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Assessing the effectiveness of nanoscale zero-valent iron particles produced by green tea for Cr(VI)-contaminated groundwater remediation

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Abstract: Nanoscale zero-valent iron particles (NZVI) produced by using green tea (GT) extract as a reductant can remove Cr(VI) from water effectively, which can be utilized in groundwater remediation. In order to define the reaction mechanism and removal effect in the aquifer, in this study, GT-NZVI particles were prepared and measured by some characterization methods to define their surface performance, and then batch and one-dimensional experiments were carried out to reveal the reaction properties of GT-NZVI and Cr(VI) in groundwater. The results showed that the prepared GT-NZVI particles were regular spherical with a diameter of 10–20 nm, which could disperse in water stably. The main component of GT-NZVI was α-Fe with superficial polyphenols as a stabilizer. GT-NZVI suspension had good ability to reduce the Cr(VI) to Cr(III) in water. When the concentration of GT-NZVI was 1 g/L, the removal efficiency of Cr(VI) with an initial concentration of 100 mg/L reached 92.8% in 1 h reaction. In column tests, GT-NZVI passed through the natural sand column successfully with an average outflow percentage of 71.2%. The simulated in-situ reaction zone (IRZ) with GT-NZVI was used to remediate Cr(VI) contaminated groundwater. The outflow concentration of Cr(VI) kept in 0.14–0.32 mg/L corresponding to the outflow rate below 0.32% within 15 days, and the removal efficiency of Cr(VI) by IRZ with GT-NZVI decreased with the increase of aquifer medium particle size, groundwater flow rate and ionic strength. Most of Cr(III) as reduzate was adsorbed or immobilized on the surface or in the lattice of GT-NZVI, which indicated effective immobilization for chromium.

Keywords: Nanoscale iron particles; Green tea; Hexavalent chromium; Groundwater remediation

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Introduction

With global economic development, the use of chromium in metal processing, electroplating, tanning and other industries has largely increased (Bhattacharya et al. 2020; Jhim et al. 2020). Chromium discharged into environment mainly exists in the form of Cr(III) and Cr(VI) (Miretzky and Cirelli, 2010). Cr(VI) not only forms highly toxic compounds, such as $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$, which has a long life-span in the environment, it is also a suspected carcinogen. Cr(VI) can be easily absorbed by the human body through the respiratory tract, skin and mucous membrane, posing a significant hazard to human health ((Duan et al. 2017; Zhao et al. 2019; Ceballos et al. 2021). Compared with Cr(VI), which is easy to migrate with water flow, Cr(III) is readily hydrolyzed into $Cr(OH)_3$ and separated from water ((Kim and Choi, 2011). Toxicity of Cr(III) is significantly lower than that of Cr(VI), and the reduction of Cr(VI) to Cr(III) can greatly decrease its baneful environmental impact (Liao et al. 2014).

As recent developments in nanotechnology, researches conducted using nanoscale zero-valent iron (NZVI) particles, including nano-FeO, nano-Fe_3O_4, nano-FeS, indicate that the reduction of pollutants occurs at a rate which is several orders of magnitude higher compared to the rates observed with granular iron particles due to the smaller

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particle size, larger specific surface area and higher surface reactivity of nanoscale particles (Kim et al. 2014; Li et al. 2015; Ju et al. 2018; Deng et al. 2020; Liang et al. 2021; Fei et al. 2022). NZVI prepared as suspension can be injected into the aquifer of any pollution depth, and hence remedial approaches involving the use of NZVI to treat the pollution in groundwater have gained popularity in the recent years (Orozco et al. 2015). However, NZVI prepared using traditional chemical reduction methods usually tend to agglomerate thereby lose reactive activation, and the preparation cost is relatively high (Badmus et al. 2018; Wang et al. 2022). Since 2008 some studies overcome these issues by using several plant extracts as reductants for Fe(III) or Fe(II) to obtain NZVI, with sizes ranging from 5 nm to 100 nm (Hoag et al. 2009; Njagi et al. 2010; Chrysochoou et al. 2010; Shahwan et al. 2011). This green synthesis method uses environmentally friendly materials (coffee, green tea, lemon balm, sorghum bran), and the synthesized products are not toxic, and it has low cost. Polyphenols in plant extract can not only be used as a reductant but also a chelating and capping agents to protect NZVI from oxidation and agglomeration and acquire a better transport ability in aquifer (Wang et al. 2021). These particles were reported to be effectively used for the removal of various dyes and heavy metals (Shahwan et al. 2011; Cheng et al. 2022). For Cr(VI), Sofija et al. (2016) found that GT-NZVI of 0.2 g/L, prepared by using oak, mulberry and cherry leaf extracts, could reduce Cr(VI) by 90% in 10 minutes. Mystrioti et al. (2015) also verified the effects of green tea, clove, mint exacts on the preparation of NZVI and found that this kind of NZVI particles had the best ability to remove Cr(VI). Nevertheless, the complicated characteristics of aquifers makes it uncertain whether polyphenol coated iron particles can keep after injection into aquifers to undertake in-situ removal of Cr(VI) from groundwater.

