PLANT MEDIATED SYNTHESIS OF ZERO VALENT IRON NANOPARTICLES AND ITS CHARACTERISATION

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Abstract

Nanoscale zero valent-iron (nZVI) particles represent an important material for diverse environmental applications because of the exceptional electron-donating properties, which can be exploited for applications such as reduction, catalysis, adsorption, and degradation of a broad range of pollutants. The search for "green" strategies leads to the advancement in the plant-mediated synthesis of ZVI nanoparticles.Within the framework of this work, the possibility of synthesis of nano zerovalent iron (nZVI) was investigated using extracts of oak, mulberry, green tea, pomelo peel, fresh orange peel and orange peel that was previously dried. Also, the subject of the investigation was the characterization of the obtained nanomaterials.

Introduction

Nanoscience and nanotechnology in recent times have purpose to minimize the negative impacts of synthetic procedures and the exploitation of different biomaterials for the synthesis of nanoparticles is considered a valuable approach in green nanotechnology. Biological resources such as plants have been used for the production of energy-efficient, low-cost and nontoxic environmental friendly iron nanoparticles *(Saif et al., 2016)*. One of the most important properties of plants that affects the production of nano zero-valent iron particles (nZVI) is the antioxidant capacity and polyphenols. Polyphenols are the most significant, essential property of plant material in the production of nZVI because antioxidant components can reduce Fe^{3+} ions to zero-valent iron (Fe^0). In order to reduce the costs of the synthesis of nanomaterials, tree leaf extracts can also be used *(Mittal et al., 2013)*. Pomelo citrus peel is characterized by a high content of pectin, essential oils, flavonoids, polysaccharides and other components that can be used in the synthesis of nZVI. Its application reduces the amount of waste caused by its consumption and thereby prevents negative impact on the environment *(Venkateswarlu, 2013)*. The size of the obtained nanoparticles as well as their reactivity depends both on the applied reagents and on the properties of the tea itself *(Chen et al., 2011)* and today, depending on the need, various tea extracts are applied. The aim of this work was to investigate the possibility of synthesizing nano zero valent iron (nZVI) using extracts of oak, mulberry, green tea, pomelo peel, fresh orange peel and orange peel that has been previously dried. Also, the subject of the investigation was the characterization of the obtained nanomaterials. The obtained extracts and nanomaterials were characterized by isoelectric point/point of zero charge (IET), zeta sizer, pH value, total phenol content and antioxidant capacity.

Methods and Materials

Nano zero valent iron was synthesized using extracts of oak and mulberry leaves (OL-nZVI, ML-nZVI), green tea (GT-nZVI), fresh orange peel (FO-nZVI), dry orange peel (DO-nZVI) and pomelo peel (P-nZVI) as a reducing agent. Preparation of Oak and Mulberry extracts were determined by previous testing and analysis *(Machado et al., 2013)*. *Huang et al., 2014* investigated the optimal time and temperature for the preparation of green tea extract so this method was used in this research. Preparation of pomelo peel (P)/fresh orange peel (FO)/dry orange peel (DO) extracts were performed by *Wei et al., 2016*. Production of nZVI was determined when solution of Fe^{3+} with a molar concentration of 0.1 M was mixed with the prepared extracts in a ratio of 3:1. Characterization of extracts from Oak, Mulberry, commercial Green Tea leaves, Orange and Pomelo Peel was determined by pH, FRAP method and by total content of phenols. pH value of the extracts was measured according to the standard method (ISO 10390:2007), by using SenTix®21 electrode. The antioxidant capacity of the extracts was evaluated by using the "ferric reducing antioxidant power" (FRAP) method *(Pulido et al. 2000)* adapted for microplates. The total content of phenols was determined by using the Folin-Ciocalteu method (ISO, 2005). The pH value of the zero charge point (IET) of nanomaterials was determined by the salt addition method *(Kosmulski, 2009)* and the IET of the samples was calculated from the dependence graph ΔpH (final pH-initial pHi) and initial pH value (pHi). The analysis of particle size distribution was performed on a Malvern Zetasizer Nano ZS device.

