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Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts

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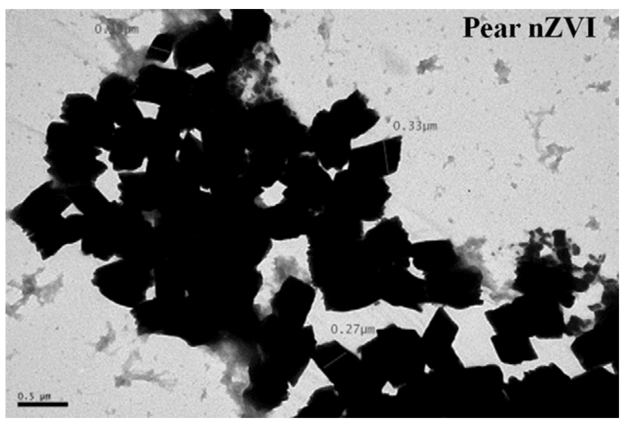
HIGHLIGHTS

- Leaves of 26 species were used to produce zero-valent iron nanoparticles.
- Each nZVI produced with the different extract showed distinct properties.
- Size, shape, reactivity, and agglomeration of the different nZVI were studied.
- Vine and medlar nZVI showed better overall results.

GRAPHICAL ABSTRACT



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ABSTRACT

In the last decades nanotechnology has become increasingly important because it offers indisputable advantages to almost every area of expertise, including environmental remediation. In this area the synthesis of highly reactive nanomaterials (e.g. zero-valent iron nanoparticles, nZVI) is gaining the attention of the scientific community, service providers and other stakeholders.

The synthesis of nZVI by the recently developed green bottom-up method is extremely promising. However, the lack of information about the characteristics of the synthetized particles hinders a wider and more extensive application. This work aims to evaluate the characteristics of nZVI synthesized through the green method using leaves from different trees. Considering the requirements of a product for environmental remediation the following characteristics were studied: size, shape, reactivity and agglomeration tendency.

The mulberry and pomegranate leaf extracts produced the smallest nZVIs (5–10 nm), the peach, pear and vine leaf extracts produced the most reactive nZVIs while the ones produced with passion fruit, medlar and cherry extracts did not settle at high nZVI concentrations (931 and 266 ppm). Considering all tests, the nZVIs obtained from medlar and vine leaf extracts are the ones that could present better performances in the environmental remediation. The information gathered in this paper will be useful to choose the most appropriate leaf extracts and operational conditions for the application of the green nZVIs in environmental remediation.

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1. Introduction

The use of nanotechnologies for environmental remediation has received substantial financial support as well as attention from service providers and the scientific community (Karn et al., 2009). This fact originated an exponential release of scientific publications, patents and research projects that supplied knowledge about the development of new materials and new applications involving nanomaterials. One of these applications, nanoremediation, is based on the use of reactive nanomaterials to degrade/transform/destroy contaminants located in distinct environmental compartments (namely soils and waters). These nanomaterials have the capacity to percolate through very small pores in the soil subsurface, or to remain suspended in the groundwater, allowing the nanoparticles to react longer, disperse better and reach locations farther than bigger particles. However, in real situations, and because of agglomeration and adsorption processes, the nanomaterials have a limited radius of influence (Phenrat et al., 2006). Nevertheless, nanomaterials have an enormous potential for environmental remediation.

Among the most common nanomaterials, zero-valent iron nanoparticles (nZVI) are one of the most widely used and have proven to be extremely effective for the removal of a wide range of pollutants such as pharmaceutical products (Machado et al., 2013b), chlorinated solvents (Choe et al., 2001), metals (Klimkova et al., 2011) among others (Crane and Scott, 2012).

