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Reduction of hexavalent chromium with polyphenol-coated nano zero-valent iron: column studies

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ABSTRACT

Nano zero-valent iron (nZVI) is considered as a highly efficient reductant with wide applicability in the remediation of contaminated sites, due to the small particle size, large specific surface area, and high reactivity. In this study, nZVI was synthesized by mixing *Camellia Sinensis* extract (green tea, GT) with a ferric iron solution. Polyphenols in the GT extract act as: (a) strong reductants, reducing thus Fe(III) to its elemental state and (b) capping agents that stabilize the Fe(0) nanoparticles and inhibit their potential rapid oxidation. The remediation potential of ZVI nanoparticles, produced with the Green Tea method (GT-nZVI), for hexavalent chromium (Cr(VI)) was evaluated by column tests. The tests were carried out using polyethylene columns, with 2.63 cm internal diameter and ~10 cm length. The columns were filled with 65 g of natural soil and pure silica sand at a ratio of 50% w/w. The reductive capacity of GT-nZVI was examined for high (5 mg L^{-1}) concentration of hexavalent chromium in aqueous solution. The soil was initially treated in the first column by introducing 11 pore volumes of GT-nZVI suspension through the packed column while in the second column 24 pore volumes were introduced. It was found that about 210 and 420 mg of ZVI nanoparticles were retained by the soil during this stage in column I and in column II, respectively. After this step, the solution of hexavalent chromium was introduced in the columns at a flowrate of 1.2 mL min^{-1}, in order to determine the breakthrough curve of Cr(VI) in the immobilized GT-nZVI on the soil. The total amount of reduced Cr(VI) was equal to 17 mg in column I and 33 mg in column II. Based on the available experimental data, it was estimated that a GT-nZVI-treated zone in the subsurface, with a length (L) of 0.75 m, could provide a sufficiently long contact time in order to reduce Cr(VI) levels from 5 mg L^{-1} to less than 5 μg L^{-1}, under the condition that groundwater Darcy velocity is either equal to or less than 0.1 cm min^{-1}.

Keywords: Nanoscale zero-valent iron; NZVI; Hexavalent chromium; Reductive capacity; Column tests

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1. Introduction

Nowadays, contamination of groundwater and soils by hexavalent chromium has become a major environmental problem. Chromium (VI) exhibits high mobility and is toxic, carcinogenic, and can cause skin ulceration. On the contrary, trivalent chromium presents lower water solubility and is an essential micronutrient for many living organisms. The toxicity, solubility, and mobility of chromium in the environment are strongly dependent on its oxidation state. For this reason, an intense research activity is in progress, aiming at the development of effective Cr(VI) reductants of the toxic and mobile Cr(VI) to the nonsoluble Cr(III).

During the last 15 years, metallic iron, at nanoscale, has been studied as one of the most promising reductants combining effectiveness and low cost [1–4]. Research conducted using nanoscale ZVI particles indicated that the reduction of pollutants occurs at a rate several orders of magnitude higher compared with the rates observed with granular ZVI particles, due to smaller particle size, larger specific surface area, and higher surface reactivity [1,2]. Many pilot and field tests have been conducted using nano ZVI for the remediation of contaminated soils and aquifers. The *in situ* treatment of contaminants by the injection of nZVI suspensions has many advantages such as less intervention in the subsurface environment, lower cost, and shorter remediation time than other remediation techniques. However, many researchers reported that nZVI presents limited effectiveness due to rapid agglomeration and oxidation effects [5]. Numerous compounds have been tested as stabilizers in order to inhibit aggregation and oxidation of nZVI, including carboxyl methyl cellulose, guar gum, xantham gum, polyacrylic acid, carbon, etc. [2,6–8]. These compounds are acting simply as stabilizers without participating in the synthesis of nZVI, which is often done by the borohydrite method. An alternative synthesis scheme using plant extracts and referred to as "green synthesis method" was recently developed. Several plant extracts, specifically those with a high polyphenol content, were found to possess the desired reducing potential, as well as appropriate surface coating properties, and were successfully used for the production of stable dispersions of iron nanoparticles [9–13]. The green synthesis method uses environmental friendly materials (coffee, green tea, lemon balm, and sorghum bran), which is of low cost and the synthesized products are not toxic.

The effectiveness of polyphenol-coated nZVI for the remediation of contaminated soils has been studied mainly for organic contaminants, such as chlorinated compounds, dyes, etc. A very limited number of studies were dedicated in the treatment of water or soils contaminated with Cr(VI) [14]. The present study was carried out using ZVI nanoparticles which were produced by the Green Tea synthesis procedure (GT-nZVI). The Cr(VI) reductive effectiveness of GT-nZVI suspensions was evaluated for a specific soil with a calcareous matrix, which is typical in the relatively arid areas of the central–eastern part of Greece.