Results and discussion

As can be seen from the table 1, the extract with the highest pH value is the oak leaf extract (pH=7.55), while the lowest pH value is the dry orange peel extract (pH=4.08). The total content of phenols in the samples of plant extracts is determined in order to obtain information on whether any plant extract can be applied for the synthesis of this type of nanomaterials (*Weng et al., 2013*). In Figure 1, it can be seen that sample GT has the highest phenolic content (64.5 mg of gallic acid equivalents per gram of dry extract), while the same total phenolic content of 1.9 mg of gallic acid equivalents per gram was detected in samples FO and P. Figure 1 show that the highest antioxidant capacity was obtained for the GT sample (60.3 mg of ascorbic acid equivalents per gram of dry extract), which can be associated with the highest total phenol content in the given sample. The lowest antioxidant capacity was obtained for samples FO and P, which are comparable results to the results of total phenol content in the given samples. In sample FO the antioxidant capacity is 0.9, while in sample P, the antioxidant capacity is 0.2 mg of extracts made from dried plants have been proven to have higher antioxidant capacities ascorbic acid equivalents per gram of dry extract. Because the water evaporates from the plants during drying, which leads to an increase in the concentration of antioxidants in the plants *(Machado et al., 2013)*. This claim was also proven by this test, because the extract of dry orange peel has a higher antioxidant capacity compared to the extract of fresh orange peel.

<u>Characterization of synthesized nanomaterials</u>

The point of zero charge (IET) is defined as the condition at which the surface charge is equal to zero, the surface of metal oxides and other materials. The IET of nanomaterials depends on several factors such as chemical modifications, surface modifications, particle size and particle transformation (*Mwaanga et al., 2014*). When the surface of the material is exposed to the environment in an aqueous solution, the layer of hydroxyl groups breaks down due to the interaction with water molecules.

Table 1. pH values of plant extracts

Extracts	**pH**
DO	4,08
FO	5,00
P	5,06
OAK	7,55
ML	7,30
GT	5,09

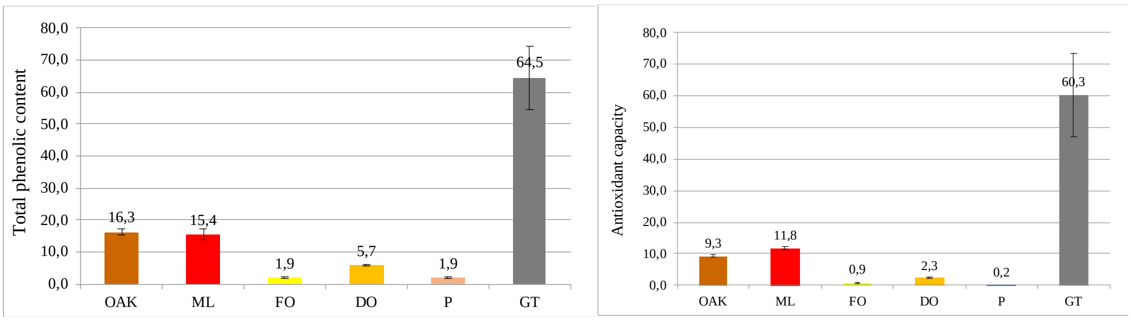

Figure 1. Comparison of the results of the antioxidant capacity of the extracts and total phenol content

