Arsenic removal by iron-based nanomaterials

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ABSTRACT: Processes based on the use of iron-based nanoparticles (FeNPs) have proved to be a promising technology for the removal of a wide range of pollutants including metals and metalloids in water, being simple and low-cost procedures for removal of As(III)/As(V). FeNPs such as zerovalent iron nanoparticles (nZVI), nanoparticles of iron oxides (FeONPs) as hematite or magnetite, and iron-based nanoparticles prepared from natural extracts of plants or seeds (as *yerba mate* and green tea) have a larger surface area/volume ratio and exceptional adsorption properties compared with micro- or macrosized materials, with the advantages of an effective removal of pollutants at very low concentrations and a low generation of sludge. Laboratory experiments have been performed to evaluate the efficiency of some iron-based nanoparticles for removal of As(III)/(V), studying the influence of the initial concentration of the pollutant, the NP mass, the pollutant:FeNP molar ratio, pH, the presence of O₂, among other variables. In this presentation, a brief review on the use of FeNPs for As removal from water and some results of our laboratory will be presented.

1 INTRODUCTION

Processes based on the use of iron nanoparticles (FeNPs) can be simple and low-cost procedures for removal of As(III)/As(V) in the pH range typical of groundwaters (Lata & Samadder, 2016). FeNPs such as zerovalent iron nanoparticles (nZVI), nanoparticles of iron oxides (FeONPs) as hematite or magnetite, and iron-based nanoparticles prepared from natural extracts of plants or seeds have a larger surface area/volume ratio and exceptional adsorption properties compared with micro- or macrosized materials, with the advantages of an effective removal of pollutants at very low concentrations and a low generation of sludge. The use of FeNPs has proved to be a promising technology for the removal of a wide range of pollutants including metals and metalloids in water (Crane & Scott, 2012; Quici *et al.*, 2018). These nanomaterials can be used to develop low-cost nanotechnologies for *in situ*, on site and *ex situ* water treatments, including drinking water provision, residual effluents and remediation of contaminated sites.

2 MECHANISMS OF REMOVAL OF METALS AND METALLOIDS WITH IRON NANOPARTICLES

Figure 1 shows the possible mechanisms for removal of metals and metalloids by FeNPs, including surface adsorption, complexation, redox processes, precipitation and coprecipitation.

When different FeNPs are compared, As removal capacity is higher for the samples of higher Fe

content, i.e., usually the most reduced materials: nZVI > Fe₃O₄ > Fe₂O₃ > FeOOH (Crane & Scott, 2012).

Mixed metal oxide nanoparticles, with Fe combined with other metals, have been also tested for As removal (Lata & Samadder, 2016).

As(V) adsorption is higher than As(III) adsorption at acid and neutral pH values because As(III) species are neutral up to pH 9, while As(V) species are charged. As(V) adsorption is always higher under acidic conditions, as the anionic species are dominant even at pH 2.

Figure 1. Proposed removal mechanisms of metals and metalloids taking place on nFe surfaces (based on Simeonidis *et al.*, 2013). M: metal or metalloid, N: oxidation state.

Some studies report that the optimal As(III) adsorption on magnetite and maghemite nanoparticles takes place at pH 2 (Quici *et al.*, 2018).

In the presence of dissolved oxygen, arsenite adsorption over magnetite is followed by As(III) partial oxidation to As(V) by the action of reactive oxygen species formed after Fe(II) oxidation by O₂; incomplete As(III) oxidation was ascribed to magnetite passivation (Ona-Nguema *et al.*, 2010).

One alternative low-cost, green method of synthesis of FeNPs is the reaction of iron salts with extracts of leaves or grains of natural plants, such as green tea (GT, *Camellia sinensis*), yerba mate (YM, *Ilex paraguayensis* Saint Hilaire), coffee and wine, where the active compounds are polyphenols and other reducing or complexing species (Oakes, 2013). The preparation of these green FeNPs has been reviewed (Genuino *et al.*, 2013; Herlekar *et al.*, 2014). Hoag *et al.* (2009) reported the first synthesis of FeNPs prepared from GT extracts and Fe(NO₃)₃ solutions. Later, similar products using a variety of natural materials and other Fe common salts were reported (Wang, 2015). However, a discrepancy exists on the composition and chemical structure of these materials, some authors claiming the presence of zerovalent iron (Fe(0)), others indicating the formation of amorphous iron complexes and some others presenting the formation of iron oxides. YM has been recently used for producing iron-based nanomaterials (Trotte *et al.*, 2016; Mercado *et al.*, 2017). There are few reports on As removal by green FeNPs (Martínez Cabanas *et al.*, 2016; Poguberović *et al.*, 2016), but the informed As removal capacity (up to 300 mg g⁻¹) makes these low-cost materials very interesting.