In light of above researches , in this study, batch and column experiments were conducted to evaluate feasibility of Cr(VI)-contaminated groundwater remediation with NZVI prepared using green tea extract (GT-NZVI). The overall objectives of this work were to (1) ascertain the major components and structure of GT-NZVI prepared using green tea; (2) confirm the transport ability of GT-NZVI in simulated aquifer; (3) determine the removal effect of Cr(VI) in water and the stability of immobilized Cr in simulated aquifers through in-situ reaction zone with GT-NZVI. This study will provide an important basis for the application of GT-NZVI in the removal of Cr(VI) from contaminated groundwater.

1 Materials and methods

1.1 Materials

All chemicals used in this study, including ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ethanol and potassium dichromate were purchased from Technology Development Corporation (Tianjin, China), and they were analytical pure grade (99+%) and used without further purification. Green tea used as a reductant for preparation of GT-NZVI originated from Chunxiang Tea Plantation (Xinyang, China). The natural sand used for simulating the groundwater aquifer was collected from a sandpit in Shijiazhuang. The sand was put through different graded sieves ranging in grain size from 0.25–0.5 mm.

1.2 Preparation and characterization of GT-NZVI

GT-NZVI was prepared according to the patented methods (Han et al. 2015; Deng et al. 2019). 100 mL of solution was prepared by mixing water with ethanol at a volume ratio of 1:1.2 g of green tea was then added to the solution which was sealed with plastic wrap and heated to 85℃ for 10 minutes. The extract was separated from the leaves by vacuum filtration, using a filter paper of 0.45 μm pore size. A solution of 4 g/L $FeCl_3$ was prepared by dissolving certain amount of $FeCl_3 \cdot 6H_2O$ in 50 mL deionized water. Subsequently, 50 mL of $FeCl_3$ solution was decanted into the same volume of green tea extract with a stirring for 40 minutes at room temperature, and the preparation of GT-NZVI suspension was completed. To evaluate the production rate of GT-NZVI, a portion of 20 mL suspension was subjected to centrifugal ultrafiltration using a ultracentrifuge (Sigma-Aldrich, 3K15, US) and the filtrate was analysed for total Fe concentration using a UV spectrophotometry (Shimadzu, UV-2550, Japan) with phenanthroline spectrophotometric method.

Transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used to evaluate the composition and structure of GT-NZVI. To make these microscopic measurements, samples were prepared by dispersing the suspension in ethanol in an ultrasonic bath for 10 minutes. One drop of obtained suspension was dispersed and dried onto a copper grid at a low temperature, and then observed by TEM (Hitachi TitanTM G2 60-300, Japan) and measured by FTIR (Thermo Scientific Nicolet iS10, US). XRD (Bruker, D8 Advance, Germany) with copper target was used for phase analysis of GT-NZVI, and the scanning angle was 10°–90° at a tube voltage of 40 kV and tube current of 30 mA. The valence content of GT-NZVI elements was determined using XPS (Thermo Fisher Scientific K-Alpha, UK) with a 180° hemispherical energy analyzer. The energy range was 0–5 000 eV, and the X-ray beam spot of 500 μm was continuously adjusted from 900 μm to 200 μm under a monochrome condition of 1 486.6 eV, 150 W.

1.3 Batch tests of Cr(VI) removal from water by GT-NZVI

Batch experiments for hexavalent chromium reduction were conducted in duplicates in 250 mL flasks. An aqueous solution containing 100 mg/L of Cr(VI) and 0.01 mol/L of Na^+ was prepared using a $K_2Cr_2O_7$ and NaCl salt. The tests were carried out by adding 5 mL of the GT-NZVI suspension in 100 mL of Cr(VI) solution (5% v/v). With this addition, theoretical molar ratio of total iron versus hexavalent chromium is equal to 5, i.e. Fe/Cr(VI)=5 mole/mole. The reaction solution in a 250-mL conical flask was sealed and placed on an oscillator for shaking at 150 rpm at ambient temperature (−25℃). The sample was drawn from the flask at a specific time interval, and filtered through a 0.45 μm membrane to measure the concentration of Cr(VI) and Cr(III), as well as pH and oxidation-reduction potential (ORP) of the solution were determined by the UV spectrophotometry and a pH meter (Sartorius, PB-10, Germany).

Control experiments were also conducted by adding 2.5 mL of pure GT extracts in 100 mL of Cr(VI) solution (2.5% v/v) to evaluate eventual contribution of initial polyphenols to the reduction of Cr(VI). Added volume of plant extracts was the 1/2 of the added volume of GT-NZVI suspensions, equal to the ratio of solutions during the synthesis procedure.

