



# Investigation of iron reduction by green tea polyphenols

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## ABSTRACT

The green synthesis of iron nanoparticles (Fe-NP) using plant extracts that are rich in polyphenols has become increasingly popular in recent years and a wide variety of plants have been used to this end. Although the reactivity of these Fe-NPs towards different contaminants has been shown, the exact composition of the nanoparticles remains controversial. Early studies claimed the formation of zero-valent iron, while others reported iron oxides such as magnetite and ferric oxyhydroxides and a variety of characterization techniques have been applied on solids recovered from the suspensions. This study reports on characterization conducted on original suspension produced from ferric iron reacted with three stoichiometries of green tea solution, utilizing X-ray Absorption Near Edge Structure (XANES) and Mössbauer spectroscopy. In addition, the suspensions were fractionated using nanofiltration and a host of techniques were applied to characterize the solid and the liquid fractions. Approximately 15% of the original Fe remained in solution, both as Fe(II) and Fe(III), while the remaining Fe formed nanoparticles that consist of primarily ferrous and ferric tannates, which have substantial reductive capacity for hexavalent chromium. Iron oxides were observed by Mössbauer spectroscopy only for the highest ratio of iron to green tea solution.

## 1. Introduction

The green synthesis of nanoparticles of iron (Fe-NP) and other metals (Ag, Au) using plant extracts has become increasingly popular in recent years (Herlekar et al., 2014; Nadagouda et al., 2014) and has been one of the key technologies for green and sustainable remediation (Virikutyte and Sharma, 2014), especially in light of their very low risk of ecotoxicity (Plachtova et al., 2018). The principle behind this technology is that the polyphenols contained in these extracts react with ferric iron (Fe(III)) to reduce it and produce zero-valent iron (Hoag et al., 2009). While the first studies employed green tea solution as the source of polyphenols (Hoag et al., 2009; Nadagouda et al., 2010), a wide variety of plant extracts have been utilized for the same purpose, including eucalyptus (Wang et al., 2014), sage (Wang et al., 2015), red wine and pomegranate juice (Mystrioti et al., 2016), blueberries (Manquian-Cerda et al., 2017), and twenty six different kinds of tree leaves (Machado et al., 2013a), to mention only a few of the available studies in the literature. Herlekar et al. (2014) provide a review of the relevant literature, which has continued to grow. Various authors have utilized the resulting suspensions to treat diverse contaminants and media, including domestic wastewater (Herlekar et al., 2014; Devatha et al., 2016), chlorinated solvents (Smuleac et al., 2011), hexavalent

chromium (Chrysochoou et al., 2012; Fazlzadeh et al., 2017; Mystrioti et al., 2016), arsenic (Manquian-Cerda et al., 2017), nitrate (Wang et al., 2014a) and ibuprofen-contaminated soils (Machado et al., 2013b).

While the reactivity of Fe-NP suspensions produced with green synthesis has been demonstrated through these treatability studies, the nature of the nanoparticles and the reaction pathways are less clear. Earlier studies utilized X-ray Diffraction (XRD) and transmission or scanning electron microscopy (TEM/SEM) to characterize the resulting nanoparticles and reported the presence of zero-valent iron (ZVI) (Hoag et al., 2009; Nadagouda et al., 2010). Njagi et al. (2011) and Machado et al. (2013a) failed to observe crystalline ZVI peaks in the XRD patterns and attributed this to the formation of an amorphous iron oxide shell around the nanoparticles upon drying. Mystrioti et al. (2016) utilized electron diffraction analysis in combination with TEM for Fe reacted with polyphenol-rich solutions and reported the presence zero-valent iron.

However, several other studies used a combination of techniques and reported the presence of iron oxide phases, specifically magnetite (Phumying et al., 2013; Singh et al., 2017), ferric oxide and oxyhydroxide (Shahwan et al., 2011), and mixtures thereof (Wang et al., 2014b, Herlekar et al., 2014). Markova et al. (2014) utilized Mössbauer spectroscopy and reported the presence of only Fe(II) and Fe(III)

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compounds; Machado et al. (2014) also found Fe(II) and Fe(III) using Mössbauer, but attributed the loss of ZVI to the sample preparation that induced oxidation.

This study focuses on the investigation of the composition and reactivity of Fe-NPs produced through a green tea synthesis, going beyond previous studies with two approaches: a) utilization of XANES spectroscopy directly on the suspension, avoiding any drying and sample preparation that could change the speciation of Fe; and, b) conducting fractionation tests with the use of nanofiltration and applying a suite of analytical and spectroscopic tests to the separated fractions, in order to obtain more detailed insight into the properties and reactivity of the Fe-NPs.

## 2. Materials and methods

### 2.1. Preparation of reagents

The green tea-iron suspension was prepared based on the method proposed in Hoag et al. (2009). Chunmee Special Grade #1 green tea (GT) leaves from Imperial Tea Garden were used in all experiments. The tea was prepared fresh daily and was brewed at 80 °C for 30 min. The leaves were pre-filtered using a Millipore prefilter (> 5 µm). The resulting filtrate was then vacuum filtered using a Millipore Durapore sterile, plain, white filter with a pore size of 0.22 µm. The average polyphenol concentration of this solution was determined to be 2.6 g/L gallic acid equivalents, using the Folin-Ciocalteu method (International Organization for Standardization (ISO) method 14502-1). The 0.1 M Fe solution was prepared using ferric chloride hexahydrate (ACS grade, Fisher Scientific). The two solutions were mixed together at room temperature at three volumetric ratios: one volume of green tea solution to two volumes of iron solution (1GT:2Fe) to form a solution with 66 mM total Fe, 2GT:1Fe to form 33 mM Fe, and 5GT:1Fe to form 16.7 mM Fe.