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), hydrogen peroxide (30%, Carlo Erba), hydrochloric acid (i ≥ 37%, Sigma Aldrich), and 1,5-diphenylcarbazide (Sigma Aldridge). 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). The natural soil was collected from a location close to Asopos river banks and away from potentially contaminating industrial activities (coordinates: 38.296329 N, 23.722548 E). The sampling procedure involved the collection of surface soil (0–20 cm depth) from five different positions covering an area of about 100 m^2. Collected soil was then 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 59% sand, 30% silt, and 11% clay. The chromium content of soil, as determined by X-ray Fluorescence, was found to be very high, i.e. 929 $mg\,kg^{-1}$, and this is probably related with the specific geochemical background of Asopos river basin, which is characterized by the presence of ultramafic rocks [15]. It is noted that all Cr occur in the trivalent state since no Cr(VI) was detected in the soil sample. Similar levels of total chromium in Asopos soils have been reported also by other researchers. For example, in the sampling campaign of Lilli et al. [16], the concentration of Cr in soils was found to be $885 \pm 570\ mg\,kg^{-1}$, based on XRF analysis of 18 samples. To minimize potential clogging problems during the column experiments, the soil was mixed with silica sand at a ratio of 50% per weight. Quartz sand (from Egypt) was obtained from Mevior SA. Sand grains were of spherical shape and particle size ranged between 0.1 and 0.4 mm. The physical and chemical properties of the mixed soil–sand material are presented in Table 1.

As seen in the Table, the mixed soil–sand material used in the column comprises 79.4% sand, 14.8% silt, and 5.8% clay. It is a calcareous material, with neutralizing potential equivalent to 103 g $CaCO_3$ kg^{-1} of soil and a slightly alkaline pH (7.65). Its organic carbon content is rather low (0.33%). Preliminary experiments which were carried out mixing the soil material with Cr(VI) solutions at several proportions and concentrations indicated that the soil material is not able to reduce or adsorb any appreciable amount of Cr(VI).

2.2. Synthesis of nZVI

In the present study, the green tea extract was prepared by immersion of 20 g L^{-1} green tea leaves to water at a temperature of 80˚C for 5 min. The extract was then 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 $FeCl_3·6H_2O$ 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 [10]. 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 further analyzed to determine the concentration of residual aqueous Fe(III). It was found that only a part of total Fe, i.e. ~27%, was reduced to the elemental state, which means that the produced GT-nZVI suspensions contained about 1 g L^{-1} of Fe in the form of nZVI solid particles and around 2.7 g L^{-1} of iron in the form of Fe(III) aqueous ions. The characteristics of GT-nZVI particles were determined using Transmission Electron Microscopy (TEM, Jeol 2100 HR). TEM samples preparation involved sonication of the suspension and subsequent deposition of just one drop of it onto a carbon-coated grid. Observation was carried out at an accelerating voltage of 200 kV. Selected area electron diffraction (SAED) analysis was also conducted for several particles.

2.3. Column experiments

In the present study, column experiments were carried out using polyethylene columns, with 2.63 cm internal diameter and ~10 cm length. The columns were filled with about 63–66 g of the soil–sand mixture that occupied a volume of 46 mL. The mixture was placed manually and gently vibrated at several stages to ensure uniform packing. The final bulk density, which is an indicator of the obtained packing, was 1.38 and 1.43 g cm^{-3} in Column I and II, respectively (Table 2).

The main investigated parameter during the column tests was the amount of GT-nZVI introduced in the soil material. A previous experimental study [13] had indicated that this solid porous medium can retain a maximum amount of nZVI, corresponding to the introduction of 7.6 mL of the GT-nZVI suspension per gram of solid. To evaluate the effectiveness of GT-nZVI under relatively low and high loading conditions, two column tests were conducted introducing 210 mL in column I (3.3 mL g^{-1}) and 420 mL in column II (6.4 mL g^{-1}).

The packed column was connected to a peristaltic pump (Alitea, Sweden) and to a reservoir, which

Table 1
Physicochemical characteristics of the soil material used for column experiments

Physical properties		Chemical components (%)			
Texture(a)					
Sand, (%)	79.4	Fe_2O_3(c)	2.83		
Silt, (%)	14.8	CaO(c)	8.68		
Clay, (%)	5.8	MgO(c)	2.88	Total C(g)	1.48
pH, NP(b)		Al_2O_3(c)	4.38	Organic C(f)	0.33
pH	7.65	SiO_2(c)	47.95	Inorganic C	1.15
NP, $gCaCO_3$ kg^{-1}	103	Cr_2O_3(c)	0.068		
		LOI(d)	7.1		

(a) Determined by screening and Laser particle size analyses.

(b) Neutralizing potential (NP), according to [17].

(c) Determined by XRF.

