

# Evaluation of chromate removal by green iron nanoparticles in a pilot scale application

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## Abstract

In this study the results of a pilot-scale injection of green iron nanoparticles (GT-nZVI) and the formation of a reaction zone (RZ) for Cr(VI) removal are presented. A pilot scale tank was constructed with dimensions 1.5m (height) × 2.5m (width) × 3.75m (length) which was filled with 24 tons of soil. A network of 48 sampling points was installed inside the tank to monitor water quality. Nano ZVI was synthesized on-site by batches of 300 L. A total amount of 2.8 m<sup>3</sup> GT-nZVI suspension was injected via 3 injection wells in order to create a RZ zone, perpendicular to the groundwater flow. After the injection of GT-nZVI suspension, the supply of contaminated water containing 5 mg/L Cr(VI) was initiated. Pore water samples taken upstream and downstream of the RZ indicated that the zone operated effectively, since all the downstream samples were not found to contain any Cr(VI) and Cr(tot) had very low concentrations varying between <6 and 15 µg/L. Monitoring data for a period of 12 months indicated that the reactive wall maintained its effectiveness during this period of time.

**Keywords:** pilot scale, iron nanoparticles, nZVI, chromate reduction, green iron nanoparticles.

## 1. Introduction

In-situ injection of nano zero valent iron (nZVI) nanoparticles for the remediation of contaminated aquifers is applied in USA and Canada since 2000 (U.S. EPA 2005). The first known case is a manufacturing site in Trenton, NJ, USA, contaminated with chlorinated hydrocarbons, namely TCE and daughter compounds. An initial pilot test using bimetallic nanoparticles (Fe/Pd nanoparticles) was conducted in 2000. A larger scale injection followed in year 2003 and the final full scale application took place in 2007. The later application involved injection of 224 kg of surface-modified nZVI (Elliot *et al.*, 2010). By the year 2009, injection of nZVI was recorded in 44 sites worldwide (Karn *et al.*, 2009). The majority of sites were in North America, one site is in Asia (Taiwan) and 4 sites in Europe (Germany, Czech Republic, Italy and Slovakia). Many pilot tests have taken place in Europe. The majority of pilot tests were carried out using commercial types of nZVI, namely Nanofer produced by the Czech company NANOIRON Ltd and

RNIP produced by the Japanese company TODA Inc. The total amount of nZVI injected during the pilot tests varied between 1 and 150 kg per site. The results of these pilot tests differ significantly. According to Mueller *et al.* (2010, 2012) at the Spolchemie site in the Czech Republic, contaminant concentrations remained low for 6 months after treatment, but increased thereafter to the original concentration. At the Kurivody site (also in the Czech Republic), the contaminant concentrations were reduced permanently by 75–95%. The remediation in Biella (Italy) led to a reduction of the original total chlorinated solvent concentrations (20,000–50,000 µg/L) by about 20–50% within 1 month. The pilot test in Thuringia (D) conducted by Golder Associates also showed significant reductions of contaminants. In Kortan (CZ) the concentration of Cr(VI) decreased from 1.9-2.5 mg/L to less than 0.05 mg/L inside the 3 injection wells and in a short distance of 3 meters downstream of the injection wells. Moreover Cr(VI) remained below detection limit in these wells for the entire monitoring period (~6 months). However, the beneficial effect of nZVI was limited to a short distance. Groundwater samples from wells located at a distance of 10 meters or more downstream of the injection points indicated that the concentration of Cr(VI) was still very high (e.g. 1.7 mg/L) after the 6 months period (Němeček *et al.*, 2014). In France, the type of nZVI injected in the site was prepared from a commercial nZVI product which was previously coated with polyacrylic acid (PAA) to increase its mobility. The pilot tests indicated that the radius of influence (ROI) of the coated nanoparticles (PAA-nZVI) was approximately 2.5 to 4 m. Injection of nZVI was carried out in two phases. Within the limits of ROI, after the second injection of nZVI the TCE concentration decreased by 97% and the concentration of hexavalent chromium was reduced completely (Dumestre *et al.* 2013). All the previously reported pilot applications were based on the use of commercial nZVI products, where the synthesis of nZVI is carried out using either energy intensive or environmentally non friendly processes. An alternative “green” procedure was developed during the last decade for the synthesis of nZVI based on the use of plant extracts, including the extract of *Camellia sinensis*, the well-known beverage green tea (Hoag 2009, Mystrioti *et al.*, 2016). Until now the effectiveness of “green” nZVI for the remediation of contaminated waters has been tested

only by laboratory scale tests. To our knowledge the present study is the first pilot scale evaluation of GT-nZVI for the treatment of Cr(VI) polluted water. The pilot test was carried out using a calcareous soil material simulating the geochemistry of aquifers at Asopos River basin. Previous laboratory experiments (Mystrioti *et al.*, 2014a) indicated that the travel distance of GT-nZVI in calcareous soils is very limited and the iron nanoparticles remain entrapped closely to the injection point. Based on these results it was deduced that the optimum mode of nZVI application in this type of soils is the formation of a reaction zone (RZ) perpendicular to the flow of contaminated groundwater. This mode of GT-nZVI application was tested in the pilot tests.