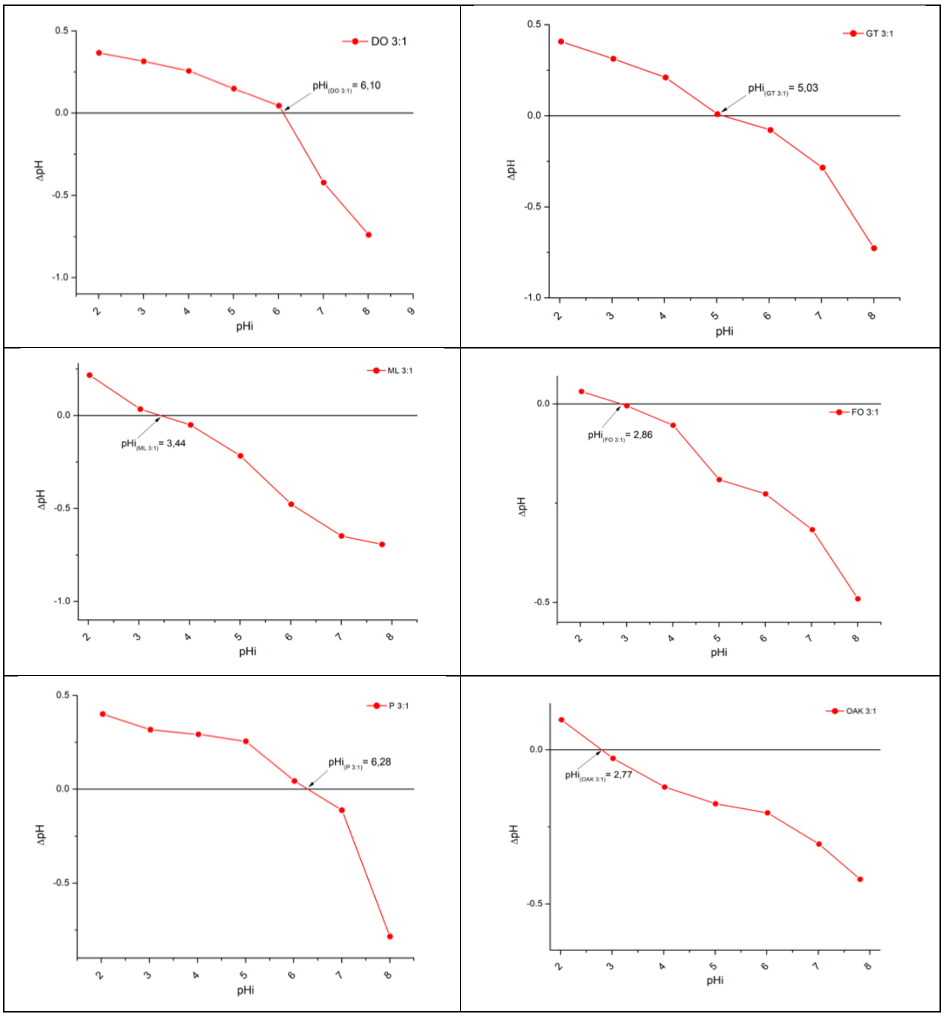

Figure 2. pHi values for synthesized nanomaterials using dry orange peel, fresh orange peel pomelo bark, oak leaf, mulberry leaf, green tea

When the surface hydroxyl groups remain undissociated in aqueous solution, the oxide surface reaches the isoelectric point (pHi) and has zero charge. If the pH is less than pHi the surface will be positively charged and if the pH is greater than pHi the surface will be negatively charged (*McCafferty, 2010*). The values of the pH point of zero charge (pHi/IET) of nanomaterials are presented in Figure 2. Point of zero charge or isoelectric point of nZVI synthesized using dry peel oranges is 6.10, for fresh orange peel is 2.86, for pomelo bark is 6.28, for oak leaf is 2.77, for mulberry leaf is 3.44, for green tea is 5.03.

