



## Comparative evaluation of five plant extracts and juices for nanoiron synthesis and application for hexavalent chromium reduction



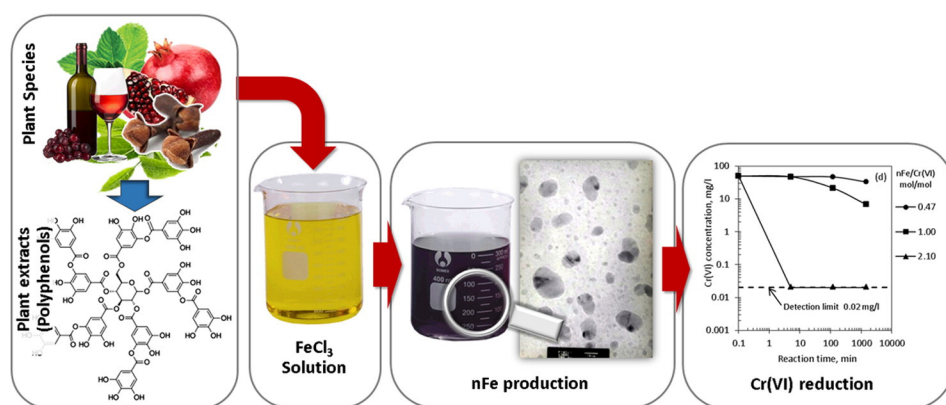
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### HIGHLIGHTS

- Herb extracts, pomegranate juice and red wine were evaluated for nanoiron synthesis
- Parameters affecting polyphenols extraction from herbs were systematically examined
- Pomegranate and Red Wine were the most efficient agents for nanoiron production
- Only a portion of total iron in the solution is bound to form iron nanoparticles
- Cr(VI) reduction efficiency was 500 mg/g nFe, higher than conventional nZVI

### GRAPHICAL ABSTRACT



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### ABSTRACT

The effectiveness of five plant extracts and juices, i.e. extracts of *Camellia sinensis* (green tea, GT), *Syzygium aromaticum* (clove, CL), *Mentha spicata* (spearmint, SM), *Punica granatum* juice (pomegranate, PG) and *Red Wine* (RW), for the production of nanoiron suspensions and their application for Cr(VI) reduction was investigated. Polyphenols contained in extracts act as reducing agents for iron ions in aqueous solutions, forming thus iron nanoparticles, and stabilize the nanoparticles produced from further oxidation and agglomeration. The maximum amount of polyphenols extracted per g of herbs was obtained at herb mass to water volume ratio varying from 10 to 20 g/L. Suspensions of nanoparticles with sizes below 60 nm were produced by mixing iron chloride solution with the plant extracts and juices investigated. The maximum concentration of nanoiron in suspensions was estimated to 22 mM, obtained using RW and PG at a mixing ratio of iron solution to extract equal to 2. Lower concentrations, up to 18 mM, were achieved using GT and CL extracts. Therefore, PG juice and RW were considered as more effective for nanoiron production, and, together with GT extracts, they were selected for the production of nanoiron suspensions, which have been proven effective for Cr(VI) reduction, reaching removal capacity as high as 500 mg Cr(VI) per g of iron in nanoparticles.

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## 1. Introduction

Chromium is widely used in many industrial processes such as leather tanning, metal electroplating, manufacturing of products for corrosion protection and wood preservation. Release of chromium containing solutions, accidentally or due to inefficient waste stream management, may lead to groundwater, surface water and soil contamination. Although the presence of high concentrations of Cr(VI) in soil and groundwater was, for many years, mainly attributed to anthropogenic activities, recent studies indicated that hexavalent chromium in groundwater can be also of geogenic origin, resulting from the oxidation of naturally-occurring Cr(III) in certain geologic formations by Mn-oxides (Oze et al., 2004; Panagiotakis et al., 2015; Moraetis et al., 2012).

Hexavalent chromium contamination either of anthropogenic or geogenic origin has become a serious environmental problem in many countries (Panagiotakis et al., 2015). Technologies for both groundwater and surface water treatment are mainly based on chemical reduction of Cr(VI) to Cr(III), since trivalent chromium presents lower solubility and mobility than the toxic, mobile and carcinogenic Cr(VI), and besides, it is an essential micro-nutrient for the diet of many organisms (O'Carroll et al., 2013).

Microscale granular metallic iron (Zero Valent Iron, mZVI) has been widely used as a reducing agent for the remediation of a variety of contaminants in permeable reactive barriers. However, the cost of this method is considered high and the process duration can be at least 15 years (O'Carroll et al., 2013; Guan et al., 2015).

During the last 15 years, the field application of nanoscale zero valent iron (nZVI) has become more promising due to its small particle size, high surface area and, thus, chemical reactivity (O'Carroll et al., 2013). Moreover, nZVI can be directly injected as a slurry in the sub-surface for the remediation of a variety of contaminants such as azo dyes, chlorinated solvents, chlorinated pesticides, inorganic anions and transition metals (Crane and Scott, 2012). Iron nanoparticles have been injected in at least 26 sites worldwide for the remediation of a variety of organic and inorganic contaminants (O'Carroll et al., 2013; Crane and Scott, 2012).