1.4 Column tests of Cr(VI) removal from simulated aquifer by GT-NZVI

One-dimensional simulation tests were carried out in polymethyl methacrylate columns with an inner diameter of 2.5 cm (Fig. 1). Medium sand of 0.25–0.5 mm was packed into the columns with compression to a height of 20 cm, and then the sand column was saturated with background solution of 0.01 mol/L NaCl for 24 h using a peristaltic pump. Pore volume (PV) of the sand column could be obtained by water release or calculated through the mass difference value before and after saturation. Afterwards, 20 PV GT-NZVI suspension and 16 PV background solution was introduced successively from the bottom of the column. The suspension of each test was applied at a certain constant flow rate of 0.266 m/d, and the effluent was collected continuously using a fraction collector and total iron concentration was measured.

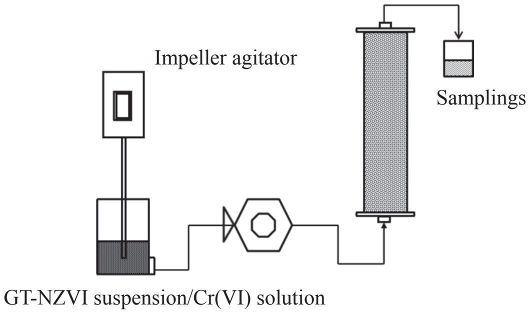

Fig. 1 Schematic diagram of the column experimental setup

When there was no iron concentration could be detected in the sample solution, some of the columns were divided into sections for exploring the deposition of GT-NZVI in the sand. The bottom end-piece was removed without disturbing the packed bed and the sand was removed at 2 cm intervals. The iron in each section was digested with 4 mL HCl (1:1 volume ratio of HCl:DI water) and total iron concentration was measured in the spectrophotometer, and the mass balance of GT-NZVI was calculated using the following equations:

$$M_d + M_o = M_t \tag{1}$$

$$M_d = 0.004 \cdot \sum_{k=1}^{10} C_k \tag{2}$$

$$M_o = \sum_{i=1}^{n} C_i V_i \tag{3}$$

Especially, M_d, M_o and M_t were the deposition mass of GT-NZVI on the sand (mg), the outflow mass of GT-NZVI in effluent (mg) and the total mass of GT-NZVI (mg), respectively. C_k was the mass concentration of GT-NZVI in each digestion solution (mg/L). C_i and V_i were the mass concentration (mg/L) and volume (mL) of GT-NZVI effluent.

For other sand columns, 10 PV Cr(VI) solution of 100 mg/L was injected into the columns and the effluent was collected and the concentration of

Cr(VI) and Cr(III) were determined. The sand column was washed with deionized water again until the concentrations of Cr(VI) and Cr(III) in the effluent were constant. One blank test and two parallel tests were carried out simultaneously. In addition, three groups of experiments were conducted to examine the effects of porous media size, groundwater flow rate and ionic strength on the removal rate of Cr(VI). Table 1 summarizes the experimental conditions for column operation. The injection concentration and volume of GT-NZVI suspension were constant, consistent with the aforementioned tests.

After completing the transport process, the sand was removed from the column for exploring the morphology and composition of GT-NZVI deposition. The deposition was scraped from the surface of the sand and dissolved in ethanol. A sample of deposition suspension for Cs-corrected STEM (FEI, Titan ETEM G2 80-300, US) was prepared as the same method as TEM, and the test voltage was 200 kV.

2 Results and discussion

2.1 Characterization of GT-NZVI

Formation of GT-NZVI during the mixing of plant extracts with the $FeCl_3$ solution was characterized by a very rapid kinetics. As shown in Fig. 2, the initially yellow color of the ferric chloride solution turned to black immediately after the addition of the extract, which indicated the formation of iron particles forcefully. The GT-NZVI suspension was found very stable without any indication of sedimentation as time passed, and conventional laboratory techniques, such as vacuum filtration and low speed (<5 000 rpm) centrifugation were proven ineffective for the separation of nanoparticles from the aqueous solution. However, the result of total Fe concentration in GT extract shows that the reduction of ferric iron was not complete, and approximately 1.35 g/L were found to remain in solution, suggesting that only 0.65 g/L of the initial 2 g/L of Fe (32.5%) were reduced to the elemental state Fe(0).

Morphology image of GT-NZVI was given in Fig. 3. It shows that GT-NZVI were spherical with a diameter of 10–20 nm, and the particles were uniform in shape and had good dispersion. Generally, NZVI particles produced using chemical reduction method in liquid phase present in chain shape with a size of few tens (Liu and Lowry, 2006). Hence, green tea used as reductant in the preparation process of GT-NZVI not only could make the particles size smaller, but also could effectively reduce the agglomeration of the particles and increased their dispersity.

