Biology and Medicine

Murgueitio et al., Biol Med (Aligarh) 2016, 8:3
http://dx.doi.org/10.4172/0974-8369.1000282

Research Article Open Access

Synthesis of Iron Nanoparticles through Extracts of Native Fruits of Ecuador, as Capuli (*Prunus serotina*) and Mortiño (*Vaccinium floribundum*)

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Received date: March 16, 2016; **Accepted date:** March 31, 2016; **Published date:** April 05, 2016

Abstract

This study describes an eco-friendly synthesis for the production of zero-valent iron nanoparticles (nZVIs). Extracts of capulí (*Prunus serotina*) and mortiño (*Vaccinium floribundum*) were used as reducing and stabilizer agents. Freshly prepared nanoparticles were characterized with Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectrometry (FTIR). Zero-valent iron nanoparticles with mortiño extract (*V. floribundum*) resulted in 13.2 nm diameter; while diameter of the nZVIs prepared with capulí extract (*P. serotina*) was 11.9 nm. On the other hand, XRD spectra showed peaks that are associated with hematite and zero-valent iron. FTIR patterns displayed functional groups in both nZVIs prepared with the extracts and only fruit extracts. Polyphenols are the key compounds for the nanoparticles growth.

Keywords: Zero-valent iron nanoparticles; nZVI, Mortiño; *Vaccinium floribundum*; Capulí, *Prunus serotina*; Ecofriendly synthesis

Introduction

Nowdays, nanoparticles show promising potential for environmental remediation [1-3]. The high reactivity due to the nanoscale size (<100 nm) is associated with the successful application of nanoparticles in different fields of science and engineering [4,5]. Equally important, it is the enormous flexibility for applications "in situ" [1,6]. A notable field of application is the removal of organic and inorganic contaminants from aqueous solutions. However, a few investigations have been applied on soil remediation. One application of ZVI nanoparticles is in the removal of pyrene from soil [7-10]. Nevertheless, in this research, the preparation of the nanoparticles has been done using conventional chemicals such as sodium borohydride to reduce the metallic ions [10,11]. Unfortunately, this reagent can be toxic for microorganisms and human health [12,13]. In the last years, some researchers have developed new methods for synthesizing iron nanoparticles, replacing the dangerous and expensive reagents with extracts of plants and fruits such as the balm of lemon (Melissa officinalis), parsley (*Petroselinum crispum*), sorghum bran (*Sorghum* spp.), coffee and green tea [14-17]. The extracts of these plants and fruits contain molecules with alcoholic functional groups, mainly phenolic type. These molecules can be exploited for the reduction and formation of stable complexes with iron [18]. This study focuses on the development of an economic, simple and eco-friendly synthesis of iron nanoparticles using fruit extracts from capulí (*Prunus serotina*) and mortiño (*Vaccinium floribundum*) as reducing agents and their characterization.

Materials and Methods

Extract preparation

Mortiño and capulí fruits were chosen for their high content of polyphenols [20]. The fruits were purchased in a local market of Quito and the cherries were selected close to senescence. These cherries were cleaned three times with water and distilled water to avoid any contamination during the extraction process. The extraction was performed with ethanol (96% EtOH). The ratio fruit/EtOH was 3:1 (w/v). The content was soaked during 48 h. The cherries' pulp was filtered three times to eliminate aggregated particles with sizes above 0.22µm using a Whatman paper. Ethanol was removed with a rotary evaporator (Buchi-850) for further reuse.

Synthesis of iron nanoparticles

A solution of 0.5M $FeCl_3.6H_2O$ was prepared in a 500 mL flask connected with a nitrogen gas line. Then, the fruit extract was added slowly into the flask keeping a ratio of 10:1 (w/v). The content was agitated in an orbital shaker at 100 rpm and the final pH was 10 for *V. floribundum* and 12 for *P. serotina*, respectively. The formation of a black precipitate in the flask was an indication of the growth of Fe(0) nanoparticles. Finally, nanoparticles were dried by evaporation using a hot plate (Freed Electric) and the resulting solid was stored for further characterization.

