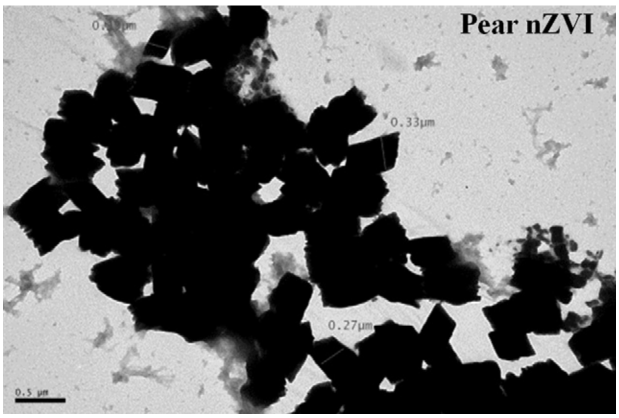
Characterization of green zero-valent iron nanoparticles produced with tree leaf extracts

S. Machado, J.G. Pacheco, H.P.A. Nouws, J.T. Albergaria, C. Delerue-Matos

GRAPHICAL ABSTRACT



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.

Keywords:
Zero-valent iron nanoparticles
Green synthesis method
Tree leaves
Size
Reactivity
Agglomeration

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 determine the composition of the nZVIs. The nZVI sizes were measured directly on the TEM image using the software of the equipment.

2.6. nZVI reactivity

The use of nZVI for environmental remediation is based on the particles' reactivity which enables the degradation of certain contaminants. This parameter is therefore essential to evaluate and predict the nZVI's performance. The reactivity of the different nZVI was evaluated through the monitoring of the extent of its reaction with a 2 mg L^{-1} chromium(VI) solution. The quantification of chromium(VI) was performed using the diphenylcarbazide method (EPA, 1992). A calibration curve was constructed using eight chromium(VI) standards with concentrations between 0.05 and 2.5 mg L^{-1} ($r = 0.9955$).

In each test 100 μL of leaf extract and 5 μL of 0.1 mol L^{-1} iron(III) solution were added to 25 mL of a 2 mg L^{-1} chromium(VI) solution. After 10 min 2.5 mL of sulfuric acid 1.0 mol L^{-1} and 1.25 mL of 1,5-diphenylcarbazide 2.0×10^{-2} mol L^{-1} were added to the mixture. After 10 min the absorbance of the solution was measured at $\lambda =$ 543 nm. All experiments were performed in triplicate for each leaf extract.

2.7. nZVI agglomeration and particle settling

The reactivity of nZVI is linked to their particle size: smaller sizes lead to higher reactivities (Wang et al., 2009). It is also known that nZVIs have the tendency to agglomerate, forming bigger structures that tend to settle, reducing their reactivity due to the decrease of the surface area (Phenrat et al., 2006). Therefore, the study of the agglomeration/settling tendency of the different green nZVIs is essential. The settlement of the particles represents the time when the nZVI have agglomerated to a certain point that will affect their function as remediation agent. This study was performed by producing the nZVI in a UV–vis cuvette and monitoring the turbidance of the resulting suspension ($\lambda = 750$ nm) for 90 min. The first test conditions were 1.5 mL of extract and 0.5 mL of iron (III) solution which corresponds to a concentration of 1396 ppm. Nanoparticle settlement occurred in all extracts. Then the tested amount of iron (III) was decreased and the tests were performed until the settlement was observed at least after 90 min. The nZVI is highly reactive within the first 1–2 h, after which the surface of the particles is mostly oxidized and has a reduced reactivity (Jing et al., 2015). This test allows the identification of when and at what concentration the nZVI starts to settle.

2.8. XRD analysis

The X-ray diffraction (XRD) analysis was performed on a solid nZVI sample in the 2θ angle range (0°–90°) with a step size of 0.04°.

3. Results and discussion

3.1. Size determination of the nanoparticles

All the nZVIs produced using the 26 types of leaves were analyzed by TEM (178 images). All the analyses identified iron nanostructures with different shapes, sizes and agglomerate forms.

