

Application of Iron Nanoparticles Synthesized by Green Tea for the Removal of Hexavalent Chromium in Column Tests

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Abstract

Nano zero valent iron particles (nZVI) are popular the last few years because of the numerous applications in remediation of a wide range of pollutants in contaminated soils and aquifers. The nZVI particles can be 10 - 1000 times more reactive than granular or micro-scale ZVI particles due to the small particle size, large specific surface area and high reactivity. An alternative green synthesis procedure was used for the production of nano zero valent iron particles (nZVI) using green tea (GT) extract, which is characterized by its high antioxidant content. Polyphenols in green tea extract possess double role in the synthesis of nZVI, because they not only reduce ferric cations, but also protect nZVI from oxidation and agglomeration as capping agents. The objective of current study was to simulate at a laboratory scale the attachment of GT-nZVI particles on soil material and study the effectiveness of attached nanoparticles for removing hexavalent chromium (Cr(VI)) from contaminated groundwater flowing through the porous soil bed. Column tests were carried out with various flowrates in order to examine the effect of contact time between the attached on porous medium nZVI and the flow-through solution on Cr(VI) reduction. After the completion of column tests the soil material in each column was split in 5 vertical sections, which were further subjected to chemical analyses and leaching tests. According to the results of the study increasing the contact time favors the reduction and removal of Cr(VI) from the aqueous phase. The reductive precipitation of Cr can be described as a reaction that follows a pseudo-first order kinetic law, with rate constant equal to $k = 0.0243 \pm 0.0011 \text{ min}^{-1}$. Leaching tests indicated that precipitated chromium is not soluble. In the examined soil material, the total amount of precipitated Cr was found to range between 280 and 890 mg/(kg soil), while soluble Cr was less than 1.4 mg/kg and most probably it was due to the presence of residual Cr(VI) solution in the porosity of soil.

Keywords

Nanoscale Zero Valent Iron, nZVI, Hexavalent Chromium, Reductive Capacity, Column Tests

1. Introduction

Chromium is widely used in a variety of industrial processes such as metal electroplating, leather tanning, man-

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ufacturing of products for corrosion protection and wood preservation. The contamination of groundwater, surface waters and soils by hexavalent chromium, due to accidents or inefficient waste management practices related with the above industrial activities, has become a high priority environmental problem. Hexavalent chromium presents high toxicity and can cause severe health problems due to its strong oxidizing properties. On the contrary, trivalent chromium (Cr(III)) is not toxic and presents lower water solubility and mobility than Cr(VI). Furthermore, Cr(III) is referred to be an essential micro-nutrient for many living organisms (Ghejou, 2011). Consequently the chemical reduction of Cr(VI) to Cr(III) is an effective method for Cr(VI) remediation.

Nanoscale zero valent iron has been studied extensively the last 15 years as a remarkable reductant for a variety of pollutants, including Cr(VI). Metallic iron, at nanoscale, combines many properties such as, small particle size, large specific surface area and high surface reactivity. As a consequence, it can reduce the pollutants at a rate several orders of magnitude higher compared to the rates observed with granular ZVI particles (Ghejou, 2011). Also the colloidal suspensions of nZVI can be injected directly inside the hotspot area of contaminated aquifer, a technique which is considered to ensure lower costs and shorter remediation time compared to other remediation options, such as pump and treat methods or permeable reactive barriers (He, 2009).

However, nZVI particles, if not appropriately coated, tend to aggregate and are rapidly oxidized. In order to inhibit aggregation and oxidation of iron nanoparticles many compounds have been tested as surface modifiers and stabilizers, such as hydrophilic biopolymers, carboxymethyl cellulose—CMC, chitosan, natural organic matter such as humic acid, polyelectrolytes, ion-exchange resins, and block copolymers (Bardos et al., 2011).