XRD pattern for GT-NZVI particles were performed to determine its composition in Fig. 4. It can be seen that the crystallinity of the synthetic product was relatively poor for an amorphous state. It is similar to other synthetic products of nanoscale iron particles prepared by using plant extracts (Gao, 2018; Liu, 2018). The characteristic diffraction peaks were marked with a strong peak at 2θ=21.8°, corresponding to the organic matter in GT extract. A weak peak at 2θ=44.5° was the characteristic diffraction peak of body-centered cubic α-Fe corresponding to the (110) plane. Characteristic peak of FeO was weaker than that of organic matter, this is because the surface of the GT-NZVI particles was coated with a layer of organic material, which had the effect on the dispersion of iron nanoparticles, just as the results of TEM. Another peak at 2θ=35.7° pointed to Fe_2O_3, suggesting the slight oxidation of GT-NZVI in the preparation process. As to the reduction products of polyphenol extracts to valence state iron, some studies have suggested that there was only zero-valent iron in the reduction products (Wang et al. 2014; Wang et al.

Table 1 Experimental conditions for column operation

Influence factors	Media size (mm)	Groundwater flow rate (m/d)	Ionic strength (Na^+, mol/L)
Media size (mm)	0.1–0.25	0.266	0.01
	0.25–0.5		
	0.5–1		
Groundwater flow rate (m/d)	0.25–0.5	0.130	0.01
		0.266	
		0.545	
Ionic strength (Na^+, mol/L)	0.25–0.5	0.266	0.01
			0.05
			0.10

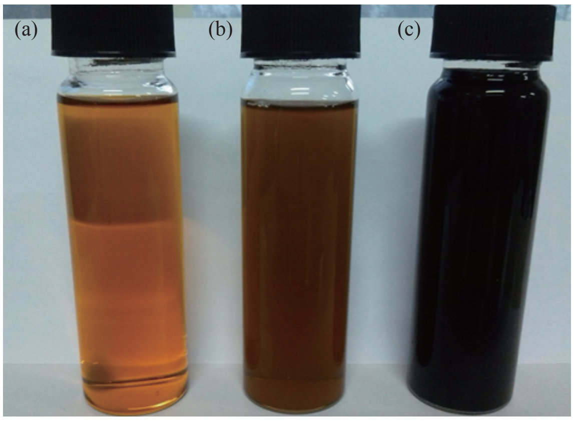

Fig. 2 The characteristic colours of $FeCl_3$ solution, GT extracts and GT-NZVI suspension: (a) Initial $FeCl_3$ solution (b) Green Tea (c) GT-NZVI suspension

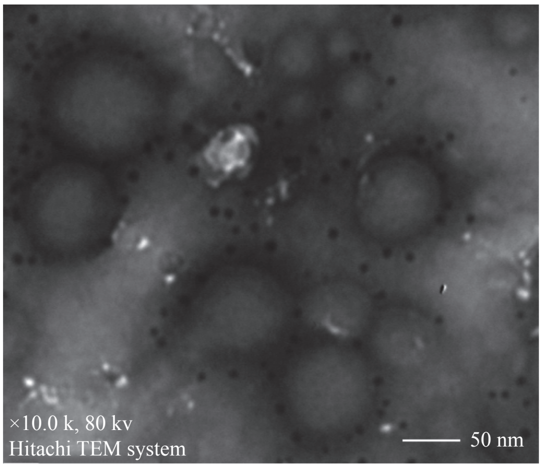

Fig. 3 TEM image of GT-NZVI

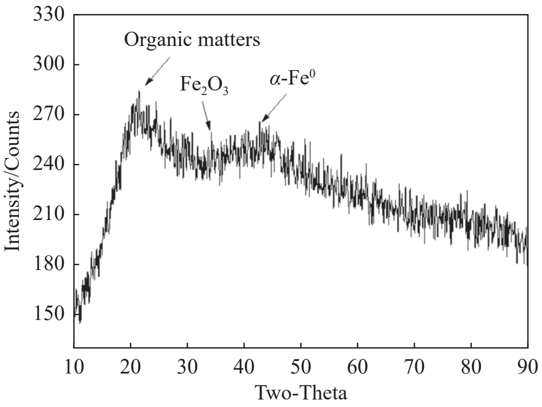

Fig. 4 XRD pattern of GT-NZVI

2017), while other studies highlight that the reduction products contained none or very small amount of zero-valent iron and the main iron products are trivalent and divalent irons (Shahwan et al. 2011; Truskewycz et al. 2016). This can be attributed to the extreme different reducibility of plant extracts. Species and parts of the plants have significant influence on the final products of valence state iron reduction.

For further confirmation, FTIR spectrum of GT-NZVI was recorded in Fig. 5. It shows the absorption peaks at about 3 369 cm^{-1} (O-H stretching) and 1 144 cm^{-1} (O-H bending) for the -OH group which mainly belonged to polyphenol. O-H groups are effective molecular structures for unpaired electrons detachment, and thus the content of O-H group has a positive correlation relationship with the reducibility of polyphenol extract (Fazlzadeh et al. 2016). Moreover, there was an absorption peak at 841 cm^{-1} (Fe-O stretching) instead of 895 cm^{-1} because of the deviation resulting from an interaction between the Fe-O and the ingredients in green tea (Huang et al. 2013). The absorption peak at 2 923 cm^{-1} (CH_3-stretching), 2 852 cm^{-1} (CH_2-stretching) , 1 640 cm^{-1} (C=C stretching) and 1 068 cm^{-1} (C-O stretching) were attributed to the polyphenolic compounds which are common in the alcoholic hydroxyl group or others. The result proved that the main plant chemicals including hydrophilic catechins in green tea might play an important role in the functionalization process of GT-NZVI, and as well as a stabilizer, which had been confirmed the in the result of TEM image.