Considering the nZVI shape, the ones produced with pear tree leaf extracts were the only ones that presented a rectangular shape (Fig. 1a), eucalyptus and nut tree leaf extracts provided a cylindrical-type shape (Fig. 1b), mulberry, cherry, pomegranate, pine, mandarin, orange, and strawberry leaf extracts resulted in spherical forms (Fig. 1c) and the rest of the leaf extracts provided nZVIs with irregular forms.

Wang et al. (2014a) concluded that the sizes and morphologies of nanoparticles (namely Fe_3O_4) are influenced by temperature, reaction time and the concentration of the reagents. In the present work the nZVI production occurred under similar conditions by using extracts with the same antioxidant capacity that were mixed with the same iron(III) solution. Therefore, the different sizes and shapes of the nZVIs can be a result of the distinct antioxidants (free amino acids, caffeine and polyphenols, among others) present in each of the extracts that can react differently, even when they have the same antioxidant power. This different chemical composition can also interact with the nZVI by hindering or enhancing the growth of the nanoparticles, originating different sizes and shapes.

Each obtained TEM image was analyzed and the observed nanoparticles were measured instrumentally. All extracts allowed the production of nanosized particles; the mulberry and pomegranate tree leaf extracts produced the smallest nZVIs (5–10 nm) with clear individual clusters and the pine, apple and plum tree leaf extracts produced the largest nZVIs (near 100 nm).

Different agglomeration types were also observed: cloud-type, net-type and large-structured. The large-structured type agglomeration was observed for the pear tree leaf extracts (Fig. 1a), the net-type agglomeration was observed for the extracts of black (Fig. 1e) and green tea, apple tree, avocado, vine and peach leaf extracts. All the other extracts presented a cloud-type agglomeration, e.g. cherry (Fig. 1f). The physical and chemical nature of the solution (the natural extract) influences the aggregates' structure (Elimelech et al., 1998), meaning that the observed nanostructures are also related to the type of leaf, namely its origin, maturation stage of the leaf, moisture and also soil fertility and pH, light intensity and temperature stress (Barrajón-Catalán et al., 2010).

To fully understand what defines the size and shape of these green nZVIs, a more detailed study on the chemical composition of the extracts, namely the polyphenol profile, is required (Mystrioti et al., 2015; Nadagouda et al., 2010). With this it would be possible to evaluate if there are specific compounds or groups of compounds that could be linked to certain nZVI physical or chemical properties (such as reactivity or agglomeration tendency).

The EDS analysis performed on the produced nZVIs showed that the nanoparticles were constituted by iron but also presented a high carbon, oxygen (originated from the polyphenols of the extract) and chlorine (originated from the iron chloride used to produce the nZVI) background. Fig. 2a and b presents the EDS analysis of nZVI produced using mandarin and oak leaf extracts, respectively.

These results are in accordance with the observations of other authors such as Wang et al. (2014b), who produced green nZVI with eucalyptus leaf extracts, and Kuang et al. (2013) and Chrysochoou et al. (2012), who used tea extracts to produce nZVI.

3.2. nZVI reactivity

The reactivity was defined as the percentage of the initial amount of chromium(VI) that was reduced by the nZVI solution. The chromium(VI):iron(III) ratio used in these tests was 1:2, however for molar ratios above 1:20 complete conversion of the chromium(VI) was observed. The tests with the 1:20 ratio originated complete reduction of the chromium(VI), which does not allow the perception of the different behaviors of the nZVIs (most of them presented 100% degradation).

Fig. 3 presents the results of the reactivity tests performed with the nZVI solution of all the studied leaves.

Fig. 3 shows that the reactivity depends on the type of extract; the peach, pear and vine leaf extracts are the ones that produced the nZVIs with the highest reactivities (decreasing 78% of the initial amount of chromium (VI)) while the lemon and pine leaf extracts produced nZVIs with the lowest reactivities (converting 29 and 23% of chromium (VI), respectively). This indicates that the chemical composition of the extracts, namely the antioxidants have a decisive influence on the nZVI production and reactivity.