(d) LOI, loss of ignition: weight loss following heating at 1,000˚C for 30 min.

(g) Analysis with LECO.

(f) Walkey-Black method [18].

Table 2
Properties and operating conditions of columns

Parameter	Column I	Column II
Soil material dry mass, M (g)	63.7	65.8
Column diameter, D (cm)	2.63	2.63
Bed height, L (cm)	8.50	8.50
Bed volume, BV(cm^3)	46.2	46.2
Particle density, $\rho_p{}^{(a)}$ ($g\,cm^{-3}$)	2.30	2.30
Dry bulk density, $\rho_b{}^{(a)}$($g\,cm^{-3}$)	1.38	1.43
Porosity, $\theta^{(c)}$	0.40	0.38
Pore volume size, V_{PV} (cm^3)	18.4	17.5
GT-nZVI load (mL)	210	420
Flowrate, Q ($mL\,min^{-1}$)	1.2	1.2
Residence time of Cr(VI) solution, $\tau^{(d)}$ (min)	15.4	14.6

(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: $\theta = 1 - \rho_b/\rho_p$.
(d)Residence time: $\tau = (BV \cdot \theta)/Q$.

contained the fluids prepared for introduction in the columns. All fluids were supplied in the columns in up-flow mode and at a constant flowrate (1.2 $mL\,min^{-1}$). The whole procedure included the following steps:

(A) The two packed columns were first saturated with a $CaCl_2$ background solution (6.6 mM). The total volume of background solution introduced in the columns during this step was about 140 mL.
(B) Then Column I was loaded with 210 mL and Column II with 420 mL of GT-nZVI suspension. Loading time was 3 h for Column I and 6 h for Column II.
(C) Background solution, 70 mL in column I and 140 mL in column II, was again introduced to elute eventual residual species of the iron suspension.
(D) A synthetic solution simulating Cr(VI)-contaminated groundwater was finally introduced in the columns (10.4 L for column I and 15.4 L for column II). The solution contained 5 $mg\,L^{-1}$ of Cr(VI) and 6.6 mM of $CaCl_2$.

Experiments in columns were conducted by interrupting the feeding of Cr(VI) solution during the nights and the weekends. The total duration corresponding to the supply of Cr(VI) solution (step S4), without considering the interruptions, was equivalent to 6 d in column I and 9 d in column II.

Column effluents were sampled and analyzed for pH, Eh, conductivity, dissolved oxygen, and concentrations of total Fe (Fetot), total Cr (Cr tot), and Cr(VI). Total Fe and Cr concentrations were determined by atomic absorption spectroscopy-flame emission, AAS-FE. Chromate analysis was carried out using the diphenylcarbazide method. pH and redox potential were measured using a pH meter Metrohm 827 pH Lab and a redox electrode 691 with a reference electrode Ag/AgCl/3 M KCl (Metrohm). Dissolved oxygen and conductivity were monitored using an electrode DO (WTW, Oxi 330i) and conductivity meter (WTW, LF 95).

3. Results and discussion

3.1. Characteristics of GT-nZVI

A representative TEM image of the GT-nZVI suspension is shown in Fig. 1(a). The sample is characterized by the presence of spherical nanoparticles with sizes ranging between 5 and 50 nm. Particles are surrounded by a material which is semi-transparent in TEM and can be attributed to the polyphenols of Green Tea extract. Observation of the sample at several points indicated that the particles were not agglomerated confirming the positive role of tea polyphenols in hindering aggregation.

SAED analysis was carried out with several nanoparticles. A representative SAED spectrum is shown in Fig. 1(b). The arrangement of bright spots is typical of the face-centered cubic crystal system of elemental iron. It should be noted that due to the high stability of GT-nZVI suspension, it was not possible to separate effectively the nanoparticles from the aqueous phase, either by filtration or by centrifugation. For this reason, it was not possible to collect a solid sample and proceed to its characterization by other conventional techniques such as powder X-ray diffraction.

3.2. Results of column tests

The results of column tests are presented in Fig. 2 where the amount of fluids introduced in the columns was expressed as number of pore volumes (PVs). This expression is often used in column and hydrogeological studies because it facilitates scale-up calculations, based on the porosity of contaminated aquifers. The size of one PV, V_{PV}, is a characteristic property of each column (see Table 2) and is calculated from the total bed volume (BV) and the porosity (θ) of the column (Eq.1):