## 2. Materials and methods

### 2.1 Synthesis of GT-nZVI

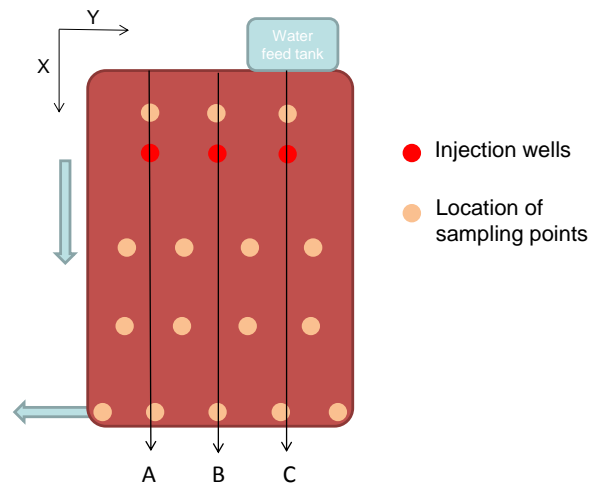
Ferric chloride solution (10% w/w, supplier Feri Tri SA, Greece) commonly used as a flocculation-sedimentation medium in wastewater treatment plans, was used as a source of iron to prepare the 0.1 M ferric chloride solution required for nZVI production. Commercially available dry leaves of green tea (Hunan Co., Ltd, China) were also purchased by local distributors. The GT-nZVI suspension was produced on site in batches of 300 L. The GT extract was first prepared by immersing 2 textile bags each one containing 1 kg of green tea for 10 min in 100 L water at temperature 75°C for 10 minutes. The GT extract was cooled to ambient temperature with cold water which circulated in helical coils and then was transferred to a 500 L tank. There it was mixed with 200 L of 0.1 M ferric chloride solution under vigorous agitation.

### 2.2 Tank construction

Pilot tests were conducted in a tank constructed inside the Campus of the National Technical University of Athens (Zografos, Greece) with dimensions  $L=3.75$  m,  $W=2.5$  m,  $H=1.5$  m. The tank was filled with a soil material consisting of a mixture of riparian silica sand and limestone at a ratio of 4/1 w/w. The objective was to obtain a calcite content equal to that of Asopos soils, i.e. 2.2 mol  $\text{CaCO}_3/\text{kg}$  (Mystrioti *et al.*, 2014a). The mixture was placed in 15 cm layers and compacted to give a final bulk density of 1.7 kg/L. The tank was saturated with tap water up to 1.1 m from the bottom of the tank and this level of water is kept constant. The detailed properties of the tank are given in Table 1. A network of 48 sampling points were installed inside the tank to monitor the quality of pore water. The sampling points were distributed in 16 locations at three levels per location (see Figure 1). A perforated plastic cylinder (diameter 1 cm, length 10 cm) covered with geotextile was installed at each sampling point. The cylinder was connected with a plastic tube of 2 mm internal diameter. The other free end of each tube was directed out of the soil at the upper surface. At each sampling event the tubes were connected to a peristaltic pump to pump out the pore water from the 48 sampling points. Following the removal of few first milliliters using the peristaltic pump, pore water was then collected by taking advantage of siphoning effects.

**Table 1.** Properties of pilot scale tank

Parameter	Value
Soil Bed Volume, BV (m <sup>3</sup> )	14
Length, L (m)	3.75
Height, H(m)	1.5
Width, W(m)	2.5
Particle density, $\rho_p$ (kg/m <sup>3</sup> )	2.57
Dry bulk density, $\rho_b$ (kg/ m <sup>3</sup> )	1.7
Porosity, $\theta$	0.34
<i>Reaction zone (RZ)</i>	
GT-nZVI loading (m <sup>3</sup> )	2.75
Width, $W_{RZ}$ (m)	2.5
Height, $H_{RZ}$ (m)	1.1
Estimated length parallel to GW flow, $L_{RZ}$ (m)	0.8



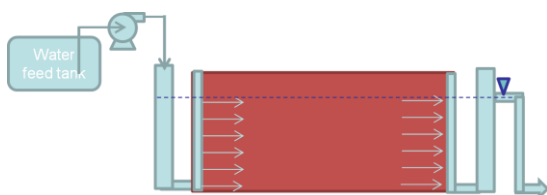
**Figure 1.** Plan indicating the 16 locations of sampling points. Samples taken at three height levels,  $Z=0.3$ ,  $0.6$  and  $0.9$  m. The isoconcentration curves of Cr(VI) in figures 4 and 5 are presented at vertical sections (A)  $Y=0.5$  m, (B)  $Y=1.25$  and (C)  $Y=2.0$  m.