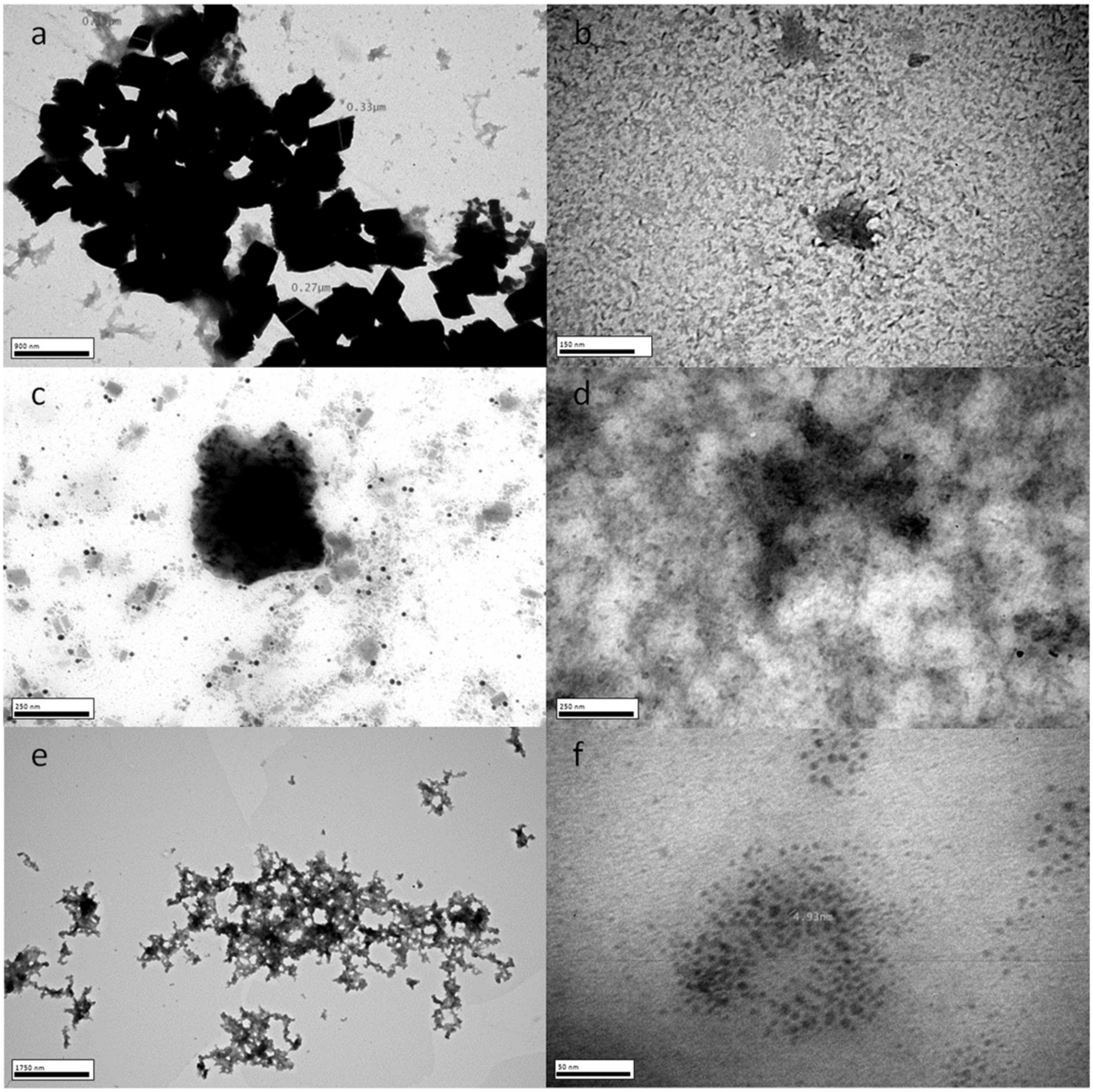


Fig. 1. Representative TEM images of the nZVIs synthesized using (a) pear tree, (b) eucalyptus, (c) mulberry, (d) kiwi, (e) black tea and (f) cherry leaf extracts.