Characterization of the nanoparticles

The iron nanoparticles produced were characterized with the help of a UV–visible, single beam spectrophotometer (Thermo Spectronic, GENESYSTM 8, England, Quartz Cell, path length 10 mm). The hydrodynamic size distributions of nanoparticles were analyzed by a Dynamic Light Scattering (DLS) instrument (HORIBA LB-550).

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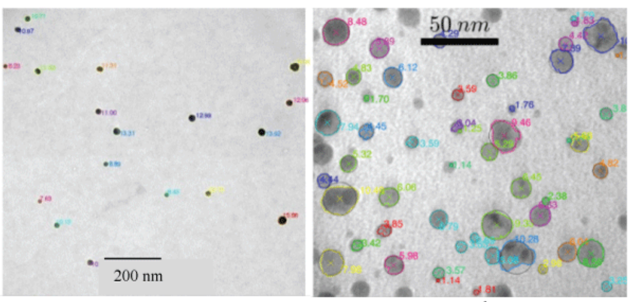
Transmission electron microscopy (TEM) was performed in a support film of 2% polyvinyl formal solution stabilized with carbon. Pictures were recorded digitally (FEI Tecnai G2 spirit twin). In addition, X-ray diffraction (XRD) studies on thin films of the nanoparticle were carried out using a PANalytical brand θ-2θ configuration (generator-detector) X-ray tube copper k=1.54 Å and EMPYREAN diffractometer. Also, FTIR total reflectance spectra were recorded on a Spectra Two IR spectrometer (Perkin Elmer, USA) to identify the functional groups. The total content of polyphenols (TCP) was determined as gallic acid equivalent (GAE) following the Folin-Ciocalteu method (ISO 14502-1).

Chemicals

Folin Ciocalteu's reagent, anhydrous sodium carbonate and gallic acid were purchased from Sigma Aldrich. Iron chloride hexahydrate was purchased from Merck.

Results and Discussion

Polyphenols in the capuli and mortiño extracts were in concentrations of 1494 ± 385 (mg GAE/100 g sample) and 2167 ± 835 (mg GAE/100 g sample), respectively. These results are similar to those found in another study [19]. When the synthesis of the nanoparticles was completed, the aqueous solutions showed a blackish-brown and a black color for mortiño (*V. floribundum*) and capulí (*P. serotina*) extracts which can be related to the formation of iron oxides and zero-valent iron nanoparticles, respectively. This clearly indicates the formation of nanostructures that are characteristic of zero-valent and iron oxides nanoparticles. The color change is due to the shift of the plasmon resonance wavelength [20]. The resulting nanoparticles are similar to those reported in Mystrioti et al. [21]. Thus, extracts of *P. serotina* and *V. floribundum* are a great source of natural antioxidants [19]. The mechanism of formation and stabilization of the iron nanoparticles might be associated to their -OH and -COOH groups contained in the biomolecules of polyphenols extracted from the cherries. TEM images of nanoparticles prepared with *P. serotina* and *V. floribundum* are shown in Figure 1. Using statistical calculations and an algorithm developed by Rodríguez et al. [22], nZVIs prepared with mortiño extract showed diameter of 13.2 nm ± 5.9 nm; fractal dimension of 1.52 ± 0.14 and roundness of 0.85 ± 0.14. Whereas, the morphological properties of nZVIs synthesized with capulí extract were 11.9 ± 7.9 nm in diameter, 1.50 ± 0.10 in fractal dimension and 0.97 ± 0.03 of roundness (Figure 1a and 1b).



a b

Figure 1: TEM micrographs: (a) nZVI 0.1M *P. serotina* and (b) of 0.1M nZVI *V. floribundum*; ratio 10:1 (v/v).

As seen the particles are in the nanosized range and roundness approaches to spherical. From the experimental and an accounting analysis performed with the TEM and a free software, it was demonstrated that the number of nanoparticles is related to the concentration of $FeCl_3$ (Table 1). The mineral structure of nanoparticles was characterized in deep using XRD. Peaks in the diagram were identified as iron oxides and zero-valent iron, respectively (Figure 2a and 2b). Also the percentages of nanoparticles Fe^0 produced with fruit extracts at different stoichiometric ratios of 0.1M $FeCl_3$, were estimated using XRD measurements (Table 2).