### 2.3 GT-nZVI injection

Preliminary column experiments were carried out to determine the capacity of soil material to retain within its pores the iron nanoparticles of GT-nZVI suspension. It was found that one gram of soil was able to retain the nZVI contained in approximately 0.75 mL of suspension. The injection of GT-nZVI in the pilot tank aimed at creating a reaction zone with dimensions  $W_{RZ}=2.5$  m,  $H_{RZ}=1.1$  m and length parallel to groundwater flow approximately  $L_{RZ}=0.8$  m. Based on the laboratory tests, it was calculated that the required volume of GT-nZVI suspension was  $\sim 2.8$  m<sup>3</sup>. This volume was introduced in the soil through three perforated tubes of high-density polyethylene with a diameter of 50 mm, which were located at a distance of 75 cm from the tank wall (see Figure 1). The injection was conducted by gravity under a hydraulic head in the range of 0.5 to 2 m. The process was slow in order to avoid upward movement of GT-nZVI and development of preferential flow channels in the saturated and unsaturated zone. The average injection rate was 20 L/h (varying in the range of 5 to 50 L/h).

### 2.3 Introduction of Cr(VI) contaminated water

After the GT-nZVI injection and the removal of soluble constituents with clean GW, water containing hexavalent chromium was introduced in the pilot tank in order to evaluate the reductive capacity of the reactive wall. Contaminated water with a concentration of Cr(VI) 5 mg/L was synthesized in batches of 300 L using potassium dichromate (>99.0%, Mallinckrodt Chemical Works, USA). The water was supplied in the pilot tank with a mean flowrate 100 L/d. This flowrate corresponds to a Darcy velocity equal to 0.36 m/d. The flowrate was regulated with a pump at the inlet and a level controller was placed at the outlet of the tank as illustrated in Figure 2.



**Figure 2.** Equipment set-up for regulation of GW flow during the introduction of Cr(VI) contaminated groundwater.

### 2.4 Pilot test monitoring

Feeding of contaminated GW started on July 2014 and continued until the end of June 2015. Samples were taken systematically from the effluent of the tank. The initial frequency of sampling was 2 or 1 sample per day, but it was lowered to 2 or 1 sample per week after the initial 3 weeks. Samples of pore water from the 48 sampling points inside the tank were also taken at several time intervals. All the samples were analyzed for the main physicochemical parameters, i.e. pH, EC, ORP, and Cr(VI). Total Cr and Fe were determined in a subset of samples. A detailed elemental analysis was also carried out in some samples of the effluent stream. The redox potential was measured with an Ag/AgCl (3M KCl) reference electrode and pH was measured with Metrohm 827 pH meter. The electric conductivity was determined using a portable conductivity/temperature meter (Bante 520). Cr(VI) was measured using a spectrophotometer UV-VIS (Hitachi U-1100) according to the USEPA 7196a method. Total Cr and Fe were analyzed by AAS-FE (Atomic Absorption Spectroscopy-Flame Emission). Low values of total Cr concentration, below the detection limit of AAS-FE (0.3 mg/L), were measured by ICP-MS (Thermo X Series II) or AAS equipped with Graphite Furnace/Analyzer (AAS-GF).

## 3. Results and discussion

### 3.1. Properties of nZVI suspension

The main properties of synthesized GT-nZVI are presented in Table 2. As seen in the table, the reduction of ferric iron with green tea polyphenols is not complete. The resulting suspension contains about 1.0 g/l as suspended nZVI particles and 2.7 g/l as dissolved iron in the aqueous phase

[Fe(aq)]. The pH of the GT-nZVI is strongly acidic, varying between 1.06 and 1.14. This is primarily due to the generation of acidity during the reduction of trivalent iron by the polyphenols. The redox potential of the final solutions exhibited high values 532-562 mV, which can be attributed to the presence of residual ferric iron in the suspension.