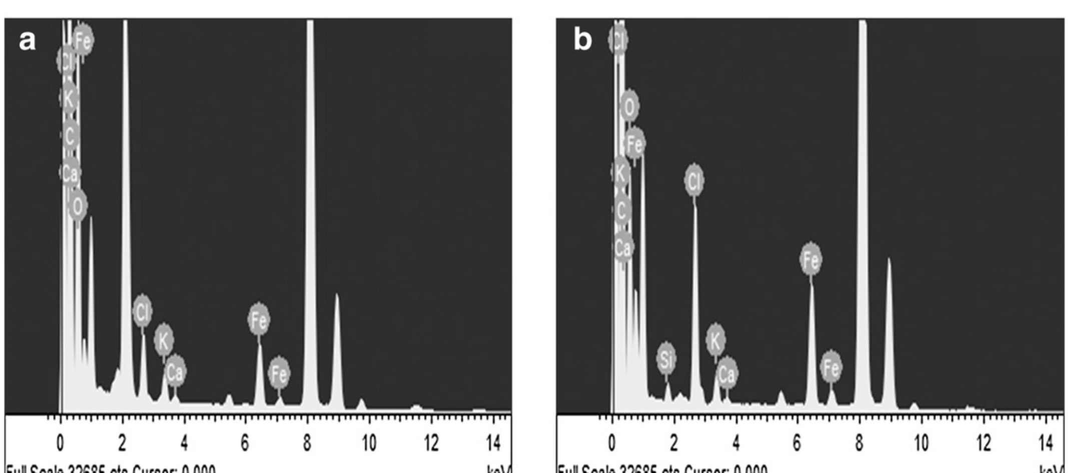


Fig. 2. EDS analysis of nZVIs produced with mandarin (a) and oak (b) leaf extracts.

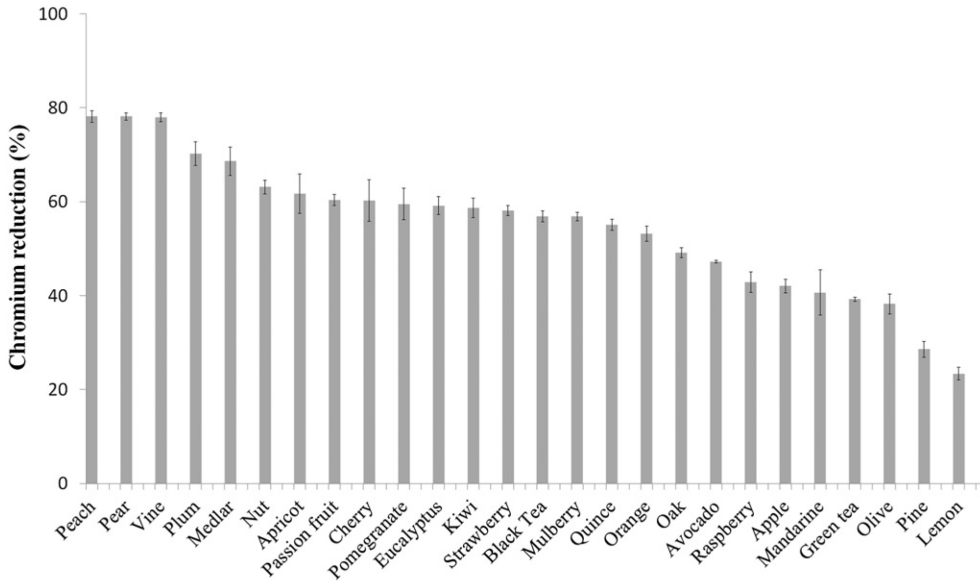


Fig. 3. Conversion of 2 mg L^{-1} of chromium(VI) achieved by each produced nZVI.

Wang et al. (2014b) found that some polyphenols of the extract solution bound to the surfaces of the green nZVI as a capping/stabilizing agent. This can hinder or delay the reaction between the nZVI and the surrounding contaminant. Once more it can be concluded that different extracts with similar antioxidant capacities can interact differently with the nZVIs, also affecting their reactivity. This is supported by Machado et al. (2013b) who observed that the extracts of pear and lemon leaves have low antioxidant capacities, but in this work they presented very different reactivities. Huang et al. (2014) evaluated the reactivity of nZVIs synthesized using three different tea leaves (green, oolong and black) and also observed different behaviors that were attributed to the caffeine/polyphenol content that acted as both reducing and capping agents.