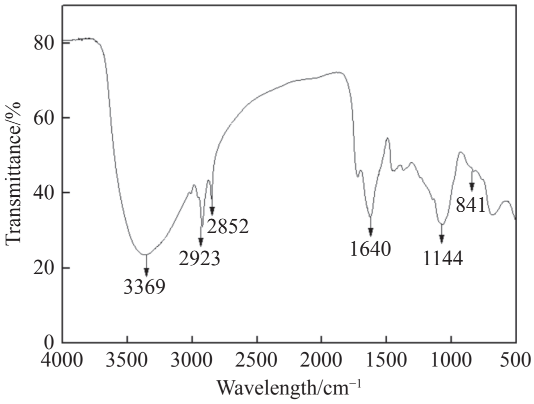

Fig. 5 FTIR spectrum of GT-NZVI

2.2 Removal efficiency of Cr(VI) by GT-NZVI in water

To confirm the removal efficiency of Cr(VI) with GT-NZVI in water, the bath tests were carried out by adding a constant volume of GT-NZVI suspensions and equal volume of GT extract as blank control. According to the reaction between Fe(0) and Cr(VI), excess amount of Fe(0) was added for its consumption by O_2 oxidation or pH corrosion reactions to ensure the complete reduction of Cr (VI) .

Results in Fig. 6(a) shows that the concentration of Cr(VI) rapidly decreased from 100 mg/L to 8.2 mg/L in 1 h reaction with GT-NZVI suspension, and the removal efficiency of Cr(VI) was 92.8%. In the reaction process of 552 h, the concentration of Cr(VI) always remained below 5.5 mg/L and the removal efficiency was 94.8%–95.9%. Corresponding concentration of Cr(III) in Fig. 6(b) increased from 0 mg/L to 88.7 mg/L in 1 h reaction and then stabilized at 80–90 mg/L. GT extract possesses a high reducing potential and is able to transform almost instantly the ferric iron to the elemental state. It is thus reasonable to consider whether they can reduce Cr(VI) directly. A blank control test by adding GT extract as a reductant was carried out to test this hypothesis. As seen in Fig. 6, the highest Cr(VI) reduction rate of 27.5% and Cr(III) production rate of 8.6% were obtained, suggesting that polyphenols remaining in the GT-NZVI suspension from the first synthesis step were not capable to reduce all Fe(III) to Fe(0) but might be able to contribute in the reduction of Cr(VI) to Cr(III), in spite of less efficient compared to GT-NZVI. Moreover, it can be seen that the whole reaction process could be divided into two phases: The concentration of Cr(VI) decreased rapidly within the first hour of the experiment, and then rebounded slightly before it stabilized. It is because heavy metals reduction by nanoscale iron particles usually comprises two processes of surface adsorption and chemical reduction (Zhang et al. 2012). Cr(VI) was adsorbed quickly onto the surface of GT-NZVI particles in the first phase, and then the adsorbed Cr(VI) was continuously reduced to Cr(III) in the second phase. Thus, chemical reduction is the final mechanism for Cr(VI) decrease by GT-NZVI.

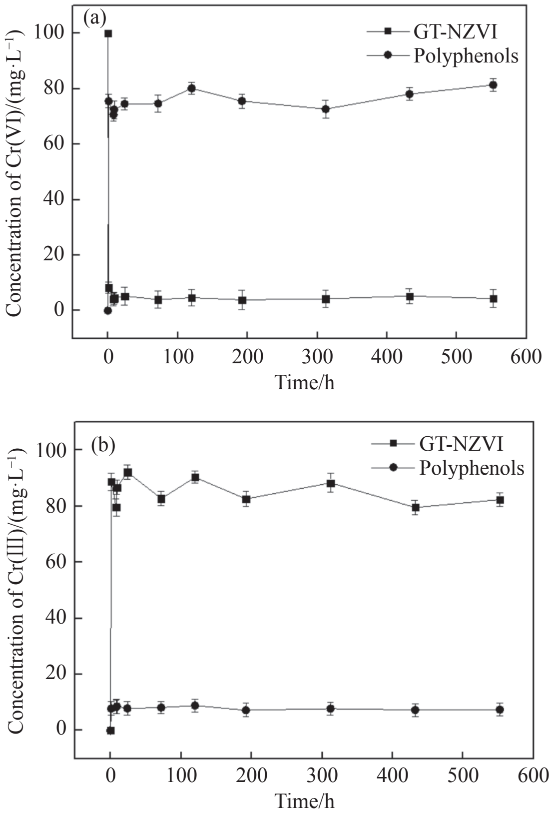

Fig. 6 Effects of polyphenols and GT-NZVI on the removal of Cr (VI)