A novel green procedure was used for the synthesis and stabilization of iron nanoparticles (nZVI) using plant extracts with high antioxidant content. The mixing of plant extracts with ferric solutions results in the production of stable dispersions of iron nanoparticles. The polyphenols of the raw materials act both as reducing and surface coating agents of nano iron particles (Hoag et al., 2009; Shahwan et al., 2011). Many environmentally friendly materials, such as green tea, pomegranate, apple and oak tree leaf, etc., have been evaluated for their reducing capacity (Machado, 2012; Hoag et al., 2009). The use of nZVI was evaluated for the treatment of water or soils contaminated with organic contaminants in numerous studies (O'Carroll et al., 2012). In comparison, the hexavalent chromium reduction with nZVI was examined in a rather limited number of studies and most of them involved only batch experiments in shaking flasks or agitated reactors (Wang et al., 2010; O'Carroll et al., 2012).

In this study the reduction of Cr(VI) by nZVI was evaluated under flow conditions by conducting column tests. GT-nZVI was initially fed in the soil columns to obtain the attachment of iron nanoparticles on the soil grains. After this, groundwater contaminated with Cr(VI) was introduced in the columns to evaluate the reductive capacity of attached nZVI under variable flowrate conditions.

2. Materials and Methods

2.1. Materials

The following chemicals were used during the experimental work: ferric chloride hexahydrate (>99.0%, Merck, Germany), calcium chloride (>99.5%, Merck, Germany), potassium dichromate (>99.0%, Mallinckrodt Chemical Works, USA), 1,5-diphenylcarbazide (Sigma Aldrich), potassium phthalate (>99.5%, Sigma-Aldrich) and 1,1-phenanthroline (>99.0%, Sigma-Aldrich). Commercially available dry leaves of green tea (Twinings of London) were used as sources of polyphenols.

Column experiments were conducted using a soil material which was a mixture of silica sand and natural soil from Asopos area (Central Greece). Collected natural soil was air dried, homogenized and sieved at -2.5 mm. Particle size analysis of the -2.5 mm part of soil indicated that it consisted of 58.9% sand, 29.6% silt and 11.5% clay. To minimize potential clogging problems during the column experiments, the natural soil was mixed with silica sand at a ratio of 50% per weight. Silica sand (origin Egypt) was obtained from Mevior SA. Sand grains were of spherical shape and their particle size ranged between 0.1 and 0.4 mm. The physical and chemical properties of the final mixed soil sand are presented in **Table 1**. The soil-sand mixture was found to be calcareous with a neutralizing capacity equivalent to 103 g of CaCO_3 per kg and exhibiting an alkaline pH around 8.0. The chromium content of the mixture, as determined by X-Ray Fluorescence, was found to be very high, i.e. 929 mg/kg. It is noted that all Cr occurs in the trivalent state, because no Cr(VI) was detected in the sample (detection limit 0.4 mg/kg).

2.2. Synthesis of nZVI

The green tea extract was prepared by immersion of 20 g/L green tea leaves in water at 80°C for 5 minutes. The

extract was separated from the leaves by vacuum filtration, using a filter paper of 0.45 μm pore size. A solution of 0.1 M FeCl_3 was prepared by dissolving 27 g of solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 L of deionized water. For the production of nZVI, the GT extract was introduced to the ferric ion solution at a 1:2 volume ratio (Hoag, 2009). Mixing was carried out at room temperature applying a vigorous agitation. To evaluate the effectiveness of nZVI production, samples of the resulting suspensions were submitted to centrifugal ultrafiltration and the ultrafiltrate was analyzed to determine the concentration of residual aqueous Fe(III) and Fe(II). It was found that only part of total Fe, i.e. $\sim 27\%$, was reduced to its elemental state. Namely, the produced GT-nZVI suspensions contained approximately 1 g/L of Fe in the form of nZVI solid particles, 2.6g/L in the form of Fe(III) aqueous ions and 119 mg/L in the form of Fe(II) aqueous ions.