$$V_{PV} = BV \times \theta \tag{1}$$

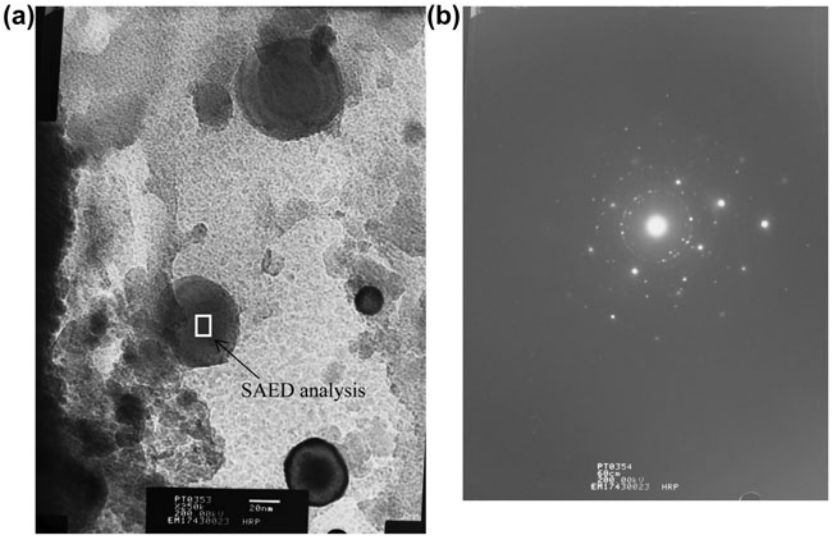

Fig1. (a) Representative TEM micrograph of GT-nZVI suspension (scale bar 20 nm), (b) SAED spectrum taken from the area indicated in (a).

Fig. 2(a) and (b) show the evolution of pH in the effluents of columns I and II, respectively. The pH of the background solution (6.6 mM of $CaCl_2$) is slightly acidic, i.e. pH 5.47. The pH increases to the value of 6.4 when the background solution passes through the soil–sand mixture, due to the presence of $CaCO_3$ in the soil. GT-nZVI suspension has acidic pH (1.7), due to the generation of H^+ during the reduction of Fe(III) to the elemental state, Fe(0), as shown in reaction (2):

$$\mathrm{n\,Fe^{3+} + 3\,(Ar\text{ - }OH)_n \rightarrow n\,Fe^0 + 3n\,(Ar = O) + 3n\,H^+} \tag{2}$$

where $(Ar\text{-}OH)_n$ represents GT polyphenols. When the acidic GT-nZVI suspension was fed to the columns, the acidity was neutralized by the $CaCO_3$ of soil and the pH of the effluent was initially buffered to values between 5.8 and 5.2. In column I, which was fed with 11 PVs of GT-nZVI, effluent pH did not drop below the value of 5.2. In column II, effluent pH decreased to around 2.6 after the introduction of the 24th PV portion of GT-nZVI suspension. This indicates that the available neutralizing capacity of soil was exhausted. After the addition of the Cr(VI) solution, the pH values in the effluents were between 7 and 7.5 in both columns.

The evolution of redox potential (ORP) in the effluents of the two columns is shown in Fig. 2(c) and (d), in comparison with the ORP of influents solutions. As seen in the figures, the ORP of influent background solution (S1, S3), as well as of the Cr(VI) solution (S4), is close to 350 mV (Ag/AgCl/3 M KCl). The GT-nZVI suspension has a high redox potential 550 mV, which is due to the presence of residual Fe(III) in the aqueous phase. In the effluent solutions of column I (Fig. 2(c)), ORP dropped from the initial value of 256–80 mV after the addition of GT-nZVI, remained at these values up to the introduction of 75 PVs of solution, and increased again to values 200–290 mV until the end of the experiment. In column II (Fig. 2(d)), the effluents presented a high redox potential, 499 mV, just after the introduction of the 24th PV of the GT-nZVI suspension, which is due to the fact that part of aqueous Fe(III) was not retained inside the column, but was recovered in the effluents.

As already mentioned, the reduction of Fe(III) according to reaction (2) is partial and the resulting suspension contains approximately 2.7 $g\,L^{-1}$ of Fe in the form of aqueous Fe(III) and 1.0 $g\,L^{-1}$ in the form of nZVI solid particulates. Only aqueous Fe(III) was detected in the effluents, indicating that all the amount of nZVI particles was retained in the porous medium in both columns. On the other hand, mass balance calculations indicated that only a small part of aqueous Fe(III) was recovered in the effluents, while the major part was retained in the columns, probably due to the precipitation of $Fe(OH)_3$ according to reaction (3):

$$\begin{aligned}&\mathrm{2Fe^{3+}(aq) + 3CaCO_3(s) + 3H_2O}\\&\quad\mathrm{\rightarrow 2Fe(OH)_3(s) + 3CO_2(g) + 3Ca^{2+}(aq)}\end{aligned} \tag{3}$$

Summarizing the results regarding mass balance calculations of iron, the following distribution was recorded in the two columns: column I, which was