$FeCl_3$	Nanoparticles prepared with *P. serotina*	Nanoparticles prepared with *V. floribundum*
0.001 M	10	12
0.01 M	32	57
0.5 M	100	

Table 1: Amount of nZVIs produced varying the concentration of $FeCl_3$.

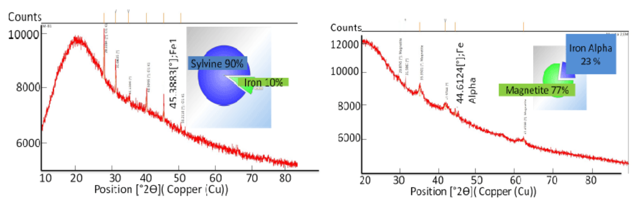


Figure 2: XRD spectra for: (a) nZVI 0.1M with *P. serotina*, (b) nZVI 0.1M with *V. floribundum*, ratio 10:1 (v/v).

Ratio of $FeCl_3$: fruit extract	Percentage of nZVIs
10:01	<1%
10:05	1%
01:10	10-11%
01:20	10-11%
01:40	10-11%

Table 2: Percentage of nZVIs produced using different ratio of $FeCl_3$: fruit extract.

It is clearly noted that when the amount of fruit extracts is higher more metallic iron is produced. This behavior can be attributed to the amount of polyphenols (reducing agent) contained in the extracts. Finally, the role of the biomolecules on the formation of nanoparticles was analyzed using the FTIR spectra. Peaks in the range 1800 cm^{-1} for both the fruit extracts and the nanoparticles solutions are attributed to functional groups of polyphenols. Whereas peaks approximately at 1000 cm^{-1} that correspond to vibration of CO are observed in both extracts but these are not shown in the nanoparticles samples (Figure 3A and 3C).

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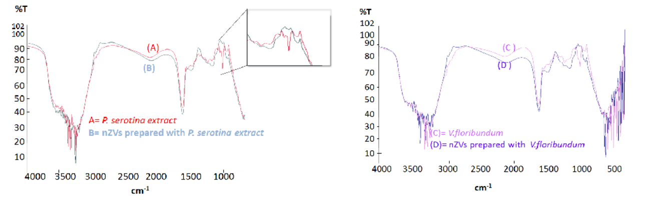

Figure 3: FTIR spectra: A) *P. serotina* extract, B) nZVIs prepared with *P. serotina* extract, C) *V. floribundum* extract, D) nZVIs prepared with *V. floribundum*, 10:1 (mL fruit extract:mL$FeCl_3$) ratio.

Conclusions

Two fruit extracts capulí (*Prunus serotina*) and mortiño (*Vaccinium floribundum*) were selected based on their antioxidant activity as reducing agents for the production of iron nanoparticles suspensions. From the results it can be concluded that the structure of polyphenols plays the key role in the formation of nanoparticles of iron. The synthesis of nanoparticles of zero-valent iron and iron oxides is strongly influenced by the amount of extracts of antioxidant compounds of capuli and mortiño. The synthesized nanoparticles have mainly spheroidal shape. The measured diameter was around 13 nm for zero-valent iron nanoparticles with mortiño extract (*V. floribundum*) whereas for capuli extract (*P. serotina*) the measured diameter was around 12 nm. In addition, increasing the concentration of the precursor salt the amount of the synthesized nanoparticles increases. In conclusion, it was demonstrated that the production of metallic nanoparticles using green synthesis is an efficient, inexpensive and environmentally friendly alternative to classical chemistry.

Acknowledgements

Authors acknowledge the assistance of Dr. Carlos Arroyo and Eng. Andrea Vaca with the TEM imaging, data processing software and XRD analysis. In addition, we thank the Universidad de la Fuerzas Armadas-ESPE for funding for the project 2015-PIC-004.

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This article was originally published in a special issue, entitled: **"Recent Advances in Biology & Nanotechnology"**, Edited by Saurabh RamBihariLal Shrivastava