2.3. Column Experiments

The detailed properties of the columns are given in **Table 2**. The experiments were carried out using polyethylene columns, with 2.63 cm internal diameter and ~ 10 cm length. The columns were filled with 60 - 64 g of the soil material and occupied a total volume of approximately 46 mL. The soil was placed manually and gently vibrated at several stages to ensure uniform packing. The final bulk density, which is a measure of the obtained packing, ranged between 1.32 and 1.38 g/cm^3 .

Each packed column was connected to a peristaltic pump (Alitea, Sweden) and to a reservoir, which contained the fluids prepared for introduction in the column. Introduction of fluids was carried out in an upflow mode.

Table 1. Physicochemical characteristics of soil material.

Properties	
Sand/Silt/Clay, %	79.4/14.8/5.8
pH	7.65
NP ^(a) , gCaCO ₃ /kg	103
Organic Carbon ^(b) , %	0.33
Fe, mg/kg	19760
Ca, mg/kg	62000
Cr, mg/kg	929

^(a)Neutralizing Potential (NP), according to Lawrence and Wang (1997); ^(b)Nelson and Sommers (1996).

Table 2. Properties and operating conditions of columns.

Parameter	Columns		
	Control	I	II
Soil material dry mass, M (g)	60.3	63.7	60.9
Column diameter, D (cm)	2.63	2.63	2.63
Bed height, L (cm)	8.50	8.50	8.50
Bed Volume, BV (cm ³)	46.2	46.2	46.2
Particle density, ρ_p ^(a) (g/cm ³)	2.30	2.30	2.30
Dry bulk density, ρ_b ^(b) (g/cm ³)	1.32	1.38	1.32
Porosity, θ ^(c)	0.43	0.40	0.43
Pore volume size, V_{PV} (cm ³)	19.9	18.4	19.7
GT-nZVI loading (mL)	--	210	210
Cr(VI) solut. flowrate, Q (mL/min)	1.2	1.2	4.8

^(a)Calculated based on the particle densities of sand 2.50 g/cm^3 and soil 2.16 g/cm^3 . ^(b)Dry bulk density: $\rho_b = M/BV$. ^(c)Porosity: $\theta = 1 - \rho_b/\rho_p$.

Three similar columns were prepared. The first column served as control, which means that it was not loaded with nZVI. The other two columns were loaded with the same amount of GT-nZVI, i.e. 210 mL of suspension, which is equivalent to approximately 11 pore volumes (PVs). The size of pore volume is calculated from the total bed volume (BV) and the porosity (θ) of each column:

$$V_{PV} = BV \cdot \theta \quad (1)$$

A previous study had indicated that this soil material can retain a maximum amount of nZVI corresponding to the introduction of ~40 PVs of the GT-nZVI suspension (Mystrioti et al., 2014). Current experimental work was carried out applying a lower loading, corresponding to ~28 % of the maximum retention capacity of soil.

A Cr(VI) contaminated water was introduced in all three columns. Feeding flowrate was equal to 1.2 mL/min in the Control column and in column I and 4.8 mL/min in column II.

The whole experimental procedure included the following steps:

S1. The packed columns were first saturated with a background solution containing 6.6 mM CaCl₂, by introducing 140 mL (~7.4 PVs) of the solution in the column.

S2. An amount of 210 mL (~11 PVs) of GT-nZVI suspension was introduced in columns I and II.

S3. Background solution, 70 mL (~3.7 PVs), was again introduced to elute eventual residual species of the iron suspension

S4. Finally a solution simulating Cr(VI) contaminated groundwater was introduced in the columns. The solution contained 5 mg/L of Cr(VI) and 6.6 mM of CaCl₂. The total volume was 2120 mL (107 PVs) in the case of Control column, 10,400 mL (565 PVs) in column I and 9350 (475 PVs) in column II.

The fluids in steps S1, S2, and S3 were introduced with a constant flowrate of 1.2 mL/min. Varied flowrate was applied only in step S4. It is also noted that steps S2 and S3 were omitted in the Control column.

Column effluents were sampled and analyzed for pH, Eh, conductivity, dissolved oxygen and concentrations of total Fe, total Cr and Cr(VI).