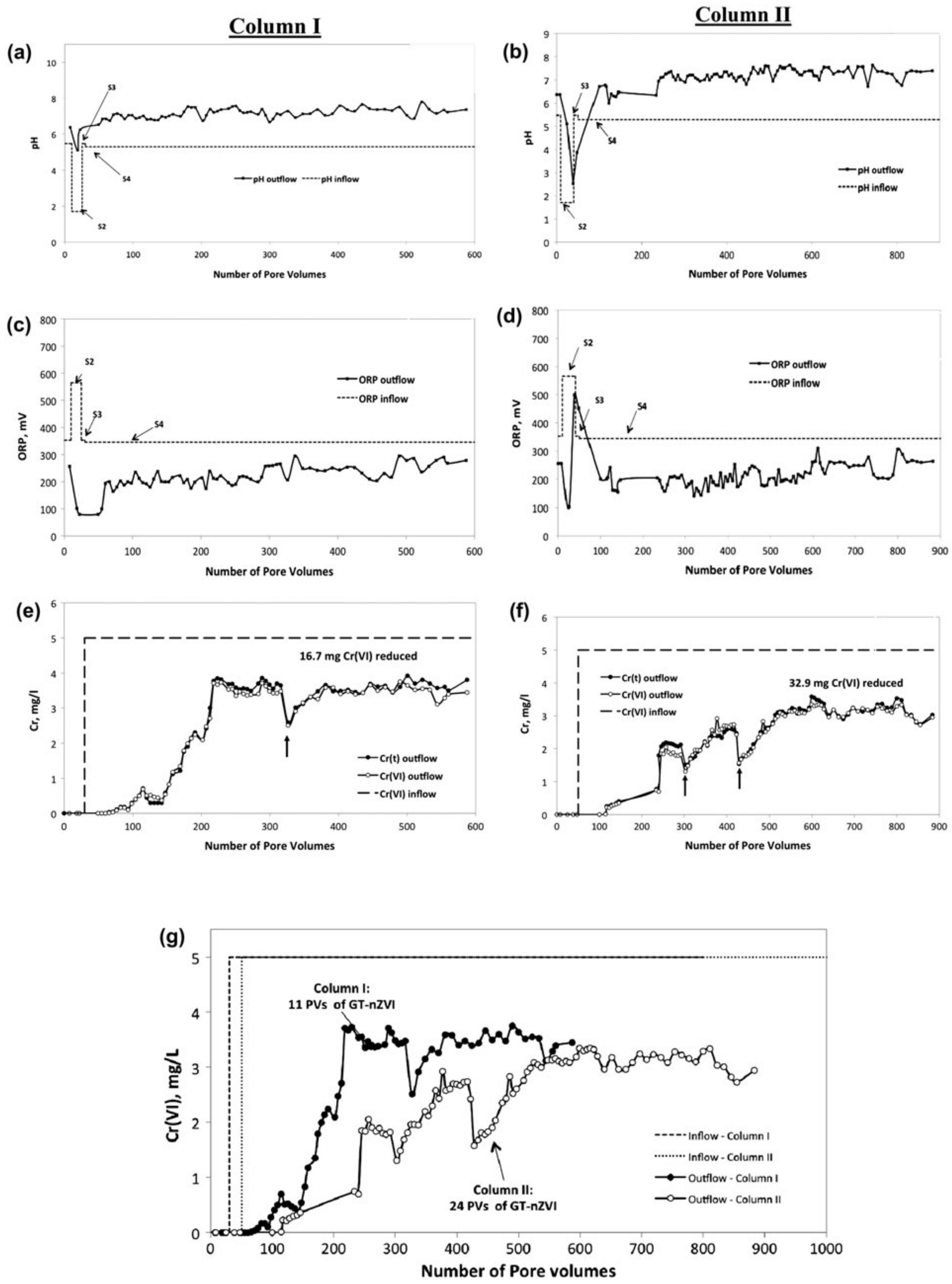

Fig. 2. Evolution of pH, redox potential (ORP), Cr(VI) and Cr(tot) in the outflow of the two columns. Column I: treated with 11 PVs (210 mL) of GT-nZVI, Column II: treated with 24 PVs (420 mL) of GT-nZVI. Introduced fluids: S1, S3: background solution 6.6 mM $CaCl_2$, S2: GT-nZVI suspension, S4: Cr(VI) 5 mg L^{-1} in 6.6 mM $CaCl_2$.

treated with 11 PVs of GT-nZVI, retained 211 mg of iron as nZVI and 455 mg of Fe as $Fe(OH)_3$, while 114 mg were eluted with the background solution; column II, treated with 24 PVs, retained 421 mg of iron as nZVI and 609 mg Fe as $Fe(OH)_3$, while 529 mg were eluted with background solution.