The nZVI particles can be 10 to 1000 times more reactive, compared to the granular or micro-scale ZVI particles (Gheju, 2011). However, there are a number of constraints inhibiting the full scale application of nZVI, including (a) the limited mobility of the suspension due to its aggregation and rapid oxidation of iron nanoparticles, and (b) the cost of iron nanoparticle production, usually involving chemical reduction of iron ions with costly reagents such as NaBH<sub>4</sub>, which also generates unsafe by-products (e.g. hydrogen gas) (Gheju, 2011).

An innovative, environmentally-friendly ("green") way to synthesize iron nanoparticles using natural materials used for human consumption such as lemon balm (*Melissa officinalis*), parsley (*Crispum crispum*), sorghum bran (*Sorghum* spp.), coffee and green tea, has been developed in the last few years (Hoag, 2009; Njagi et al., 2011; Genuino et al., 2013). Extracts of these herbs contain molecules bearing alcohol functional groups mainly of phenolic type, which can be exploited for reduction as well as formation of stable complexes with iron (Nadagouda et al., 2010). The latter is well known in the medical science where many studies have indicated that iron absorbance in the humans cells is inhibited when tea or red wine is simultaneously consumed, which has been attributed to the formation of polyphenol-iron complexes (Hurrell et al., 1999; Disler et al., 1975). In this method, polyphenols in extracts when mixed with iron bearing aqueous solutions can reduce iron cations leading to the formation of suspended iron nanoparticles. This green synthesis procedure for producing iron nanoparticles is considered as the most environmental friendly process (Nadagouda et al., 2010), however, it is not yet clearly defined in terms of exact reduction mechanism of ferric iron to its ferrous and elemental state using polyphenols, as well as the nanoiron suspension properties, the size, and, mainly, their reduction efficiency when different extracts are used as source of polyphenols.

The aim of this research study is to comparatively evaluate green tea, spearmint and clove extracts, as well as pomegranate juice and red wine as sources of polyphenols for the green synthesis of iron nanoparticles, and their subsequent application for hexavalent chromium reduction. The selection of the five different materials was based on data available in the literature (Carlsen et al., 2010) and web databases (Rothwell et al., 2013) as regards their antioxidant properties and, consequently, their reducing capacity to produce iron from ferric or ferrous solutions, thus forming iron nanoparticles. Green tea was selected as a reference material, due to the wide published information about its effectiveness for iron nanoparticles production.

## 2. Materials and methods

### 2.1. Materials

Commercially available dry leaves of *Camellia sinensis* (green tea, GT, Twinings of London, pure, moisture content 0.26% w/w dry basis), *Mentha spicata* (spearmint, SM, origin Greece, moisture content 0.29% w/w) and *Syzygium aromaticum* (clove, CL, origin Madagascar, moisture content 0.27% w/w) were used to extract polyphenols, which were subsequently used for iron nanoparticles production. Pomegranate juice from commercially available *Punica granatum* (pomegranates, PG, origin Greece) and commercially available red wine produced in Crete by Peza Union were used as polyphenol sources.

Ferric chloride hexahydrate of analytical grade (>99.0%, Merck, Germany) was used as a source of iron for nanoiron production. Folin-Ciocalteu's phenol reagent (Sigma Aldrich, Swiss), anhydrous sodium carbonate (Sigma Aldrich, Swiss) and gallic acid (Sigma Aldrich, China) were used for the determination of total polyphenol content in solution. Potassium dichromate (>99.0%, Mallinckrodt Chemical Works, USA) was used as a source of Cr(VI). ACS grade 1,5-diphenylcarbazine (Sigma Aldrich) was used for chromate analysis. Phthalic acid (≥99.5%, Sigma Aldrich, Japan) and phenanthroline (>99% Sigma Aldrich, Swiss) were used for the determination of ferrous iron in aqueous solutions.

### 2.2. Preparation of extracts

The green tea (GT), spearmint (SM) and clove (CL) samples were immersed to deionized water at 80 °C for 5 min at various herbs mass to water volume ratios (5, 10, 20, 50 and 100 g/L) resulting in the production of polyphenol-rich extracts. Extraction temperature was selected based on previous studies mainly on polyphenols extraction from green tea (Hoag, 2009; Ziaedini et al., 2010). In order to investigate the effect of retention time on polyphenols extraction, green tea extraction tests were conducted for 5, 10, 20 and 30 min at a fixed rate of its weight per water volume (20 g/L). All tests were performed in duplicate. The repeatability of the extraction process was also verified by performing 7 replications of green tea extraction at the same conditions (addition of 20 g in 1 L of water at 80 °C for 5 min). The green tea, spearmint and clove extracts were filtered by vacuum filtration using a 0.45 μm filter paper. Although wine and pomegranate juice were used as received, given that their initial total polyphenol content was high, a series of tests were also performed by diluting the original juice with distilled water at a ratio of 1:5.

### 2.3. Analysis of extracts, juices and red wine

All reducing media were analyzed for their Total Organic Carbon (TOC) content by the colorimetric method (U.S. Patent 6.368.870), which is based on controlled digestion/diffusion in a sealed glass assembly, with a spectrophotometer Hach DR/2500. The Total Polyphenol Content (TPC) was determined as gallic acid equivalents (GAE) following the Folin-Ciocalteu method (ISO 14502-1).

A UV-vis spectrophotometer (Hitachi U-1100) was used to measure the absorbance of the standards/samples at wavelength (λ) equal to

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