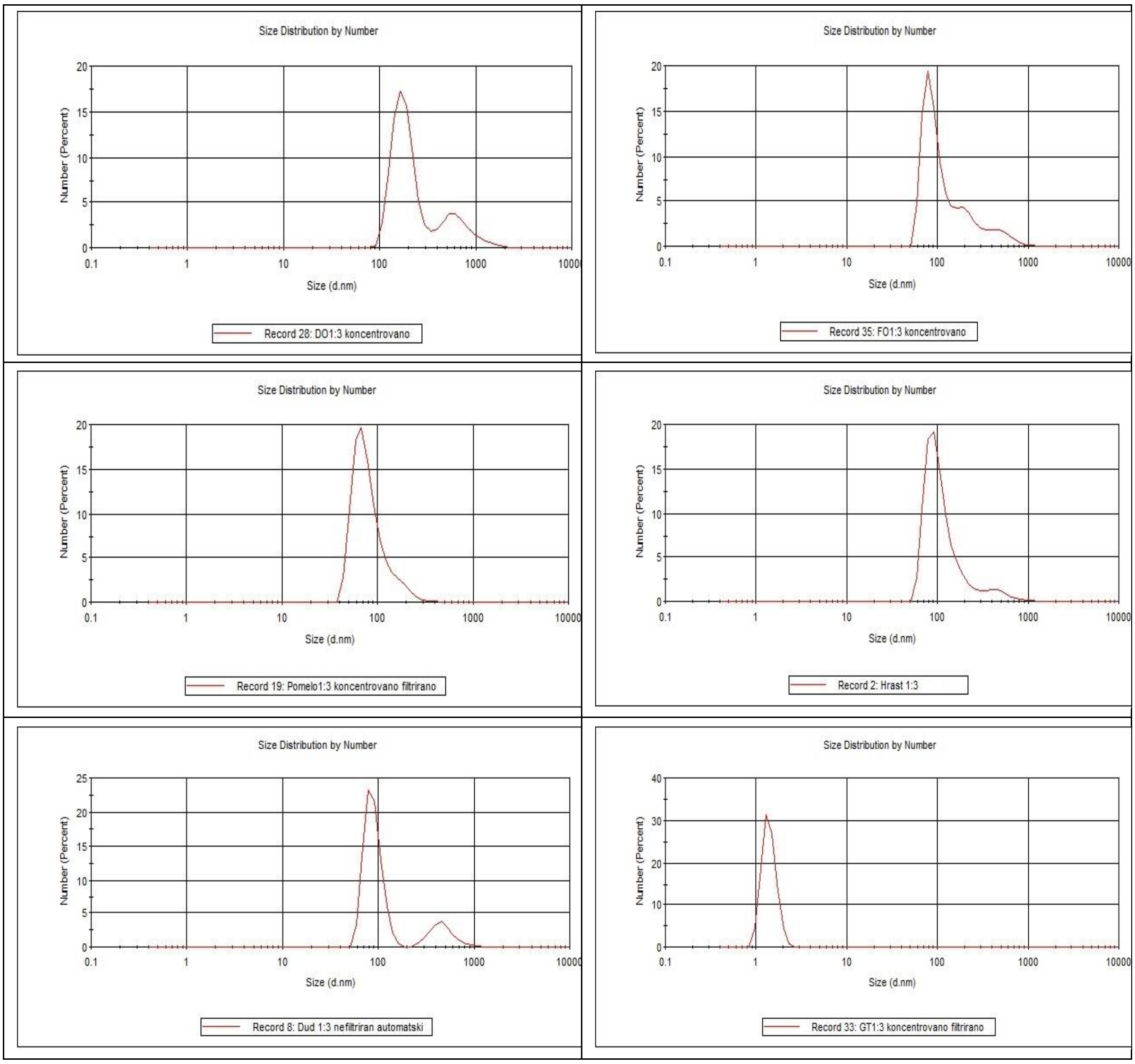

Figure 3. Particle size distribution of nZVI synthesized using plant according to their total number using a zetasizer

Poguberović, 2016 obtained comparable results for the IET sample of green synthesized nZVI from an oak leaf, pHi= 2.4, and for the mulberry leaf obtained a pHi value of 3.80 pH units. The obtained low pHi values of this type of nanomaterial can be explained as a result of the high acidity of the prepared extract of fresh orange peel *(Poguberović, 2016)*. Analysis using a zetasizer was performed in relation to the total number of particles in the sample. The results of the analysis (Figure 3) showed that the size range of nZVI particles in the samples were from **0,7 to 2000** nm, depending on plant using for synthesis. The largest number of particles having smallest diameter of about 2nm are detected for GTnZVI, and the largest number of particles having biggest diameter of about 90 nm are detected for FOnZVI. The other samples have the largest number of particles of around 70nm.

Conclusion

Dry orange peel, fresh orange peel, pomelo peel, oak leaf, mulberry leaf and green tea have been shown to be suitable plants for the synthesis of nano zero valent iron due to their relatively high content of total phenolics which is related to their antioxidant capacity.The most acidic extract was the dry orange peel extract, while the most alkaline extract was the oak leaf extract.

Using the Folin-Ciocalteau method, it was determined that green tea extract has the highest phenol content, while fresh orange peel and pomelo extracts have the lowest phenol content. The results of the FRAP method showed similar trend, where the green tea extract has the highest antioxidant capacity, while the pomelo extract has the lowest antioxidant capacity. The sample with the lowest isoelectric point is the OAK 3:1 sample, while the sample with the highest isoelectric point is the P 3:1 sample. Zetasizer, by analysing the total number of particles, showed that there are particles of different sizes in the samples. The particle size range identified by the zetasizer is from 0.7 to 2000 nm.

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