2.4. Soil Material Examination after the End of Column Tests

After the completion of Cr(VI) flow through the columns, the soil material of columns was split in 5 vertical sections, which were examined by detailed chemical analyses. Representative samples of the 5 soil sections were also subjected to the EN12457.02 standard leaching test procedure, to evaluate the stability of precipitated Cr compounds. The leaching tests were conducted by adding 3 grams of sample in 30 mL of deionized water and the suspensions were kept under agitation for 24 hours. After this period, the suspensions were filtered and the aqueous solutions were analyzed for total Cr and Fe.

2.5. Analytical Methods

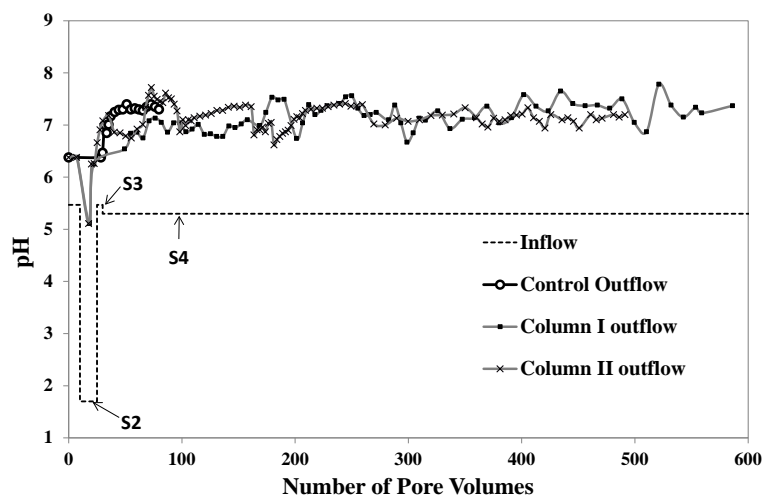
Elemental analysis of soil material before and after the column tests was conducted applying the X-Ray Fluorescence (XRF) technique. The measurements were carried out using a XEPOS spectrometer equipped with xlab-pro software.

Total Fe and Cr concentrations in aqueous solutions were determined by Atomic Absorption Spectroscopy-Flame Emission, AAS-FE. Low Cr concentrations were measured by ICP-MS (Thermo Scientific, X Series II). Ferrous ion was measured by the phenanthroline method. Chromate analysis was carried out using the diphenylcarbazide method. The pH and redox potential were measured using the pH meter Metrohm 827 pH Lab and a redox electrode 691 with a reference electrode Ag/AgCl/3 M KCl (Metrohm). The dissolved oxygen and the conductivity were monitored using an electrode DO (WTW, Oxi 330i) and conductivity meter (WTW, LF 95).