3 RESULTS OF OUR LABORATORY

3.1 Introduction

In our laboratory, the efficiency of FeNPs has been evaluated for removal of As(III)/(V), studying the influence of the nature and amount of the iron material, the initial concentration of the pollutant, the pollutant: FeNP molar ratio (MR), the pH, the presence of O₂, and other variables (Morgada *et al.*, 2009; Pabón *et al.*, 2018). Recently, FeNPs were rapidly synthesized using YM extracts and Fe(III) salts, and the applicability of the materials for the removal of As(III)/As(V) from aqueous solutions has been tested and compared with similar materials prepared from GT and with commercial nZVI (García *et al.*, 2018). The last advances of our laboratory will be briefly presented.

3.2 Experimental

3.2.1 Materials and methods

Ethanol (99.5%), NaOH (97%), FeSO₄·7H₂O (99%), FeCl₃·6H₂O (99.6%), orthophosphoric acid (85%), and H₂SO₄ (98%) were analytical grade (Biopack). K₂Cr₂O₇ was Mallinkrodt. Na₂HAsO₄·7H₂O, NaAsO₂, 1,5-diphenylcarbazide (UCB), acetone (99.8%,

Anedra) and gallic acid monohydrate (J.T. Baker) were used. NanoFe® was synthesized by Nanotek S.A. (Santa Fe, Argentina) by a proprietary technology based on chemical reduction of ferric salts with sodium borohydride in a stabilized multiphase nanoemulsion (www.nanoteksa.com). nZVI (NANOFE 25, hereafter N25) was provided by NANO IRON s.r.o. (Czech Rep.) as a concentrated aqueous suspension. Commercial dried YM (Taragui *sin palo*) and GT (Hierbas del Oasis, S.R.L.) leaves were purchased from a local supermarket. In all experiments, Milli-Q water was used (resistivity = 18 MΩ cm). All other chemicals were of the highest purity.

3.2.2 Synthesis of iron-based nanoparticles from GT and YM extracts

Commercial GT leaves were processed for 30 s with a hand blender (Philips, HR 1368/00) to obtain a size similar to commercial YM (around 1–3 mm diameter). A 50 g L⁻¹ suspension of each powder was extracted during 1 h at 79–85°C and filtered through a 0.22 μm pore size nylon membrane.

Fresh 0.1 M FeCl₃·6H₂O solutions were prepared and vacuum filtered through a 0.22 μm pore size nylon membrane. To 2.5 mL of the Fe(III) solution, the corresponding volume of YM or GT extract, previously diluted to 25 mL, was added at a 2.8:1 extract:Fe MR. The color of the mixture with YM changed from yellow to greenish-black, and to black for GT, indicating in both cases the formation of nanoparticles. The corresponding iron suspensions will be named YM-Fe(III) and GT-Fe(III).

3.2.3 Experiments of As removal with NanoFe®

In a typical experiment, 150 mL of an As(V) solution (1 mg L⁻¹, pH 7.8), were introduced into a 250 mL glass Erlenmeyer flask (covered by an aluminum foil to avoid the entrance of ambient light) and bubbled with air (1 mL min⁻¹) for 30 min under orbital stirring in order to reach oxygen saturation. Then, air bubbling was stopped, and a volume of the NanoFe® suspension containing the corresponding amount of the material (to have final concentrations ranging 0.005–0.1 g L⁻¹) was added, under vigorous stirring. The flask was left open to the air all throughout the run. Temperature was ambient, never higher than 30°C. Samples (2.5 mL) were taken periodically, filtered through a 0.45 μm Millipore membrane and analyzed for total As in solution by ICP-OES, using a Perkin-Elmer Optima 3100 XL apparatus.

3.2.4 Experiments of As removal with N25

Experiments with As(III) (1 mg L⁻¹, pH 6) were performed in a recirculating batch system with a cylindrical Pyrex glass reactor, adding the corresponding amount of nZVI suspension in different As:Fe RMs, 1:10, 1:20, 1:30, 1:50 and 1:100. The system was stirred, open to air and the temperature was 25°C. Changes in As(V) and As(III) concentration in solution were measured using a modified arsenomolybdate technique at 868 nm (Levy *et al.*, 2012).

