

# Evaluation of Soil Loaded with Green Iron Nanoparticles for Hexavalent Chromium Reduction

Mystrioti C.<sup>1,\*</sup>, Mpouras T.<sup>2</sup>, Papassiopi N.<sup>1</sup>, Dermatas D.<sup>2</sup>

<sup>1</sup>Sch. of Mining and Metallurgical Eng., National Technical University of Athens, 15780, Greece

<sup>2</sup>School of Civil Engineering, National Technical University of Athens, 15780, Greece

\*corresponding author:e-mail: chmistrioti@metal.ntua.gr

## Abstract

Chromate is a pollutant often found in groundwater and considered a serious threat for humans and ecosystem. Iron nanoparticles produced by green tea polyphenols (GT-nZVI) is a powerful reductant, appropriate for the reduction of Cr(VI) to Cr(III). GT-nZVI suspension was initially conceived ideal for direct injection in the contaminated aquifers. However, many studies demonstrated that this suspension presents very low mobility in calcareous aquifers, which are typical in Mediterranean countries. An alternative mode of GT-nZVI application is the incorporation of nanoiron in a permeable reactive barrier. This option was evaluated experimentally, assuming that the permeable barrier is filled with a calcareous soil previously loaded with nZVI. Namely an amount of soil was loaded with 0.40 mmol of nZVI per gram of soil (S-nZVI) and its efficiency for Cr(VI) removal was evaluated by conducting batch and column tests. Batch tests were carried out by mixing S-nZVI with contaminated groundwater (GW) containing 1300 µg/L Cr(VI), at five doses from 5 to 50 grams of S-nZVI per liter of GW. Chromate concentration dropped below detection limit within 1 day at the highest dose. Reduction kinetics was slower with the other doses but after 20 days Cr(VI) dropped below the limit of 50 ppb at all doses except the lowest. Column tests confirmed the effectiveness of S-nZVI. Chromate concentration in column's effluents remained below detection limit after the introduction of 390 pore volumes of GW.

**Keywords:** hexavalent chromium, soil loaded nZVI, green nano-iron, calcareous soils.

## 1. Introduction

The groundwater and surface water contamination by organic and inorganic pollutants is considered as a major environmental issue. At Eastern Greece, high Cr(VI) concentrations have been detected in groundwater. Hexavalent chromium is ranked 119<sup>th</sup> in the EPA list of 126 Priority Pollutants due to its toxicity and mutagenicity. Various technologies have been tested for hexavalent chromium removal, such as electrochemical remediation, chemical reduction, adsorption and membrane filtration. The removal of heavy metals using nanoparticles has been successfully tested the last years (O'Carroll et al., 2013). The elemental metals (Fe, Ag, Zn) in nanoscale are more effective compared to their

granular forms due to the larger specific surface area and high reactivity. The efficient reduction of Cr(VI) to Cr(III) by green iron nanoparticles have been evaluated at laboratory tests and at pilot scale application (Mystrioti et al., 2018). However iron nanoparticles suspension present limited mobility to calcareous soils which are commonly encountered in the aquifers of Mediterranean countries. In this study an alternative mode of using nZVI was evaluated. The calcareous soil was loaded with iron nanoparticles and used for the treatment of Cr(VI) contaminated waters by conducting batch and column tests, simulating the function of a permeable reactive zone.

## 2. Methods

### 2.1. S-nZVI synthesis

Thirty (30) grams of calcareous soil and 400 mL of a FeCl<sub>3</sub> solution (0.1M) were mixed for 1 h. Due to the calcareous matrix of soil, Fe(III) was quantitatively removed from the aqueous phase by precipitation and/or adsorption. It is calculated that the soil is loaded with 0.40 mmol of Fe(III) per gram of soil. The soil containing the freshly precipitated Fe(III) cations was then filtrated and mixed with 200 mL of green tea extract (GT) for 24 hours, in order to obtain the reduction of Fe(III) to the elemental state by the polyphenols of GT.

### 2.2. Batch experiments

The nZVI loaded soil (S-nZVI) was mixed with simple soil at 5 proportions varying from 10% up to 100%. The resulting mixtures were mixed in polyethylene bottles with contaminated groundwater GW at a constant solid to liquid ratio 1/20. The GW originated from Asopos area (Central Greece), and contained 1300 ppb Cr(VI). Samples were taken from all the bottles at predetermined time intervals and analyzed for pH, ORP, electric conductivity (EC), Cr(VI), total Fe and total Cr. The final aqueous solutions were also analyzed for Mn, Ni, Co and As, to evaluate potential mobilization of other metals. Representative samples of the washed solid residues from the batch tests were subjected to the EN12457.02 standard leaching test procedure (L/S = 10 L/kg).