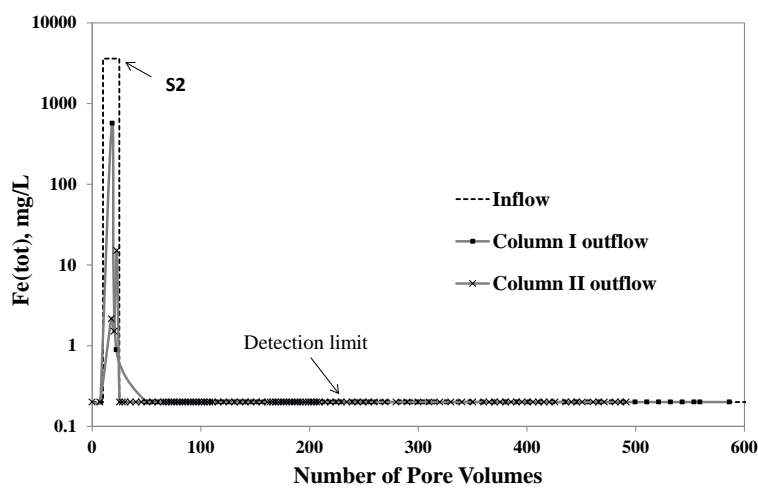
3. Results and Discussion

3.1. Column Experiments Results

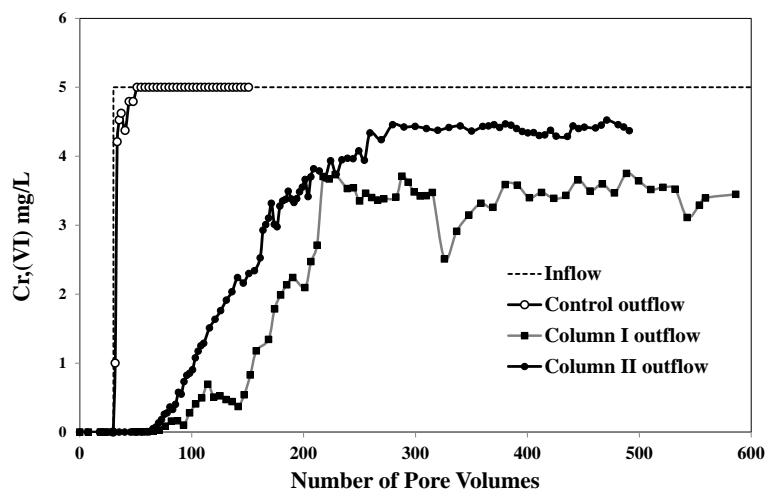
Representative results of column tests are shown in the charts of **Figure 1**. In these charts the amount of fluids supplied in the columns was expressed as number of Pore Volumes (PVs). This expression, which is often used in column and hydrogeological studies, facilitates scale-up calculations, based on the porosity of contaminated aquifers.



(a)



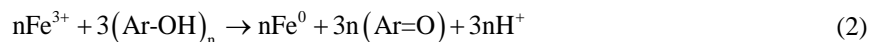
(b)



(c)

Figure 1. (a) Evolution of pH during the 4 steps of operation; (b) Total concentration of Fe in the effluents of Columns I and II; (c) Breakthrough curves of Cr(VI) in the three columns. The volume of fluids supplied in the columns is expressed as number of pore volumes.

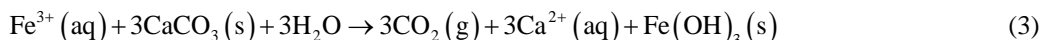
The evolution of pH in the columns during the 4 steps of operation and the concentration of Cr(VI) in the effluents of the 3 columns is shown in **Figure 1(a)**. The dotted curve represents the pH of inflow solutions. The background solution, which was supplied during steps S1 and S3, has a pH of 5.5. GT-nZVI suspension, which was fed in Columns I and II during step S2, has a very acidic pH equal to 1.7. The acidity of GT-nZVI suspension is due to the generation of H⁺ during the reduction of Fe(III) to the elemental state, Fe(0), as shown in reaction (2):



where (Ar-OH)_n represents GT polyphenols.

The soil material neutralizes part of the introduced acidity due to the contained CaCO₃. The pH of effluents is systematically higher compared to that of influents. During the introduction of acidic GT-nZVI suspension in Columns I and II the pH of effluents becomes slightly acidic, but it does not drop below the value of 5.2. During the addition of Cr(VI) solution the pH of effluents is buffered close to neutral values, ranging between 7.0 - 7.5 in all the columns.

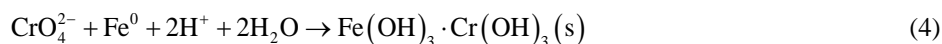
Iron was detected in the effluents of Columns I and II only for a few number of pore volumes during the introduction of GT-nZVI in step S2 (**Figure 2(b)**). Speciation analyses of effluents indicated that all eluted iron was only in the form of aqueous Fe ions. As already mentioned, the reduction of Fe(III) according to Equation (2) during the synthesis of nZVI is partial and the resulting suspension contains approximately 2.6g/L of Fe in the form of aqueous Fe(III), and 1.0 g/L in the form of nZVI solid particles. Mass balance calculations during column experiments indicated that only a small part of aqueous Fe(III) was recovered in the effluents, while the major part was retained in the columns, due to the precipitation of Fe(OH)₃ according to reaction (3):



Summarizing the results regarding mass balance calculations of iron, from the 280 mg of iron fed to Columns I and II, approximately 210 mg were retained inside the soil material as nZVI and 460 mg as Fe(OH)₃, while 110 mg were eluted with the background solution as aqueous Fe species.