(a) Concentration change of Cr(VI); (b) Concentration change of Cr(III)

The pH and ORP values of initial reaction solution were equal to 1.62 and 308.5 mV (Fig. 7). Immediately after the addition of GT-NZVI suspensions, the pH exhibited an sharp increase to approximately 2.02 and OPR decreased to 289.4 mV, which was attributed to the redox reaction. Then both rebounded gradually and pH stabilized at 1.7–1.8 and ORP at 305–310 mV. According to the study of Sanchez et al. (2007) phenol- and quinone-like compounds can be degraded by dissolved O_2 within 2–6 hours in the presence of Fe(0), which act as catalysts, and the end-products are low molecular-weight organic acids. These degradation reactions generate protons and could explain the subsequent pH and OPR changes.

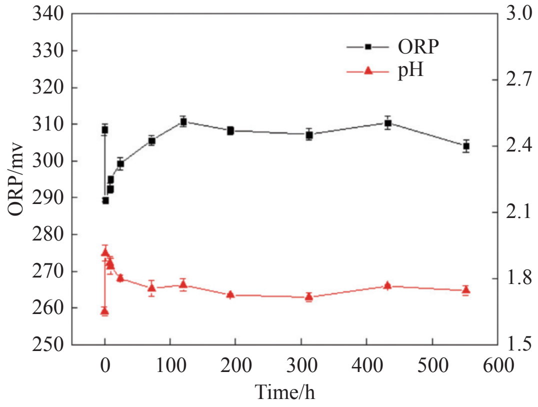

Fig. 7 pH and ORP changes in the reaction solution during the reaction

2.3 Removal and influence factors of Cr(VI) by GT-NZVI in porous media

To investigate the remediation effect of Cr(VI) contaminated groundwater by GT-NZVI injecting, GT-NZVI suspension was introduced to sand columns. The transport condition of GT-NZVI particles is shown in Fig. 8. C/C_0 (C: Iron concentration of effluent through column; C_0: initial concentration of inflow) was calculated as the normalized effluent concentration obtained from the breakthrough curves during the initial phase of particle elution. When the GT-NZVI suspension of less than 8.5 PV was injected to the sand column, the particles were not detected in the effluent due to the intercepting and adsorption effects of the natural sand. As the suspension inflow continued, the sampling concentration started to increase to a maximum of 0.74. The mass balance of the GT-NZVI during the transport process was calculated (Table 2), and the average mass ratio of effluent and influent of GT-NZVI was 71.2%, which suggests that GT-NZVI had a good migration capacity in natural sand. Most previous studies about NZVI migration used glass beads or silica sand as porous media, the results of which may be inaccurate because of ignoring the effects of the organic matters in the natural sand (Li et al. 2015; Cheng et al. 2022). The test results mentioned above adequately show that GT-NZVI prepared by plant polyphenols could well transport in actual aquifer medium, which was the precondition for groundwater remediation by NZVI injecting technology.

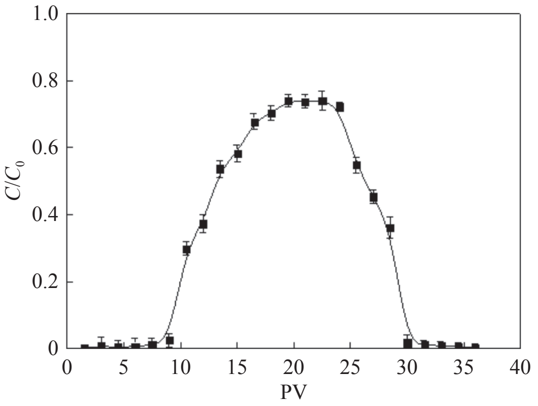

Fig. 8 The breakthrough curve of GT-NZVI in natural sand

The removal results of Cr(VI) passing through in-situ reaction zone (IRZ) with GT-NZVI was shown in Fig. 9. In the pure sand column, the effluent concentration of Cr(VI) rapidly increased, and the C/C_0 reached a maximum value of 0.992 after 4 PV injecting, suggesting limited Cr(VI) adsorption by natural sand. Compared to this, the outflow time of Cr(VI) through IRZ column was obviously hysteretic and the effluent concentration significantly declined. When injection volume of Cr(VI) was less than 3 PV, Cr(VI) concentration could not be detected in the effluent, which demonstrates that Cr(VI) flowing through IRZ with GT-NZVI was completely removed, and the removal efficiency of Cr(VI) was close to 100%. As the injection went on, the concentration of Cr(VI) gradually increased, it indicates that the activity of IRZ with GT-NZVI declined with the adsorption and reduction reaction process, and resulted in the continuous decrease of the removal efficiency of Cr(VI). After a 8 PV of Cr(VI) solution injected, the C/C_0 increased to 0.65 which meant the removal of Cr(VI) decreased to 35%. Cr(VI) solution was replaced by background solution after 10 PV injected into the column, and the effluent concentration of Cr(VI) and Cr(III) (Fig.10) were continuously monitored. The results show that the effluent concentration of Cr(VI) kept at 0.14–0.32 mg/L within 15 days, and Cr(III) concentration tended to be stable at 0.20–0.30 mg/L, which suggested that IRZ with GT-NZVI had good stability for Cr(VI) removal, and chromium was fixed in the IRZ would not be easily released to the groundwater.

