaterial in the remediation of soils and waters; however, universal acceptance has not yet been achieved (Crane and Scott, 2012). Among the reasons for the lack of acceptance that can be underlined are concerns related to the long-term fate of these particles in the environment, their ecotoxicity and the inexistence of an established, simple and fast production method.

According to Li et al. (2006) there are two general strategies for the production of nZVI: top-down and bottom-up approaches. The top-down approach uses mechanical and chemical processes (grinding, ball milling, etching, and machining) to reduce larger size ZVI (granular, macro- and microsized). The bottom-up approach promotes the 'growth' of the particles on ZVI through several processes such as chemical synthesis or self-assembling. These methods are generally expensive and require specific equipment. In one of the most widely used bottom-up processes sodium borohydride is used to reduce iron(III) or iron(II) to zero-valent iron nanoparticles (Hoag et al., 2009). This chemical process presents disadvantages related to safety issues associated with the use of a toxic reagent (sodium borohydride) and the formation of a flammable gas (hydrogen) during the process (Li et al., 2006). However, in the last years several authors have been developing a greener bottom-up method that involves the utilization of extracts from natural products (usually leaves or peels) (Hoag et al., 2009; Machado et al., 2013). These extracts have high reductive capacities and assure the reduction of the iron(III)/(II), producing nZVI. The main advantages of this method are related to the use of natural products (that in some cases are considered wastes, e.g. fruit peels or tree leaves) and non-toxic solvents, in this case water. This 'green' method also enhances the stability of the nZVIs through the capping action of the polyphenols present in the extract, which delays the agglomeration process and increases the reactivity and efficiency of the remediation (Hoag et al., 2009). However, this method is not yet universally accepted because of the lack of knowledge of the production method as well as of the nZVIs' characteristics, namely size, agglomeration, and, mainly, their reactivity.

It has been proven that nZVIs are efficient for the degradation of halogenated hydrocarbons (Wang et al., 2012), polychlorinated biphenyls (PCBs) (Petersen et al., 2012) or metals (Zhu et al., 2009), but information about their reactivity with pharmaceutical products (PPs) is scarce. PPs have been massively used and are considered emergent contaminants because they have been introduced in soils and waters through (i) human excretions in sewage collectors (especially from hospital effluents (Heberer, 2002)), (ii) disposal of unwanted, unused or expired products in the toilet or sink, and (iii) land application of animal manure (O'Connor and Aga, 2007) and treated sewage sludge (Kinney et al., 2006). PPs have been detected (at  $\text{ng L}^{-1}$  and  $\mu\text{g L}^{-1}$  levels) in a wide variety of water samples, such as effluents (from medical care units, landfills, and municipal sewage), seawater, drinking water, and surface- and groundwater, (Benotti et al., 2009; Fatta-Kassinos et al., 2011); but also in soils and sediments in concentrations ranging from  $\mu\text{g kg}^{-1}$  to  $\text{mg kg}^{-1}$  (Braganca et al., 2012; Li et al., 2012). Based on this, and to preserve water and soil quality, it is imperative to conduct experiments to study the degradation of these contaminants. In these studies the use of green nZVIs can become an efficient and sustainable option.

The present work reports the development of a new and more sustainable method for the chemical remediation of water and soil contaminated with ibuprofen (a widely used anti-inflammatory

drug and a priority substance that can present significant risk to or via the aquatic environment, according to the European Community (EC), Scientific Committee on Health and Environmental Risks (2011)) using green nZVIs. Experiments with common oxidants (potassium permanganate, hydrogen peroxide and Fenton's reagent) were performed in order to compare the results with those obtained with the nZVIs.

## 2. Materials and methods

### 2.1. Reagents and solutions

Ibuprofen (98% (m/m)) was obtained from Sigma-Aldrich, hydrogen peroxide (30% (w/v)) and sulphuric acid (98% (w/w)) were purchased from Panreac, ammonium iron(II) sulphate hexahydrate and sodium hydroxide were supplied by Pronalab, and iron(III) chloride hexahydrate and potassium permanganate were obtained from Merck. All reagents were of analytical grade or equivalent quality. Type II deionized water (resistivity = 15.0 M $\Omega$  cm) was used throughout the study and was obtained from an Elix 3 Advantage system (Millipore). Two ibuprofen solutions were prepared (70 and 10  $\text{mg L}^{-1}$ ) and diluted with water to achieve the desired concentrations. For the remediation experiments solutions of potassium permanganate (0.0100  $\text{mol L}^{-1}$ ), hydrogen peroxide (0.880  $\text{mol L}^{-1}$ ), iron(III) (0.100  $\text{mol L}^{-1}$ ), and iron(II) (0.100  $\text{mol L}^{-1}$ ) were used.

### 2.2. Analysis of ibuprofen

Ibuprofen was analyzed using liquid chromatography (LC). The LC system (JASCO, Inc.) consisted of a quaternary gradient pump (PU-2089Plus), an autosampler (AS-2057Plus), a column oven (CO-2060Plus), and a photodiode array detector (PDA, MD-2018Plus). JASCO ChromNAV software (version 1.17.01) was used to acquire and process all the chromatographic data. For the separations a Phenomenex 2.6  $\mu\text{m}$  C18 100A (100  $\times$  2.10 mm) column was used at 35  $^{\circ}\text{C}$ . The mobile phase consisted of 0.1% (v/v) aqueous formic acid (A) and 0.1% (v/v) formic acid in acetonitrile (B) using the following linear gradient program (A/B, % (v/v)): 55/45: 0–3 min, gradient: 3–5 min; 5/95: 5–7 min; gradient: 7–8 min; 55/45: 8–20 min. The other instrumental parameters were: injection volume: 20  $\mu\text{L}$ ; flow rate: 0.5  $\text{mL min}^{-1}$ ; and detection wavelength: 220 nm.

For the quantification of ibuprofen the external standard calibration method was used. Calibration curves between 0.0250 and 10.0  $\text{mg L}^{-1}$  ( $0.981 \leq r \leq 0.997$ ) were constructed at different pH values.

### 2.3. nZVI production

One of the novelties of this work is the utilization of a new generation of nanoparticles: green nZVIs. For their production, extracts from natural products with high reductive powers were used. These extracts can substitute sodium borohydride for the reduction of iron(III). The extracts were produced according to the procedures developed by Machado et al. (2013), using black tea-, grape marc-, and vine leaves. The extractions were performed in a conical flask in a water bath (80  $^{\circ}\text{C}$ ) with continuous stirring using the conditions presented in Table 1. The nZVIs were produced by mixing the obtained extracts with a 0.100  $\text{mol L}^{-1}$  iron(III) solution. Spectrometric analysis at

**Table 1**  
Most favorable extraction conditions for the studied products.

Product	Moisture content (% $\pm$ SD)	Contact time (min)	Mass <sub>leaf:volume<sub>water</sub></sub> (g/100 mL)
Vine leaves	5.0 $\pm$ 0.7	80	3.7
Black tea leaves	8.5 $\pm$ 1.0	20	0.8
Grape marc	6.3 $\pm$ 0.8	20	3.7

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