The concentration of Cr(VI) in the effluents is shown in **Figure 1(c)**. As seen in the figure, soil material in the Control column is not able to reduce or adsorb any appreciable amount of Cr(VI). Chromate concentration in the effluents becomes almost equal to that in the influents after the supply of approximately 3.5 PVs of solution. In contrast, Columns I and II, which were treated with GT-nZVI suspension, can retain an important amount of Cr(VI). Retention occurs through the reduction of Cr(VI) in the trivalent state under the action of ZVI nanoparticles, and the precipitation of Cr(III) in the form of mixed Fe-Cr oxyhydroxides.

A typical reaction describing the reductive precipitation of Cr(VI) is given in Equation (4):



The experiments in column I were conducted by interrupting the supply of Cr(VI) solution during the nights and the weekends and for this reason the shape of the breakthrough curve is not smooth. The Cr(VI) concentration in the effluents after each interruption was lower than the previous one suggesting that an increase of contact time favors the reduction and removal of Cr(VI) from the aqueous phase. The execution of experiments in column II was carried out without interrupting the inflow of Cr(VI) solution and for this reason the shape of breakthrough curve was smoother.

Three stages can be distinguished during the supply of Cr(VI) in Columns I and II. The initial stage corresponds to the complete reduction and removal of Cr(VI) from the aqueous solution. This stage lasted for approximately 50 PVs of Cr(VI) solution in Column I and 40 PVs in Column II. A gradual decline in the performance of nZVI-loaded columns was recorded after this initial stage and finally steady state conditions were established in their operation after the introduction of ~200 and 240 PVs of Cr(VI) solution in columns I and II respectively. Both columns reached a plateau which is equal to 3.5 mg/L of Cr(VI) in the effluent for column I and 4.5mg/L for column II. This value is by 1.5 mg/L and 0.5mg/L lower compared to the concentration of Cr(VI) in the feed solution, i.e. 5 mg/L. The appearance of this plateau suggests that the soil columns maintain a certain reductive capacity but there is a kinetic limitation for the reduction of Cr(VI) to the Cr(III) state during the flow of solution through the column. Assuming a pseudo-first order kinetics, the concentration of Cr(VI) in the effluent, C_{ef}, is related with the concentration in the influent, C_{in}, according to Equation (5):