3.3. nZVI agglomeration tendency

Another factor that influences the nZVIs' performance as a remediation agent is their tendency to agglomerate; originating larger particles that tend to settle and, therefore, decrease the extension of the reaction with the contaminants. Several works report that the reaction between nZVI and the contaminants mainly occurs in the first hours (Crane and Scott, 2012). If the agglomeration occurs after the most reactive phase, it could be considered an advantage because it can help the removal of the reacted particles from the remediated media. This is an important issue because of the uncertainty about the possible toxicity of the nZVI in water and soil ecosystems (Saccà et al., 2014). Therefore, and for an efficient reaction, the nZVI should remain in suspension during the required reaction time and agglomerate (and settle) later.

To evaluate the agglomeration behavior of the green nZVI the following tests were performed: the different nZVIs were produced according to the most favorable conditions (extraction temperature, contact time and mass of leaves:solvent volume ratio) described in Machado et al. (2013b), and their agglomeration (settlement) was monitored through spectrophotometric analysis for 90 min, considering the time of the highest reactivity of nZVI. With these tests it was possible to identify which was the nZVI concentration, for each extract used, at which the settling occurred after 90 min, therefore guaranteeing that the nZVIs were in suspension during their reactive period.

Table 1 presents the results obtained in the agglomeration tests, indicating when and at what nZVI concentration the agglomeration (settlement) occurred for each nZVI. In some cases no agglomeration was observed for certain conditions, indicated with "NO" in Table 1.

From Table 1 it is possible to conclude that the produced nZVIs have distinct agglomeration tendencies: the nZVIs produced using passion fruit leaf extracts, even at a high concentration (931 ppm), do not agglomerate after 90 min after their production. To avoid the settlement of the other nZVIs it was necessary to decrease their concentration. The vine nZVIs, that also presented a high reactivity towards chromium, started to settle 90 min after their formation assuring that they used most of their capacity to react with the contaminant when it was in suspension.

On the other hand, the oak and eucalyptus nZVIs showed an extremely high tendency to settle which could only be avoided by using low nZVI concentrations (9 and 4 ppm, respectively). However, when considering Fig. 2, these two examples presented medium reactivities, indicating that the agglomeration did not cause a significant impact on

Table 1
Results of the agglomeration tests.

nZVI	nZVI concentration (ppm)	Sedimentation at 90 min[a]
Passion fruit	931	No
Medlar	266	No
Cherry	266	No
Apricot	266	Yes
Vine	266	Yes
Kiwi	180	No
Mandarin	180	No
Avocado	180	No
Apple-tree	180	No
Orange	180	Yes
Green tea	180	Yes
Pine	163	No
Olive	108	No
Black tea	90	No
Pear	90	No
Lemon	90	Yes
Peach	46	No
Quince	46	No
Walnut tree	46	Yes
Strawberry	43	No
Plum	35	Yes
Pomegranate	20	Yes
Mulberry	17	No
Raspberry	17	No
Eucalyptus	9	Yes
Oak	4	Yes

[a] Not observed.

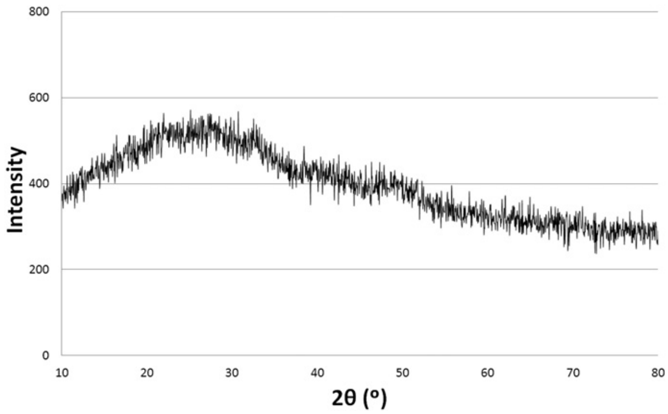


Fig. 4. XRD analysis of the green nZVI.

the reactivity of those nanoparticles when compared to the other nZVI performances.