**Table 2.** Properties of GT-nZVI

Parameter	GT-nZVI
pH	1.1±0.04
EC (mS/cm)	13.04±0.73
ORP (mV)	547±15
nZVI (g/L)	0.95±0.34
Fe(aq) (g/L)	2.56±0.29

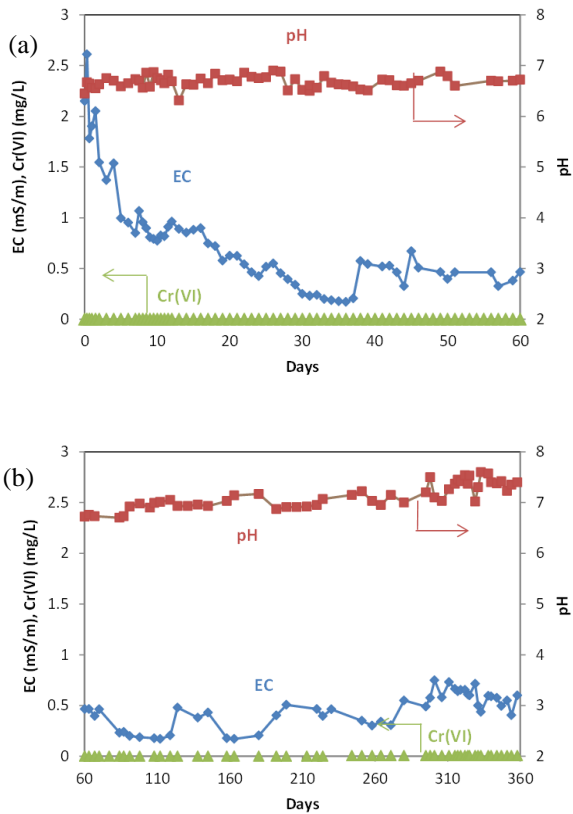
### 3.2 Injection of GT-nZVI. Pore water quality

The results of the injection of GT-nZVI suspension in the pilot scale tank have been published in detail previously (Mystrioti *et al.* 2014b). The main conclusions can be summarized below. Due to the high acidity of GT-nZVI (pH=1.1) and the relatively high concentration of chlorides (~0.2 M), the injection of GT-nZVI resulted in decreasing the pH of pore water from the initial values 7-8 to less than 5 and in increasing the conductivity from 0.5 to 13 mS/cm. Iron nanoparticles ZVI were not detected either in the pore water samples or in the effluent, indicating that nZVI particles remained attached to the soil material and/or to the iron hydroxide precipitates, which are formed due to the neutralization potential of soil calcite. As a consequence the ZVI nanoparticles cannot travel away from the initial injection point. For the removal of water soluble components from the porosity of the soil after the GT-nZVI injection, 3000 liters of clean groundwater was introduced. This quantity was approximately equal to the volume of the injected GT-nZVI suspension. By applying this washing step the pH of pore water increased to values greater than 6 and the conductivity was reduced to values below 1 mS/cm. It was thus concluded that the removal of water soluble components can be achieved relatively easily.

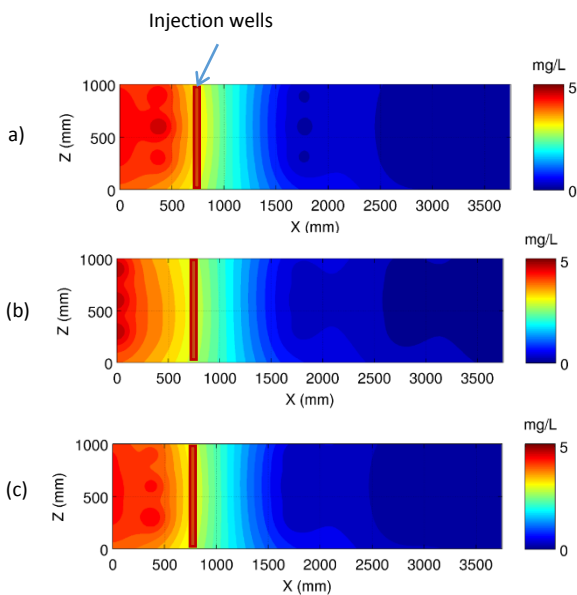
### 3.3 Effectiveness of reaction wall for hexavalent chromium reduction