At present, there are few column simulation studies on the Cr(VI) contaminated groundwater remediation by NZVI reaction zone, most of which are static batch tests for reaction mechanism studies (Li et al. 2019; Wang, 2020). In some studies, Cr(VI) contaminated groundwater was continuously injected into NZVI reaction zone to investigate the effectiveness and sustainability of the zone (Zhao, 2020; Han, 2022). However, in this study, a certain amount of Cr(VI) contaminated groundwater was injected into IRZ, which was then followed by pollution-free groundwater. On one hand, the effectiveness of GT-NZVI reaction zone for Cr(VI) pollution was defined; on the other hand, whether the chromium fixed in IRZ would be released again after remediation was investigated. In other words, in this study, the stability of Cr(VI) fixed in IRZ for remediation was explored from another perspective which has not been seen in previous studies and has great significance for the practical application of GT-NZVI reaction for Cr(VI) contaminated groundwater remediation.

In the actual contaminated sites, aquifer litho-

Table 2 GT-NZVI mass balance during the transport through natural sand in parallel tests (mg)

No.	Deposition on sand	Accumulated outflow	Total mass	Percentage of outflow (%)
1	203.41	511.79	715.20	71.6
2	208.33	501.53	709.86	70.7
3	205.22	508.16	713.38	71.2

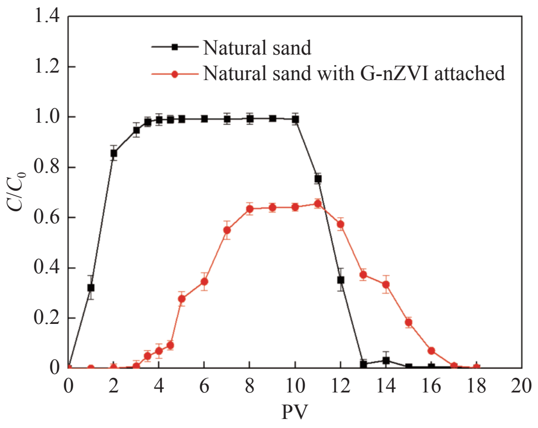

Fig. 9 Breakthrough curves of Cr(Ⅵ) in sand column

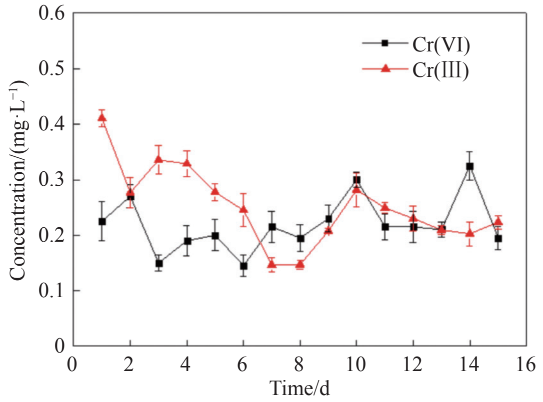

Fig. 10 Eluting concentration of Cr(VI) and Cr(III) in IRZ with GT-NZVI

logy, groundwater hydrodynamics and chemical composition have an important impact on the remediation of Cr(VI) pollution in nano-iron reaction zone. Therefore, the effects of aquifer medium particle size, groundwater flow rate and ionic strength on the reduction of Cr(VI) were studied in this paper.

Fig. 11(a) shows the influence of aquifer media size on the removal of Cr(VI) by GT-NZVI. In the reaction system with coarse sand, medium sand and fine sand, the final C/C_0 of Cr(VI) were 69.32%, 64.05% and 53.46%, respectively, which indicated that fine sand had the best Cr(VI) removal efficiency. Researches have shown that the media can affect the removal rate of pollutants by affecting the adsorption of NZVI, and the smaller the media particle size, the greater retention of NZVI particles (Zhao, 2020; Han, 2022). The main reason is that the smaller particle size increases the surface area of the media and thus increases the filtration, interception and adhesion of NZVI particles. Therefore, it can be speculated the interception mass of GT-NZVI particles in fine sand was more than that in coarse and medium sand, and thus the removal rate of Cr(VI) was the best of all three. However, in actual contaminated site, the aquifer may be blocked by NZVI particles for too small medium size and excessively low permeability. Furthermore, the reaction zone of nano iron particles formed in media of small size might be narrow which results in a short contact time for pollutant and NZVI particles (Li et al. 2015), therefore should be considered for good remediation effect in application.