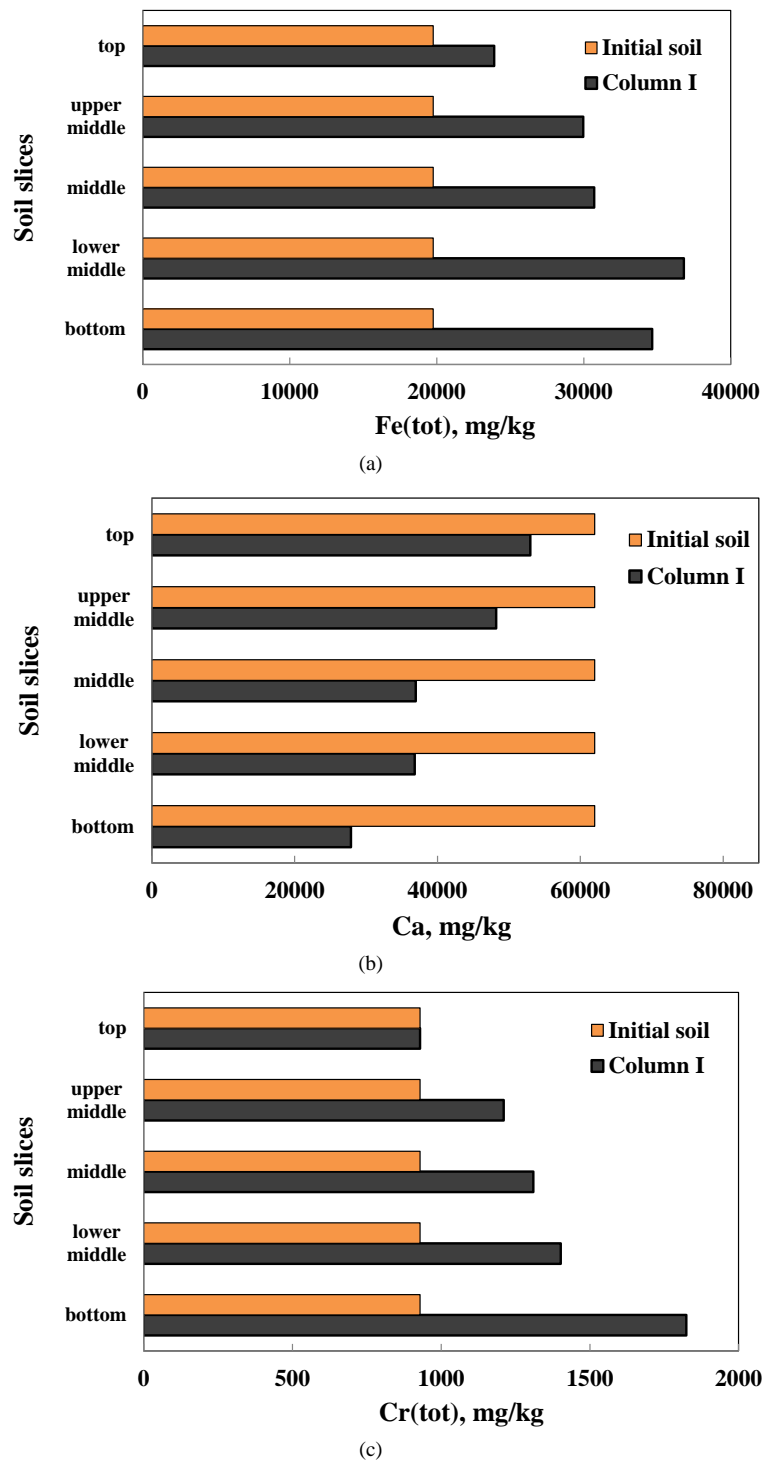


Figure 2. (a) Iron (b) calcium and (c) chromium content in the five sections of soil material in Column I after the completion of tests in comparison with the concentrations in initial soil.

$$\ln \left(\frac{C_{ef}}{C_{in}} \right) = -k\tau = -k \frac{\theta \cdot L}{u} \quad (5)$$

where k is the rate constant of the pseudo-first order kinetic law, τ is the residence time of solution in contact

with the nZVI loaded soil material inside the column, θ the porosity, L the length of soil bed and u the Darcy velocity of the solution, calculated from the volumetric flowrate Q and column cross section according to Equation (6):

$$u = \frac{Q}{\pi(D/2)^2} \quad (6)$$

In the case of Column I with $\theta = 0.40$, $L = 8.5$ cm, $C_{ef} = 3.5$ mg/L and $Q = 1.2$ ml/min, the value of rate constant k is calculated to be equal to 0.0232 min^{-1} . For Column II with $\theta = 0.43$, $L = 8.5$ cm, $C_{ef} = 4.5$ mg/L and $Q = 4.8$ ml/min, the value of k is 0.0254 min^{-1} . The two values of k are very close supporting the assumption of pseudo-first order kinetic law. Based on these experiments, the mean value of rate constant and the relative difference of estimates is $k = 0.0243 \pm 0.0011 \text{ min}^{-1}$.

