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Preparation of nanoscale iron (oxide, oxyhydroxides and zero-valent) particles derived from blueberries: Reactivity, characterization and removal mechanism of arsenate

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ABSTRACT

The application of iron nanoparticles (FeNPs) to the removal of various pollutants has received wide attention over the last few decades. A synthesis alternative to obtain these nanoparticles without using harmful chemical reagents, such as $NaBH_4$, is the use of extracts from different natural sources that allow a lesser degree of agglomeration, in a process known as green synthesis. In this study, FeNPs were synthesized by 'green' (hereafter, BB-Fe NPs) and 'chemical' (hereafter, nZVI) methods. Extracts of leaves and blueberry shoots (*Vaccinium corymbosum*) were used as reducing agents for $FeCl_3{\cdot}6H_2O$ solution in the green synthesis method. FeNPs were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), electrophoretic migration, Brunauer-Emmett-Teller (BET) surface area analysis and X-ray diffraction (XRD) and evaluated for the removal of As(V) from aqueous systems. In both synthesis methods, XRD analysis confirmed the presence of the different kinds of iron nanoparticles. SEM analysis showed that the average size of BB-Fe NPs was 52.4 nm and that a variety of nanoparticles of different forms and associated structures, such as lepidocrocite, magnetite, and nZVI, were present, while the dimensions of nZVI were 80.2 nm. Comparatively significant differences regarding the electrophoretic mobility were found between both materials pre- and post-sorption of As(V). The velocity of As(V) removal by BB-Fe NPs was slower than that by nZVI, reaching equilibrium at 120 min compared to 60 min for nZVI. The removal kinetics of As(V) were adequately described by the pseudo-second-order kinetic model, and the maximum adsorbed amounts of this analyte are in close accordance with the experimental results. The Langmuir-Freundlich model is in good agreement with our experimental data, where the sorption capacity of nZVI and BB-Fe NPs was found to be 52.23 ± 6.06 and 50.40 ± 5.90 ($mg{\cdot}g^{-1}$), respectively. The use of leaves of *Vaccinium corymbosum* affords an easy-to-synthesize, low-cost, and eco-friendly material with capabilities similar to nZVI. BB-Fe NPs are promising for arsenic remediation, which has emerged as a new alternative for water purification and sanitation.

1. Introduction

The application of nanoscale zero-valent iron (nZVI) for removing various organic and inorganic pollutants has been studied extensively over the last decade, with particular reference to heavy metals, organochlorine compounds, dyes, pharmaceuticals, and nitrates (Crane and Scott, 2012; Kanel et al., 2005). The morphology of nZVI is clearly defined as a nucleus composed of Fe^0 atoms surrounded by a layer of mixed-valence Fe oxide, whose thickness varies as a function of the conditions of the medium (pH, O_2 content, redox potential, and presence of trace elements) (Arancibia-Miranda et al., 2014a; Yan et al., 2012a). This core-shell structure promotes a series of removal mechanisms, because the functional groups presented on the outer surface can adsorb ions, forming inner or outer sphere complexes. In addition they can be potentially reduced as a result of electron transfer from the core (Calderon and Fullana, 2015; Yan et al., 2012a, 2010). Other removal mechanisms of nZVI are precipitation, co-precipitation, and oxidation, which will predominate depending on the chemical characteristics of the medium and of the analyte (Arancibia-Miranda et al., 2014a; Yan et al., 2012a, 2012b).

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In general, the synthesis of nZVI is carried out by the reduction of Fe^{2+}/Fe^{3+} salts with sodium borohydride ($NaBH_4$) (Wang and Zhang, 1997). This method has a number of disadvantages, such as high cost and the production of toxic, corrosive (BO_4^{3-}) and explosive (H_2) elements. Furthermore, the reaction produces highly agglomerated nanoparticles due to magnetic forces and van der Waals interactions, which reduces their surface area, limiting the removal processes and favouring their oxidation (Arshadi et al., 2014; Fan et al., 2009; Markova et al., 2014). The agglomeration can be reduced by adding dispersing agents, surfactants and/or chelating agents, which increase production costs and, on a large scale, are considered toxic to the environment (Li et al., 2006; Sarathy et al., 2008).

An alternative synthesis method to obtain environmentally friendly nanoparticles with less agglomeration uses aqueous extracts from various natural sources – a methodology known as *green synthesis*. The main approach in the use of plant extracts to synthesize nZVI mainly relies on the ability of polyphenols to form complexes with Fe and other metal ions (Ag^+ and Cu^{2+}) due to the presence of functional groups that increase the ability to reduce the metal ion (Machado et al., 2013a, 2013b; Nadagouda et al., 2010; Shen et al., 2016). The reducing power of an extract will depend on the solvent used and mainly the type and concentration of compounds present, especially polyphenols, which allow the reduction of the Fe^{3+} through an electron transfer mechanism (Martínez-Cabanas et al., 2016; Kumar et al., 2013). The chemical structure of polyphenols improves the stability of the nanoparticles that are formed by capping, causing an increase in the electrostatic and/or steric repulsion between the particles and a decrease in the van der Waals interactions and magnetic force, therefore leading to reduced agglomeration and oxidation of the nanoparticles (Nadagouda et al., 2010). In this context, the use of plant residues, such as leaves and shoots, with high contents of phenolic compounds will allow the production of nanoparticles with a scarce amount of toxic residues in relation to the use of synthetic reagents ($NaBH_4$). A mechanism proposed for the synthesis of nZVI from polyphenols was reported by Smuleac et al. (2011), who proposed the following Eq. (1):

$$-n\mathrm{Fe}^{2+} + 2Ar(\mathrm{OH})_n \rightarrow n\mathrm{Fe}^0 + 2nAr = \mathrm{O} + 2n\mathrm{H}^+ \qquad (1)$$

where Ar is the phenyl group and n is the number of hydroxyl groups oxidized by Fe^{2+}. The position of the hydroxyl groups in the phenolic compounds also plays an important role in the formation of nanoparticles, and it has been found that phenolic compounds with hydroxyl groups in the *ortho* position favour the reduction and formation of nanoparticles (Ryan and Hynes, 2007).