The fate of nanoparticles in the environment is an issue of concern because they are considered potentially harmful to living organisms [19]. It is thus important to avoid their uncontrolled release to aquatic systems. The present study demonstrates that GT-nZVI particles have a very limited mobility when injected in a calcareous soil material. As mentioned above, when the suspension came in contact with the soil material, the nZVI particles were removed from the aqueous phase and remained attached to the solid particles of the porous medium inside the columns. There was no indication of any remobilization of the nanoparticles during the whole duration of the experimental work.

Fig. 2(e) and (f) show the breakthrough curves of Cr(VI) and total Cr, as a function of the volume of Cr(VI) solution introduced in the two columns (expressed as number of PVs). Total Cr concentration is approximately equal to the concentration of Cr(VI), indicating that the reduction of hexavalent species to the trivalent state is followed by precipitation. The reductive precipitation of Cr(VI) under the action of elemental Fe(0) can be described by the following typical reaction:

$$CrO_4^{2-} + Fe^0 + 2H^+ + 2H_2O \rightarrow Fe(OH)_3 \cdot Cr(OH)_3 \quad (4)$$

In reaction (4), elemental iron was considered to be oxidized in the trivalent state, Fe(III), and to coprecipitate with Cr(III) in the form of a mixed $Fe(OH)_3 \cdot Cr(OH)_3$ compound [20]. However, partial reduction of Fe^0 to the divalent state Fe(II) is also highly probable, particularly under anaerobic conditions [21]. In this case, several other mixed Fe(II)-Fe(III)-Cr(III) compounds may precipitate such as chromite (FeOis·Cr_2O_3) or Cr-containing magnetite (FeO·$Fe_{(2-x)}Cr_xO_3$) [21].

According to simple mass balance calculations, the total amount of reduced Cr(VI) is equal to 16.7 mg in column I and 32.9 mg in column II. Compared with the available nZVI, i.e. 211 and 421 mg, respectively, it is evident that less than 10% of nZVI has been used for chromate reduction. It should be mentioned that Fe(0) may be consumed by many other parallel reactions including oxidation by atmospheric O_2, or corrosion by the acidic pH of the solutions [21]. However, the concentration of dissolved O_2 in the effluents was not substantially different from that in the influent solutions, suggesting that competition from dissolved O_2 is not particularly important. On the other hand, due to the calcareous matrix of soil, water pH is buffered close to neutral or slightly alkaline pHs, reducing thus the risks for the acidic corrosion of elemental Fe.

The evolution of Cr(VI) reduction in the two columns is compared in Fig. 2(g). Three stages are observed in both columns. The first stage represents the complete reduction and removal of Cr from solution and corresponds to the treatment of 50 PVs for column I and 114 PVs of solution for column II. The second stage represents a decline in the performance of nZVI retained in the columns, which is steeper for column I compared with column II. In column I, Cr(VI) in the effluents increases from 0 to around 3.5 $mg\,L^{-1}$ after the treatment of approximately 200 PVs of Cr(VI)-rich solution. In column II, this increase is more gradual lasting for ~600 PVs. The third stage corresponds to a steady state condition where Cr(VI) effluent concentration has reached a plateau, approximately equal to 3.5 $mg\,L^{-1}$ for both columns. This value is by 1.5 $mg\,L^{-1}$ lower compared with the concentration of Cr(VI) in the feed solution, i.e. 5 $mg\,L^{-1}$. The appearance of a plateau suggests that 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 Eq. (5):

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

where k is the rate constant of the pseudo-first-order kinetic law, τ is the residence time of solution in contact with the porous medium in the column, u is the mean velocity of the solution, θ is the porosity, and L is the length of the porous medium bed. In the case examined, $u = 0.221$ cm min, $L = 8.5$ cm, and $\theta = 0.39$. Using these parameters, the value of residence time τ is equal to 15 min and k is calculated to be equal to 0.0238 min^{-1}. The arrows in Fig. 2(e) and (f) point out incidents of interruption of pump operation with a relatively long duration, i.e. more than 24 h. It can be observed that the concentration of Cr(VI) in the effluents after each interruption was considerably lower due to the increase of contact time between porous medium and solution. This behavior is compatible with a limitation of kinetic nature.

Overall, the results suggest that despite the important decrease of initial rapid reactivity, the nZVI-treated soil/sand mixtures preserve a certain reductive capacity, which corresponds to slower kinetics. In this case, the effectiveness of Cr(VI) reduction depends highly on the available contact time, which is a function of the length of nZVI-treated zone and the flowrate of contaminated water through this zone. Assuming that the previously determined rate constant represents accurately the Cr(VI) reduction process in the field, it can be calculated by applying Eq. (5) in order to reduce Cr(VI) levels from 5 mg L^{-1} to less than 5 μg L^{-1}, where the required contact time is 4.9 h. If groundwater Darcy velocity is equal to or less than 0.1 cm min^{-1} and aquifer porosity is 0.4, the hydraulic residence time $\tau = 4.9$ h can be obtained by injecting GT-nZVI in a zone of the subsurface with a length of $L = 0.75$ m. However, additional experiments, using different flowrates and variable column lengths are required to confirm these results.