As presented before, and depending on the nZVI concentration, the green nZVIs tend to agglomerate and settle.

3.4. XRD analysis

XRD analyses were performed on the synthesized green nZVI (Fig. 4). In this test no peaks were observed, especially the characteristic peak of zero-valent iron (α-Fe) at $2\theta = 44.9°$, indicating that the green method produces amorphous nZVI, which was also observed in other studies (Njagi et al., 2011; Shahwan et al., 2011).

This property constitutes a difference between the green nZVI and the ones produced with sodium borohydride (Arancibia-Miranda et al., 2014; Zha et al., 2014). This could be due to the heterogeneous constitution of the leaf extracts.

4. Conclusions

The use of different leaf extracts to produce nZVI results in amorphous nZVI with different sizes, shapes, agglomeration tendencies and reactivities. The nZVIs produced using mulberry and pomegranate leaf extracts were the smallest (5–10 nm) while the nZVIs produced with pine, apple and plum tree leaf extracts were the largest (near 100 nm). Concerning the reactivities, and for the experimental conditions used, the prepared nZVIs converted between 23% (using lemon leaf extracts) and 78% (peach, pear and vine leaf extracts) of chromium(VI).

Furthermore, differences in agglomeration tendencies of nZVI were also observed: some of them started to settle at low concentrations (4 or 9 ppm, for the oak and eucalyptus leaf extracts, respectively) while others did not settle even at concentrations of 930 ppm.

All the information gathered in this paper will be useful to choose the most appropriate extracts and operational conditions to use the green nZVIs for environmental remediation. Attending to the reactivity and to the agglomeration and settlement behaviors of the nZVI produced, the nanoparticles obtained from medlar and vine leaf extracts are the ones that could present better performances in the environmental remediation.

Acknowledgments

This work received financial support from the European Union (FEDER funds through COMPETE) and National Funds (FCT, Fundação para a Ciência e a Tecnologia) through projects UID/QUI/50006/2013 and PTDC/AAG-TEC/2692/2012. To all financing sources the authors are greatly indebted.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.06.091.

References

Arancibia-Miranda, N., Baltazar, S.E., Garcia, A., Romero, A.H., Rubio, M.A., Altbir, D., 2014. Lead removal by nano-scale zero valent iron: surface analysis and pH effect. Mater. Res. Bull. 59, 341–348.

Barrajón-Catalán, E., Fernández-Arroyo, S., Saura, D., Guillén, E., Fernández-Gutiérrez, A., Segura-Carretero, A., et al., 2010. Cistaceae aqueous extracts containing ellagitannins show antioxidant and antimicrobial capacity, and cytotoxic activity against human cancer cells. Food Chem. Toxicol. 48, 2273–2282.

Choe, S., Lee, S.-H., Chang, Y.-Y., Hwang, K.-Y., Khim, J., 2001. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe_0. Chemosphere 42, 367–372.

Chrysochoou, M., Johnston, C.P., Dahal, G., 2012. A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron. J. Hazard. Mater. 201, 33–42.

Crane, R.A., Scott, T.B., 2012. Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J. Hazard. Mater. 211, 112–125.

Elimelech, M., Jia, X., Gregory, J., Williams, W., 1998. Particle Deposition & Aggregation.

EPA, 1992. Chromium, Hexavalent (Colorimetric).

Hoag, G.E., Collins, J.B., Holcomb, J.L., Hoag, J.R., Nadagouda, M.N., Varma, R.S., 2009. Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. J. Mater. Chem. 19, 8671–8677.

Huang, L.L., Weng, X.L., Chen, Z.L., Megharaj, M., Naidu, R., 2014. Synthesis of iron-based nanoparticles using oolong tea extract for the degradation of malachite green. Spectrochim. Acta A Mol. Biomol. Spectrosc. 117, 801–804.

Jing, C., Li, Y., Cui, R., Xu, J., 2015. Illite-supported nanoscale zero-valent iron for removal of 238U from aqueous solution: characterization, reactivity and mechanism. J. Radioanal. Nucl. Chem. 304, 859–865.