The advantages of green synthesis over the traditional synthesis of nanoparticles are in the use of natural products (i.e., leaves, fruit peel, shoots, and roots), the solvent used (i.e., water), its simplicity, its speed, the stability of the compound, and its cost-effectiveness. Various studies have shown that it is possible to synthesize iron nanoparticles from tea, mulberry, mint, and grape leaves, as well as the seed extract of Cnidium, for use in pollutant removal (e.g., As, ibuprofen, Pb, Cr, dyes) due to their a high sorption characteristics (Luo et al., 2016, 2015; Machado et al., 2013a, 2013b; Poguberović et al., 2016; Prasad et al., 2014; Lingamdinne et al., 2017). In this respect, it has been reported that blueberry leaves (*Vaccinium corymbosum*) contain a high concentration of polyphenols with a large reducing ability, with chlorogenic acid, ellagic acid, and rutin as the main phenolic compounds detected, which convert this plant a potential source for the synthesis of Fe nanoparticles, including nZVI (Manquián-Cerda et al., 2016), with potential for the removal of different trace elements.

The removal of As from natural systems using nZVI has been studied extensively. Findings show that these nanoparticles are highly effective for removal and stabilization (Baltazar et al., 2014; Kanel et al., 2005; Yan et al., 2012a, 2012b). Arsenic is present in various forms in nature, mainly as organic species, such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine, and arsenocholine (Lau et al., 1987; Mandal and Suzuki, 2002). In aqueous systems, inorganic forms of arsenic predominate, such as arsenate (As(V)) and arsenite (As(III)), which present the highest levels of toxicity (Kanel et al., 2005; Smedley and Kinniburgh, 2002). In this regard, the total arsenic content in drinking water recommended by the World Health Organization should not exceed 10 μg/L. However, in areas where As is geologically present in high concentrations, reaching this limit requires higher operational costs (Smedley and Kinniburgh, 2002; WHO, 2011).

Therefore, to determine whether iron nanoparticles synthesized from *Vaccinium corymbosum* extract have the same efficiency for the removal of pollutants as nanoparticles obtained by traditional methods (i.e., reduction with borohydride), the removal of arsenic (As(V)) from an aqueous matrix was evaluated and compared. In this study, Fe nanoparticles were synthesized from blueberry extracts. The obtained material was characterized structurally and superficially using various analytical methods, including TEM, SEM, XRD, BET, and surface charge analysis, and the extracts were evaluated according to their reducing power. Kinetic models and adsorption isotherms were studied in the removal of As(V) by nZVI and by nanoparticles obtained from green synthesis.

2. Materials and methods

2.1. Preparation of the extracts

Each extract was prepared with 8.0 g of blueberry plant materials. The three extracts used corresponded to 100% leaves, 100% shoots and 50–50% leaves-shoots. Extraction was performed with 400 mL of water as the solvent. The samples were subjected to continuous extraction for 0, 5, 30, 60, 90, 120, and 180 min at 90 °C, and the extracts were then filtered through 0.45 μm regenerated cellulose filters.

2.2. Evaluation of the reducing capacity of the extracts

The ferric reducing antioxidant power (FRAP) assay measures the ability of the sample to reduce Fe^{3+} to Fe^{2+} (Benzie and Strain, 1996), followed by the absorbance at 593 nm of the blue complex formed with tripyridyltriazine (TPTZ). The FRAP reagent was prepared by mixing acetate buffer (300 mM), TPTZ solution (10 mM in HCl), and $FeCl_3$ solution (20 mM) at a 10:1:1 ratio.

The FRAP reagent was kept at 37 ± 2 °C (310 ± 2 K). The absorbance of samples containing 900 μL of FRAP reagent, 80 μL of water, and 20 μL of extract was measured at 593 nm in an Agilent 8453 UV–Vis spectrophotometer. The results were expressed in ascorbic acid equivalents.

2.3. Total phenolic content (TPC)

The total phenolic content was determined using the Folin-Ciocalteu method proposed by Singleton and Rossi (1965), using gallic acid as the standard. A dilution was prepared containing 10 μL of the aqueous extract and 30 μL of Milli-Q water. Then, 100 μL of the Folin-Ciocalteu reagent was added and mixed. After 5 min, 300 mL of Na_2CO_3 (7%) was added and allowed to stand for 10 min. Finally, the reaction mixture was measured spectrophotometrically at 765 nm in an Agilent 8453 UV–Vis spectrophotometer (Palo Alto, CA, USA). The results are expressed as milligrams of gallic acid equivalent (GAE) per gram of dry weight.

2.4. Synthesis of iron nanoparticles

The synthesis of Fe nanoparticles used blueberry extracts from *V. corymbosum* cv. Legacy. First, 10 mL of extract was mixed with 5 mL of 1.0 M $FeCl_3{\cdot}6H_2O$ solution. The black solid product was then separated from solution using an ultracentrifuge (Sorvall RC-5C Plus) and washed five times with a (1:1) acetone/water solution (9000 rpm for 30 min)