There are numerous publications dealing with the kinetics of Cr(VI) reduction by granular or nanoscale ZVI, but most of them are based on batch experiments [21]. Kinetic studies based on column experiments are very limited and were all carried out with granular ZVI. Kaplan and Gilmore [22] conducted tests using mixtures of sand and ZVI particles (size = 2.5 mm), where ZVI content varied from 20 to 100%. Assuming a first-order kinetic law they determined the values of constant k varying between 86×10^{-3} and 331×10^{-3} min^{-1}. El-Shazly et al. [23] carried out tests using a fixed bed of bearing ZVI spheres (diameter 5–10 mm) and studied the effect of solution velocity and temperature. At ambient temperature the first-order kinetic constant ranged between 25×10^{-3} and 65×10^{-3} min^{-1}. Li et al. [24] used columns filled with pellets consisting of a zeolite and ZVI mixture. They described the removal of Cr(VI) with a first-order kinetic law, where k varied between 0.25×10^{-3} and 1.58×10^{-3} min^{-1}. When the pellets were treated with a cationic surfactant, Cr(VI) removal rate was enhanced and constant k reached the value of 6.27×10^{-3} min^{-1}. The value of the first-order kinetic constant, $k = 23.8 \times 10^{-3}$ min^{-1}, describing the removal rate of Cr(VI) in our study, is of the same order of magnitude as in the above-mentioned studies. It is worthwhile to mention that this performance was achieved with a very low amount of iron attached on the soil particles, namely 0.3–0.6% as nZVI and 0.7–0.9% as $Fe(OH)_3$. In comparison, the ZVI content of fixed beds in the other studies ranged from 20 to 100%.

Another option for the remediation of Cr(VI)-contaminated aquifers is the exploitation of biological processes, as demonstrated by several laboratory and field-scale tests [25,26]. In most cases, the biologically induced reduction of Cr(VI) is characterized by relatively slow kinetics. For instance, experiments that were carried out using sulfate- [25] or sulfur [26]-reducing bacteria in fixed bed bioreactors indicated that for the efficient removal of Cr(VI) (e.g. >99%), the hydraulic residence time of contaminated water in the bioreactors must be more than 7 and 17 h, respectively.

4. Conclusions

Polyphenol-coated nano Fe(0) particles have been synthesized mixing Green Tea extract with a $FeCl_3$ solution. The resulting GT-nZVI suspension was found to contain approximately 1 g L^{-1} of Fe in the form of ZVI nanoparticulates and 2.7 g L^{-1} Fe as residual aqueous Fe(III). GT-nZVI was used to reduce hexavalent chromium in columns filled with a mixture of natural calcareous soil and pure silica sand. Two columns were prepared which were treated with 11 and 24 PVs of GT-nZVI suspension. The presence of calcite caused the precipitation of aqueous Fe(III) in the form of $Fe(OH)_3$ and the retention of nZVI particles inside the soil–sand columns. The amounts of nZVI particles were retained in the porous medium, i.e. 211 mg in column I and 421 mg in column II, which are equivalent to nZVI loading of 4.2 and 8.4 kg m^{-3} of porous medium, respectively. The Cr(VI)-reducing effectiveness of the two columns, containing the nZVI particles, was evaluated by introducing a solution containing 5 mg L^{-1} of Cr(VI). Complete reduction and removal of Cr(VI) was observed for an amount of solution corresponding approximately to 60 and 140 PVs for columns I and 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 600 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. From the available experimental data it was estimated that a GT-nZVI-treated zone in the subsurface, with a length of $L = 0.75$ m, could provide a sufficiently long contact time in order to reduce Cr(VI) levels from 5 mg L^{-1} to less than 5 μg L^{-1}, if the groundwater Darcy velocity is equal to or less than 0.1 cm min^{-1}.

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References

[1] R.A. Crane, T.B. Scott, Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology, J. Hazard. Mater. 211–212 (2012) 112–125.

[2] D. O'Carroll, B. Sleep, M. Krol, H. Boparai, C. Kocur, Nanoscale zero valent iron and bimetallic particles for contaminated site remediation, Adv. Water Resour. 51 (2013) 104–122.

[3] D. Sparis, C. Mystrioti, A. Xenidis, N. Papassiopi, Reduction of nitrate by copper-coated ZVI nanoparticles, Desal. Water Treat. 51 (2013) 2926–2933.

[4] S. Chen, Y. Huang, J. Lin, M. Lin, Dechlorination of tetrachloroethylene in water using stabilized nanoscale iron and palladized iron particles, Desal. Water Treat. 52 (2014) 702–711.