### 2.2. Experimental approach

The resulting suspension consists of suspended nanoparticles in an aqueous solution. To determine the speciation of Fe in the suspension, the experimental approach was adopted as illustrated in Fig. 1. The solid fraction was separated through nano-filtration in custom-built stainless steel dead-end cells. NF270 filter paper (pore size ~ 1 nm, molecular weight cutoff 340 Da) from Dow Water & Process Solutions was cut to fit the cell diameter using an X-ACTO knife and rinsed with

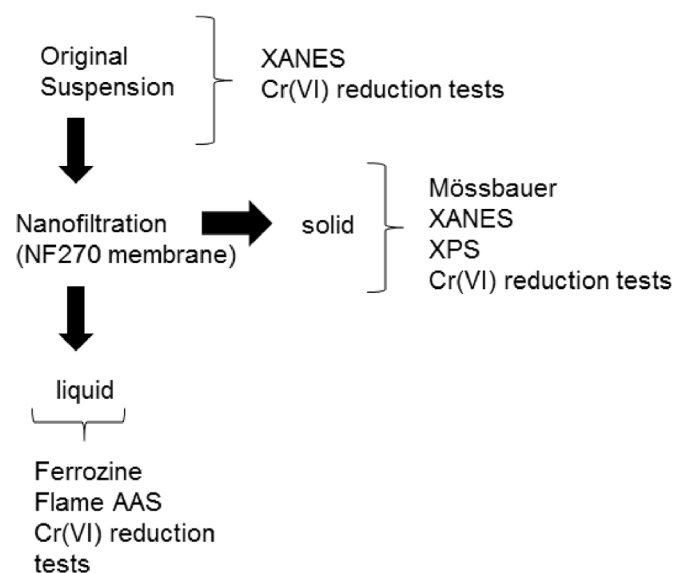


Fig. 1. Overview of experimental approach.

DI water before being fit into the cell. A 10 mL aliquot of suspension was pipetted into the cell for each test. Nitrogen from a high-pressure tank flowed into the cell at 500 psi. The cell was positioned atop a stir plate and the outflow was captured in a plastic screw-cap vial. The filtration ran to completion and the filtrate was stored at 4 °C. The filter paper and solid mass were transported to a desiccator to dry under continuous flow of nitrogen gas. A variety of methods were employed in order to determine the type and concentrations of the iron species present in the two fractions, as described in the following sections.

Finally, the reductive potential of the three fractions (suspension, solid, liquid) was evaluated using hexavalent chromium (Cr(VI)) as a probe compound. All tests were performed with 10 mL of original suspension as the reference amount of reactant, i.e. the solid and the liquid were recovered from the fractionation of 10 mL of original suspension using nano-filtration. The suspension and the solid filtrate were mixed with 200 mL of a 50 mg/L suspension, placed on a magnetic stirrer for 24 h and then filtered and residual Cr(VI) was measured with EPA method 7196a. The pH of the batch reduction tests was adjusted to ~ 3 if necessary using concentrated HNO<sub>3</sub> to run the reaction to completion without H<sup>+</sup> being a limiting factor and to prevent rapid oxidation of Fe(II) in solution or suspension. For liquid experiments, it was found that the reductive capacity was too low to accurately measure with this method, so that the volume was reduced to 50 mL of 50 mg/L stock solution for 10 mL of suspension to obtain accurate readings of the final Cr(VI) concentration.

### 2.3. Analytical and spectroscopic methods

For Fe(II) analysis in solution, the revised ferrozine method by Viollier et al. (2000) allows for the determination of Fe(II) in the presence of Fe(III) in solution and the details are provided in Supplementary Information. For total Fe analysis, flame Atomic Absorption Spectroscopy AAS (Thermo Scientific Niton iCE 3000) was employed according to EPA method 7000B, including blanks, standards and duplicates for quality assurance-quality control. All Fe-GT ratios were tested in five replicates, for which averages and standard deviations are given.

XPS analysis was carried out using a PHI Multiprobe with an aluminum anode. The full survey spectra were collected using a pass energy of 100 eV and a scan rate of 1 eV per step. High resolution spectra were collected at a pass energy of 50 eV and a scan rate of 0.1 eV per step. High resolution scans were performed on carbon, oxygen, and iron peaks. The spectra were analyzed using the CasaXPS software. Binding energy data was derived from the spectra fitting using the adventitious carbon C1s peak at 284.8 eV (Grosvenor et al., 2004). Shirley background curves were used for all fittings and specifically for Fe, separate background curves were fitted to the <sup>2</sup>p<sub>3/2</sub> and <sup>2</sup>p<sub>1/2</sub> peaks. The full-width at half maximum for peak fitting was constrained to equal values for all peaks within a fit, and the peak areas for the <sup>2</sup>p<sub>1/2</sub> peaks were constrained to half the areas of the <sup>2</sup>p<sub>3/2</sub> peaks.

XANES analysis was performed on beamline X23A2 operated by the National Institute of Standards and Technology, at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY). Incident X-ray energy was scanned across the XANES region (100 eV below the edge up to 400 eV above the edge) of the Fe K-edge (E = 7112 eV) using a Si(311) monochromator and a single-bounce harmonic rejection mirror. The monochromator was calibrated using a Fe foil. Fluorescent X-rays were collected using a Stern-Heald fluorescence detector. Samples of the GT-Fe suspensions were pipetted into a sample holder between two layers of Kapton tape for analysis. Final spectra are the result of a single scan; this was preferred because evaluation of sequential scans showed beam damage, i.e. progressive oxidation of the Fe in the sample. XANES data were processed using the Athena software (Ravel and Newville, 2005), including normalization, calibration and alignment.

Mössbauer sample mounts were made from these dried products by

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