Two different approaches can be used to produce nanomaterials, e.g. nZVI: top-down and bottom-up methods. The former consists of the reduction of the iron particle size through mechanical and/or chemical processes, and includes milling, etching, and/or machining; while the latter promotes the growth of the particles through chemical reactions, positional and self-assembling, among others (Li et al., 2006). The top-down method generally involves specific equipment and is associated with high energy costs. Within the bottom-up approach two distinct paths can be followed: traditional and green production methods. The traditional method involves the reaction between iron(III) or iron(II) solutions with sodium borohydride (Li et al., 2006). Although at first this seems like a very simple and fast procedure without the requirement of specific equipment, there are safety and health concerns associated with this method (Li et al., 2006). The use of a toxic compound such as sodium borohydride requires specific actions during the production process to protect operators, and the removal of the remaining toxic compound at the end of the synthesis. Besides this, in the traditional method hydrogen is produced which also requires safety measures to reduce/eliminate the combustion/explosion risks (Li et al., 2006). Like this, an opportunity was created for the development of new production methods, including the green production method. This method uses aqueous extracts with high reduction capacities which are obtained from natural products, such as tea leaves (Hoag et al., 2009) or tree and bush leaves (Machado et al., 2013b). The use of these extracts provides several advantages when compared to the traditional method: i) the polyphenolic matrix can act as a capping agent that protects the iron nanoparticles from premature oxidation (Hoag et al., 2009) and agglomeration, ii) it can be used as a source of nutrients and microorganisms for a possible bioremediation action after the chemical treatment (Machado et al., 2013b) and iii) the valorization of natural products, such as tree leaves, that, in some cases, are considered wastes or do not have any added value (Machado et al., 2013b). Martins et al. (unpublished results) used life cycle assessment to evaluate the environmental performance of the two synthesis methods (traditional using the sodium borohydride and the green using natural extracts) and concluded that the green synthesis method presents lower environmental impacts than the traditional method.

However, these new nanomaterials are not sufficiently characterized, especially regarding their chemical characteristics, sizes, reactivities and agglomeration tendencies. These parameters are extremely important to evaluate the nanoparticles' performance in soils because they illustrate the capacity of the particles to react and to move through the soil pores reaching locations farther from the injection point.

Therefore the objectives of this work were to characterize nZVI produced using the green method and to study the relation between the type of leaves and the characteristics of the obtained nZVIs. This information will indicate with which leaves better degradation efficiencies in water/soil remediation can be attained.

2. Materials and methods

2.1. Reagents and equipments

The following reagents were used without further purification throughout the work: ethanol (99.5%), potassium dichromate (99.0%), iron(II) sulfate heptahydrate (99.0%) and 2,4,6-Tris(2-pyridyl)-s-triazine (Sigma-Aldrich), sodium carbonate (99.8%) (Riedel-de Haën), sodium acetate trihydrate (99.0%) and sulfuric acid (96%) (Panreac), glacial acetic acid (99.7%) and hydrochloric acid (37%) (Carlo Erba), iron(III) chloride hexahydrate (99.0%) (Merck) and 1,5-diphenylcarbazide (>97%) (Fluka), and potassium hydrogencarbonate (Pronalab). Type II deionized water (resistivity >5.0 MΩ·cm) was used throughout the study and was obtained from an Elix 3 Advantage water purification system (Millipore). The determination of the antioxidant capacity of the extracts, the study of the settling of the nZVI and their reactivity were performed using a Thermo Scientific (Evolution 300) spectrophotometer.

X-ray diffraction studies were performed with a Bruker diffractometer (Bruker D8 Discover), (IBMC, Porto, Portugal).

2.2. Leaf preparation

Leaves from 26 different tree species (Apple, Apricot, Avocado, Cherry, Eucalyptus, Kiwi, Lemon, Mandarin, Medlar, Mulberry, Oak, Olive, Orange, Passion fruit, Peach, Pear, Pine, Pomegranate, Plum, Quince, Raspberry, Strawberry, Tea-Black, Tea-Green, Vine, and Walnut) were collected in the North of Portugal (Porto and Vila Real district) in September 2013. The leaves were removed from the trees using a knife. The leaves were prepared according to the procedures described in a previous study (Machado et al., 2013a) and involved drying, milling and sieving.

2.3. Determination of the reducing power of the extracts

To compare the performance of the different nZVIs, the reducing power of all the leaf extracts were all adjusted to the same value (through dilution) to assure the production of similar amounts of nZVI. The method used was the "ferric reducing antioxidant power" (FRAP) method (Pulido et al., 2000). The reaction time was 30 min, after which the absorbance was measured at 595 nm. The calibration curve was constructed using six iron(II) standards with concentrations ranging from 100 to 3000 μmol L^{-1} ($r = 0.9988$).

2.4. nZVI production

The green nZVIs were produced by mixing 1 mL of each extract with 250 μL of an iron(III) solution (0.1 mol L^{-1}) followed by gentle mixing. The formation of nZVI occurs immediately after the mixture of the extract with the iron (III) solution; this is proven by the darkening of the solution.

2.5. Size determination of the nZVIs

The produced nZVIs (178 samples) were mounted on 300-mesh nickel grids and examined using a JEOL JEM 1400 Transmission Electronic Microscope (TEM; 120 kV). Magnifications from 120,000 to 500,000× were used to determine the size of the nZVIs. Energy-dispersive X-ray spectroscopy (EDS) analyses were also conducted to