[5] T. Phenrat, N. Saleh, K. Shirk, R. Tilton, G. Lowry, Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions, Environ. Sci. Technol. 41 (2007) 284–290.

[6] F. He, M. Zhang, T. Qian, D. Zhao, Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: Column experiments and modeling, J. Colloid Interf. Sci. 334 (2009) 96–102.

[7] T. Raychoudhury, G. Naja, S. Ghoshal, Assessment of transport of two polyelectrolyte-stabilized zero-valent iron nanoparticles in porous media, J. Contam. Hydrol. 118 (2010) 143–151.

[8] L. Hoch, E. Mack, B. Hydutsky, J. Hershman, J. Skluzacek, T. Mallouk, Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium, Environ. Sci. Technol. 42 (2008) 2600–2605.

[9] G. Hoag, J. Collins, Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols, J. Mater. Chem. 19 (2009) 8671–8677.

[10] E. Njagi, H. Huang, L. Stafford, H. Genuino, H. Galindo, J. Collins, G. Hoag, S. Suib, Biosynthesis of iron and silver nanoparticles at room temperature using aqueous sorghum bran extracts, Langmuir 27 (2010) 264–271.

[11] T. Shahwan, S. Abu Sirriah, M. Nairat, E. Boyacı, A. Eroglu, T. Scott, K. Hallam, Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes, Chem. Eng. J. 172 (2011) 258–266.

[12] M. Chrysochoou, M. McGuire, G. Dahal, Transport characteristics of green-tea nano-scale zero valent iron as a function of soil mineralogy, Chem. Eng. Trans. 28 (2012) 121–126.

[13] C. Mystrioti, N. Papassiopi, A. Xenidis, D. Dermatas, M. Chrysochoou, Column study for the evaluation of transport properties of polyphenol-coated nano iron, J. Hazard. Mater. (in press), doi: 10.1016/j.jhazmat.2014.05.050.

[14] M. Chrysochoou, C. Johnston, G. Dahal, A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron, J. Hazard. Mater. 201–202 (2012) 33–42.

[15] D. Moraetis, N.P. Nikolaidis, G.P. Karatzas, Z. Dokou, N. Kalogerakis, L.H.E. Winkel, Origin and mobility of hexavalent chromium in North-Eastern Attica, Greece, Appl. Geochem. 27 (2012) 1170–1178.

[16] M.A. Lilli, D. Moraetis, N.P. Nikolaidis, G.P. Karatzas, N. Kalogerakis, Characterization and mobility of hexavalent chromium in soils and sediments, in: Proceedings of the13th International Conference on Environmental Science and Technology, Athens, Greece, September 5–7, 2013.

[17] R.W. Lawrence, Y. Wang, Determination of neutralization potential in the prediction of acid rock drainage, in: Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, BC, 1997, pp. 449–464.

[18] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon and organic matter, in: J.M. Bartells (Ed.), Methods of Soil Analysis. Part 3: Chemical Methods, vol. 5, third ed., ASA and SSSA, Madison, WI, 1996, pp. 961–1010.

[19] A. Nel, T. Xia, L. Madler, N. Li, Toxic potential of materials at the nanolevel, Science 311 (2006) 622–627.

[20] N. Papassiopi, K. Vaxevanidou, C. Christou, E. Karagianni, G.S.E. Antipas, Synthesis, characterization and stability of Cr(III) and Fe(III) hydroxides, J. Hazard. Mater. 264 (2014) 490–497.

[21] M. Gheju, Hexavalent chromium reduction with zero-valent Iron (ZVI) in aquatic systems, Water Air Soil Poll. 222 (2011) 103–148.

[22] D.I. Kaplan, T.J Gilmore, Zero-valent iron removal rates of aqueous Cr(VI) measured under flow conditions, Water Air Soil Poll. 155 (2004) 21–33.

[23] A.H. El-Shazly, A.A. Mubarak, A.H. Konsowa, Hexavalent chromium reduction using a fixed bed of scrap bearing iron spheres, Desalination 185 (2005) 307–316.

[24] Z Li, H.K. Jones, P. Zhang, R.S. Bowman, Chromate transport through columns packed with surfactant-modified zeolite/zero valent iron pellets, Chemosphere 68 (2007) 1861–1866.

[25] F. Battaglia-Brunet, S. Foucher, D. Morin, I. Ignatiadis, Chromate (CrO_4^{2-}) reduction in groundwaters by using reductive bacteria in fixed-bed bioreactors, Water Air Soil Poll: Focus 4 (2004) 127–135.

[26] E. Sahinkaya, A. Kilic, M. Altun, K. Komnitsas, P.N.L. Lens, Hexavalent chromium reduction in a sulfur reducing packed-bed bioreactor, J. Hazard. Mater. 219–220 (2012) 253–259.