Results related with the quality of effluent are presented in Figure 2. As shown in the figure, the pH values were gradually increased from 6.7 to 7.5, while the conductivity was stabilized at values close to 0.5 mS/cm. Chromium (VI) was below the detection limit of 6 µg/L in the effluent of tank. Total chromium was also occasionally analyzed by ICP-MS and was found to vary between 10 and <0.6 µg/L. Samples of pore water from the 48 sampling points inside the tank were taken after 1, 3 and 12 month of operation. Based on the measurements of the 48 sampling points isoconcentration curves were calculated by developing a code in MATLAB (matrix laboratory). The estimation of values between sampling points was made using the inverse distance squared method. In this method the estimation of a value to unknown points is calculated with

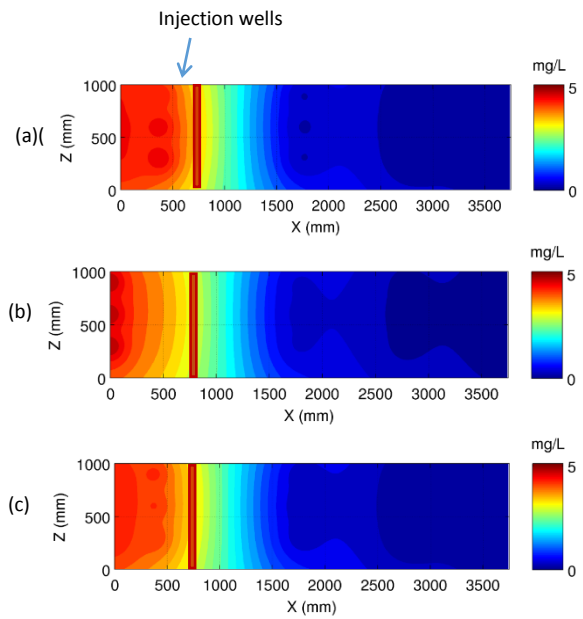
a weighted average of the values available at the known points (Lam 1983).



**Figure 2.** Evolution of pH, EC, Cr(VI) in the effluent of the tank (a) during the initial 60 days and (b) between 60 and 360 days of operation. Concentration of Cr(VI) in the inflow was 5 mg/L.



**Figure 3.** Profile of Cr(VI) concentration in the three perpendicular sections inside the tank ((a)  $Y = 0.5$  m) (b)  $Y = 1.75$  m and (c)  $Y = 2$  m) from the sampling campaign of 31/7/2014.



**Figure 4.** Profile of Cr(VI) concentration in the three perpendicular sections inside the tank ((a)  $Y = 0.5$  m) (b)  $Y = 1.75$  m and (c)  $Y = 2$  m) from the sampling campaign of 25/6/2015.

The profile of Cr(VI) along the pathway of GW flow in the three perpendicular sections (A:  $Y=0.5$  m, B:  $Y=1.75$  m and C:  $Y=2.0$  m) is shown in Figures 3 and 4. The location of nZVI injection wells are also shown in the figures. High hexavalent chromium concentrations were measured in the sampling points located at position  $X = 0.375$  m, in the upstream side of the reaction wall. Hexavalent chromium, Cr(VI), was not detected in any position at the downstream side of the wall, while total chromium, Cr(T), varied between 15 and  $<6$   $\mu\text{g/L}$ . This indicates that during the flow of contaminated water through the nZVI zone, the hexavalent chromium is reduced to the trivalent state and is removed from the aqueous phase, probably by precipitation in the form of mixed Fe(III)-Cr(III) or Fe(II)-Fe(III)-Cr(III) hydroxides and oxides.

#### 4. Conclusions

The performance of in-situ injection of nanoscale zero-valent iron, synthesized using green tea extract, for the reduction and immobilization of Cr(VI) was evaluated in a pilot scale tank, with dimensions 1.5 m (height)  $\times$  2.5 m (width)  $\times$  3.75 m (length). The pilot scale tank was filled with 24 tons of soil. Nano ZVI was synthesized on-site by mixing ferric iron solution with green tea extract. A total amount of 2.8  $\text{m}^3$  GT-nZVI was injected by gravity under a hydraulic head of 0.5 – 2 m. The mobility of GT-nZVI is limited due to the presence of calcite which causes the precipitation of aqueous Fe(III) in the form of iron oxyhydroxides and the retention of nZVI particles on soil grains. It is estimated that a permeable reactive wall was created around the injection wells with dimensions  $L \approx 0.8$  m,  $W=2.5$  m,  $H=1.1$  m. After the injection of the suspension and the removal of water soluble components, the supply of contaminated water containing 5 mg/L of Cr(VI) chromium was initiated. Pore water samples taken

upstream and downstream of the reactive wall indicate that the wall operates effectively, since all the downstream samples were not found to contain any Cr(VI). Introduction of contaminated groundwater was maintained for approximately 12 months and the results indicate that the reactive wall has maintained its effectiveness during this period of time.

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