3.2.5 Experiments of As removal with YM-Fe(III) and GT-Fe(III)

The corresponding volume of YM-Fe(III) and GT-Fe(III) suspensions was added to an Erlenmeyer flask containing 25 mL of a solution of As(V) or As(III) (1 mg L^{-1} , pH 7, As:Fe MR = 1:30), under continuous agitation. Control experiments with Fe(III), Fe(II) at As:Fe MR = 1:30 were performed. Samples (0.5 mL) were taken at periodical times, filtered through a Millipore membrane ($0.22 \mu\text{m}$) and analyzed for remaining total As in the filtrate by TXRF using a Bruker S2 Picofox spectrometer.

3.3 Results and discussion

3.3.1 Experiments of As(V) removal with NanoFe®

Experiments of As(V) (1 mg L^{-1} , pH 7.8) removal using different NanoFe® masses are shown in Figure 2. As removal was rapid and increased with NanoFe® dosage in the range $0.005\text{--}0.1 \text{ g L}^{-1}$. Removal attained more than 90% after 150 min of contact time at the highest NanoFe® concentrations; $0.05\text{--}0.1 \text{ g L}^{-1}$ were enough to reach an excellent and rapid efficiency.

3.3.2 As(III) removal with N25

Results of As(III) removal (1 mg L^{-1}) are presented in Figure 3. The removal increased with the increase of the amount of nZVI, being almost complete at 1:50 MR. As(V) was detected in the final solution in all cases but at a low concentrations compared with the initial As(III) concentration (lower than 0.4 mg L^{-1}), indicating that part of the material was immobilized on the remaining solid.

3.3.3 As removal with YM-Fe(III)-5 and GT-Fe(III)-5

In Figure 4, results of total As removal with YM-Fe(III)-5 and GT-Fe(III)-5 starting from As(III) (1 mg L^{-1} , pH 7) are shown. With both Fe(III)-5 and GT-Fe(III)-5, low removals, 22 and 32% respectively, were obtained; however, at this As:Fe MR = 1:30, N25 was not very efficient either (44%) and the removal

Figure 2. Temporal evolution of normalized As(V) concentration during treatment with NanoFe® in different iron masses. $[\text{As(V)}]_0 = 1 \text{ mg L}^{-1}$, pH 7.8, $T = 30^\circ\text{C}$.

was similar to that performed adding soluble Fe(II). Control with Fe(III) gave negligible removal.

Figure 5 shows the results of total As removal with YM-Fe(III)-5 and GT-Fe(III)-5 starting from As(V).

Figure 3. Temporal evolution of normalized As(III) concentration during treatment with N25. Conditions: $[\text{As(III)}]_0 = 1 \text{ mg L}^{-1}$, MR = 1:10, 1:20, 1:30, 1:50, pH 6-7, open to air, $T = 25^\circ\text{C}$. Inset: temporal evolution of As(V) concentration.

Figure 4. Temporal evolution of normalized total As concentration during treatment with YM-Fe(III)-5 and GT-Fe(III)-5. Conditions: $[\text{As(III)}]_0 = 1 \text{ mg L}^{-1}$, pH 7, As:Fe MR = 1:30, $T = 25^\circ\text{C}$.

Figure 5. Temporal evolution of total As concentration during treatment with YM-Fe(III)-5 and GT-Fe(III)-5. Conditions: $[\text{As(V)}]_0 = 1 \text{ mg L}^{-1}$, pH 7, As:Fe MR = 1:30, $T = 25^\circ\text{C}$.

In contrast with the results of As(III), YM-Fe(III)-5 gave a very good total As removal (83%), better than that obtained with N25 (52%), while GT-Fe(III)-5 gave only 20%. Controls with Fe(III) and Fe(II) gave removals of 28 and 7%, respectively.

4 CONCLUSIONS

Use of iron-based nanoparticles is a very efficient and low-cost method for arsenic removal from water. These nanomaterials, including those prepared from natural extracts and cheap iron salts, can be used to develop low-cost nanotechnologies for *in situ*, *on site* and *ex situ* water treatments, including drinking water provision, residual effluents and remediation of contaminated sites. Laboratory tests must be done to continue testing the efficiency of these materials and are underway.

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