3.2. Characteristics of Soil Material after Completion of Tests

The concentrations of iron, calcium and chromium in the successive layers of Column I are shown in **Figures 2(a)-(c)**. As seen in **Figure 2(a)**, the Fe content of soil after the completion of tests is higher compared to the initial soil material. Namely, initial concentration of Fe was 19,760 mg/kg and increased up to approximately 36,000 mg/kg in the two lower slices of soil bed, 30,000 mg/kg in the middle and upper middle slice and close to 24,000 in the top slice. Increase of Fe concentration occurs during the introduction of GT-nZVI suspension in the column (operation step S2) and is related with the precipitation of aqueous Fe(aq) according to reaction (3) and the simultaneous attachment of nZVI particles in the precipitates.

Figure 2(b) illustrates the gradual decrease of Ca content in the five slices of soil, which is due to the dissolution of soil calcite as described in reaction (3). Finally, **Figure 2(c)** shows the gradual accumulation of Cr, which takes place during the supply of Cr(VI) solution in the column (operation step S4) and is due to the reductive precipitation of Cr according to equation (4). The concentration of Cr in initial soil was 929 mg/kg and increased up to 1820 mg/kg in the bottom slice, and 1410, 1310 and 1210 mg/kg in the three subsequent slices of soil.

Leaching tests were carried out to evaluate the stability of precipitated chromium. The results of the tests showed that soluble chromium was almost equal in the five layers of soil column, ranging between 0.8 and 1.4 mg/kg. This is a very low amount compared to the total mass of precipitated Cr, which varied from 280 to 890 mg/kg. However, it is much higher in comparison with the theoretic solubility of $\text{Fe}(\text{OH})_3 \cdot \text{Cr}(\text{OH})_3$. According to published thermodynamic data the solubility of mixed $\text{Fe}(\text{OH})_3 \cdot \text{Cr}(\text{OH})_3$ in near neutral pHs is expected to be in the order of 0.003 mg/L (Sass & Ray, 1987; Papassiopi et al., 2014). This concentration in the aqueous phase corresponds to an amount of soluble Cr equivalent to 0.03 mg per kg soil, when the leaching tests are carried out according to the protocol of EN12457.02 test, i.e. with a liquid to solid ratio 10 mL per gram soil. The comparatively high concentrations of measured soluble Cr can be attributed to the fact that the soil layers were not washed before the execution of leaching tests. As a consequence they contained in their porosity the residual Cr(VI) solution supplied during the column experiments. Mass balance calculations justify this assumption.

4. Conclusion

Polyphenol coated nZVI particles have been synthesized mixing Green Tea extract with a FeCl_3 solution. The resulting GT-nZVI suspension was found to contain approximately 1.0 g/L of Fe in the form of ZVI nanoparticles, 2.6 g/L Fe as residual aqueous Fe(III) and 119 mg/L in the form of Fe(II) aqueous ions.

GT-nZVI suspension was introduced in columns containing a calcareous soil material. The presence of calcite caused the precipitation of aqueous Fe(III) in the form of iron oxyhydroxides and the retention of nZVI particles inside the soil columns. The Cr(VI) reducing effectiveness of soil columns, containing the nZVI particles, was evaluated by introducing a solution containing 5 mg/L of Cr(VI) with two different flowrates. Complete reduction and removal of Cr(VI) was observed for an amount of solution corresponding approximately to 50 PVs for Column I and 40PVs for Column II respectively. A gradual decline in the performance of nZVI-loaded columns was recorded after this initial stage and finally steady state conditions were established in their operation after the introduction of ~200 and 240 PVs of Cr(VI) solution in columns I and II. The performance of columns at steady state conditions suggests that there is a kinetic limitation for the reduction of Cr(VI) to the Cr(III) state at this stage. This limitation can be described as a reaction that follows a pseudo-first order kinetic law, with rate constant equal to $k = 0.0243 \pm 0.0011 \text{ min}^{-1}$.

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