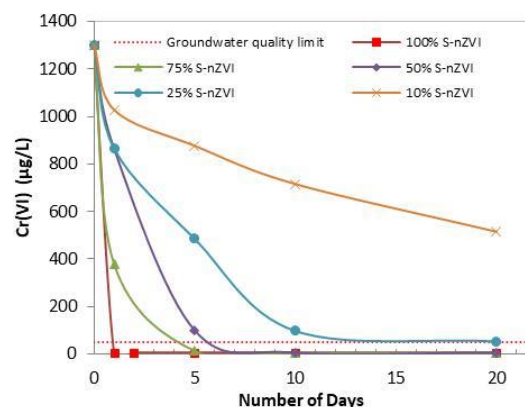
### 2.3 Column experiment

Column experiment was carried out using a polyethylene column with 2.63 cm internal diameter and ~10 cm length. The column was filled with 67.5 g of the S-nZVI. The total bed volume was 48.2 mL and the pore volume 19.7 mL. Contaminated groundwater containing 1.3 mg/L of Cr(VI) was introduced in the column in up-flow mode with a constant flowrate of 1.2 mL/min. The total volume was equal to 7650 mL, which is equivalent to ~390 pore volumes.

### 3. Results

The results of the batch tests carried out with the mixtures of soil and S-nZVI are presented in Figure 1. The Cr(VI) concentration in GW was found below detection limit (6 µg/L) from the first day of the experiment with 100% S-nZVI indicating that the reduction capacity of iron nanoparticles is high. The mixtures with 10%, 25%, 50% and 75% S-nZVI presented slower reduction of Cr(VI). The mixture with 75% S-nZVI reached a Cr(VI) concentration below detection limit (<6ppb) after 5 days, the mixture with 50% S-nZVI after 10 days and the mixture with 25% S-nZVI after 20 days. In the experiment with 10% S-nZVI Cr(VI) concentration in solution was 515 µg/L on the 20th day.

The solutions of the 20<sup>th</sup> day were analyzed for Co, Mn and Ni. The presence of nZVI caused the mobilization of Ni from soil; the concentrations measured in the aqueous phase varied between 22 and 64 µg/L without any apparent effect of the nZVI dose, while the concentration Ni in the initial GW was 15 µg/L. A similar effect was observed for Mn, whose concentration increased from below detection limit (9 µg/L) to the range 33-58 µg/L. In the case of Co (0.5 µg/L in GW) the mobilization was limited for doses 10% to 75% S-nZVI, i.e. 1.6 to 3.0 µg/L, but increased to Co 17 µg/L, at the highest dose 100% S-nZVI. The results of EN12457.02 leaching tests show the soil mixtures after the reduction and precipitation of Cr(VI) have low leachability. Namely, the leachability of As, Ba, Cd, Cr, Cu, Pb, Se, Sb and Mo meets the criteria established by Directive 2003/33/EC for the acceptance of solid residues in landfills for inert waste.



**Figure 1.** Evolution of Cr(VI) in the batch tests as a function of S-nZVI percentage in the soil mixture

In the column test, the effluent was free of Cr(VI) during the introduction of 7650 mL of GW. This amount is equal to 159 bed volumes or 390 pore volumes, indicating that the soil loaded with nZVI is very efficient for the reduction of Cr(VI). It was calculated that the total amount of reduced Cr(VI) was equal to 147 mg/g S-nZVI.

### 4. Conclusions

The technology of iron nanoparticles produced by green tea (GT-nZVI) was evaluated assuming that it will be used applying the approach of a permeable reactive barrier, where the reactive material can be prepared from local soil loaded with GT-nZVI (S-nZVI). This option was tested in the laboratory by conducting batch tests, where soil, containing five different levels of attached GT-nZVI, varying from 0.04 to 0.4 mmol nZVI per gram of soil, was mixed with contaminated GW at a solid to liquid ratio (S/L) equal to 1/20. The hexavalent chromium concentration of GW dropped from 1300 µg/L below 6 µg/L, within 1 day, 5 days, 10 days and 20 days, using the soils containing 0.4, 0.3, 0.2 and 0.1 mmol nZVI/g soil, respectively. In the experiment with the lowest nZVI load 0.04 mmol/g, the Cr(VI) was 515 µg/L after 20 days. Also S-nZVI presents high performance for chromates remediation under flow conditions.

### References

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