Karn, B., Kuiken, T., Otto, M., 2009. Nanotechnology and in situ remediation: a review of the benefits and potential risks. Environ. Health Perspect. 117, 1823–1831.

Klimkova, S., Cernik, M., Lacinova, L., Filip, J., Jancik, D., Zboril, R., 2011. Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. Chemosphere 82, 1178–1184.

Kuang, Y., Wang, Q.P., Chen, Z.L., Megharaj, M., Naidu, R., 2013. Heterogeneous Fenton-like oxidation of monochlorobenzene using green synthesis of iron nanoparticles. J. Colloid Interface Sci. 410, 67–73.

Li, X.Q., Elliott, D.W., Zhang, W.X., 2006. Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. Crit. Rev. Solid State Mater. Sci. 31, 111–122.

Machado, S., Pinto, S.L., Grosso, J.P., Nouws, H.P.A., Albergaria, J.T., Delerue-Matos, C., 2013a. Green production of zero-valent iron nanoparticles using tree leaf extracts. Sci. Total Environ. 445–446, 1–8.

Machado, S., Stawiński, W., Slonina, P., Pinto, A.R., Grosso, J.P., Nouws, H.P.A., et al., 2013b. Application of green zero-valent iron nanoparticles to the remediation of soils contaminated with ibuprofen. Sci. Total Environ. 461–462, 323–329.

Martins F., Machado S., Albergaria J.T., Delerue Matos C. LCA applied to nano scale zero valent iron synthesis. (to be published).

Mystrioti, C., Sparis, D., Papasiopi, N., Xenidis, A., Dermatas, D., Chrysochoou, M., 2015. Assessment of polyphenol coated nano zero valent iron for hexavalent chromium removal from contaminated waters. Bull. Environ. Contam. Toxicol. 94, 302–307.

Nadagouda, M.N., Castle, A.B., Murdock, R.C., Hussain, S.M., Varma, R.S., 2010. In vitro biocompatibility of nanoscale zerovalent iron particles (NZVI) synthesized using tea polyphenols. Green Chem. 12, 114–122.

Njagi, E.C., Huang, H., Stafford, L., Genuino, H., Galindo, H.M., Collins, J.B., et al., 2011. Biosynthesis of iron and silver nanoparticles at room temperature using aqueous *Sorghum* bran extracts. Langmuir 27, 264–271.

Phenrat, T., Saleh, N., Sirk, K., Tilton, R.D., Lowry, G.V., 2006. Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. Environ. Sci. Technol. 41, 284–290.

Pulido, R., Bravo, L., Saura-Calixto, F., 2000. Antioxidant activity of dietary polyphenols as determined by a modified ferric reducing/antioxidant power assay. J. Agric. Food Chem. 48, 3396–3402.

Saccà, M.L., Fajardo, C., Costa, G., Lobo, C., Nande, M., Martin, M., 2014. Integrating classical and molecular approaches to evaluate the impact of nanosized zero-valent iron (nZVI) on soil organisms. Chemosphere 104, 184–189.

Shahwan, T., Abu Sirriah, S., Nairat, M., Boyaci, E., Eroglu, A.E., Scott, T.B., et al., 2011. Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem. Eng. J. 172, 258–266.

Wang, Q., Snyder, S., Kim, J., Choi, H., 2009. Aqueous ethanol modified nanoscale zerovalent iron in bromate reduction: synthesis, characterization, and reactivity. Environ. Sci. Technol. 43, 3292–3299.

Wang, D., Yang, P., Zhu, Y.N., 2014a. Growth of Fe_3O_4 nanoparticles with tunable sizes and morphologies using organic amine. Mater. Res. Bull. 49, 514–520.

Wang, T., Jin, X.Y., Chen, Z.L., Megharaj, M., Naidu, R., 2014b. Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater. Sci. Total Environ. 466, 210–213.

Zha, S.X., Cheng, Y., Gao, Y., Chen, Z.L., Megharaj, M., Naidu, R., 2014. Nanoscale zero-valent iron as a catalyst for heterogeneous Fenton oxidation of amoxicillin. Chem. Eng. J. 255, 141–148.