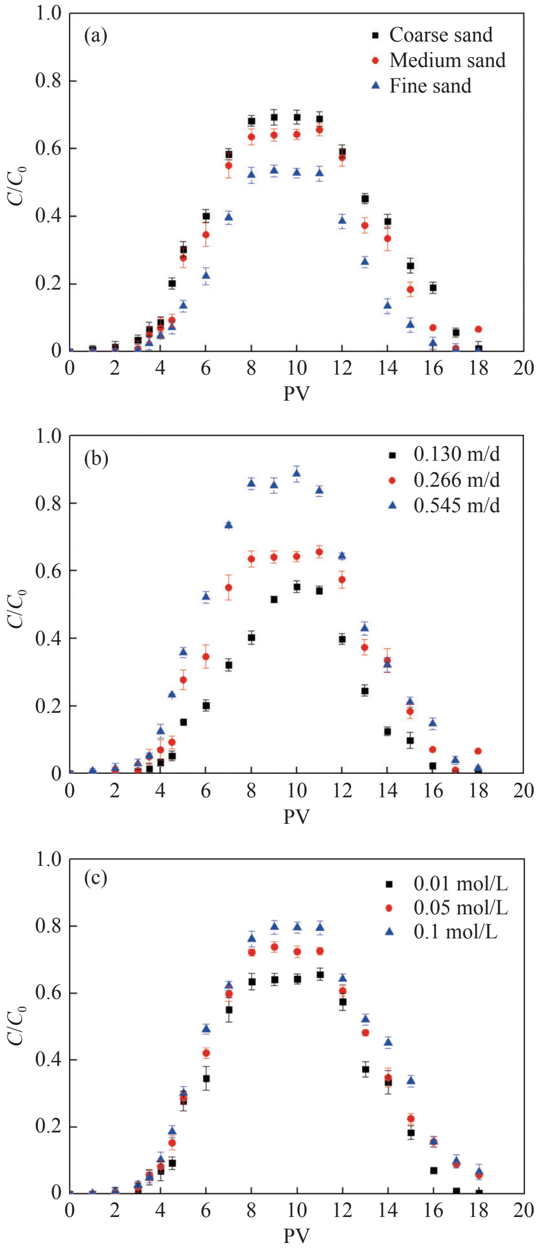

Fig. 11 Influence of medium size (a), groundwater flow rate (b) and ionic strength (c) on Cr(VI) reduction in IRZ with GT-NZVI

Fig. 11 (b) shows the influence of groundwater flow rate on the removal of Cr(VI) by GT-NZVI. It shows that the removal efficiency of Cr(VI) decreases with the increase of groundwater flow rate. When the groundwater flow rate increased from 0.130 m/d to 0.266 m/d and 0.545 m/d, the final C/C_0 of Cr(VI) by GT-NZVI increased from 55.33% to 64.25% and 88.65%, respectively. The results can be explained by the following three reasons: (1) the lager groundwater flow rate caused the faster migration of GT-NZVI and resulted a wider and lower concentration reaction zone, which meant a lower reaction ability for the pollutants; (2) with the increase of Cr(VI) injection rate and amount, GT-NZVI was rapidly consumed, and the subsequent reaction was blocked; (3) the contact time between GT-NZVI and Cr(VI) was greatly shortened for increased flow rate.

Fig. 11(c) shows the influence of ionic strength on the removal of Cr(VI) by GT-NZVI. It can be seen that the removal efficiency of Cr(VI) decreases with the increase of ionic strength. When the ionic strength increased from 0.01 mol/L to 0.05 mol/L and 0.1 mol/L, the final C/C_0 of Cr(VI) by GT-NZVI increased from 64.05% to 73.80% and 79.62%, respectively, which meant the removal efficiency decreased by 27.12% and 43.31%, respectively. The study from Li et al. (2011) showed that the high ionic strength affected the stability of NZVI particles, and the agglomeration of particles caused the decrease of their specific surface area, and the reaction rate of Cr(VI) reduction decreased. In addition, Hong (2018) found Cl^- promoted the removal of Cr(VI) by stabilized NZVI to some extent, because Cl^- would form a complex with Fe(0) which could accelerate the decomposition of oxide passivation layer. However, the results of this study show that the effect of Cl^- on the reduction of Cr(VI) by GT-NZVI was relatively small compared with the ionic strength.

In order to further verify the stability of Cr(VI) reduction with GT-NZVI, Cs-corrected STEM for sediment product on the surface of natural sand was measured. As shown in Fig. 12. The size of GT-NZVI particles after the reaction became bigger with a diameter of about 60 nm (Fig. 12a), this was due to the oxidation and agglomeration of GT-NZVI particles during the reaction process. Moreover, element Cr had the similar distribution range as element Fe and O (Fig. 12b-d), especially coincided with Fe, signifying that Cr was bound and buried either on the surface or in the crystal lattice of iron hydroxide or iron oxide. Papassiopi et al. (2014) have shown that Fe(III) and Cr(III) could form mixed hydroxides, $Cr_xFe_{(1-x)}(OH)_3$, with relatively low solubility even in the acidic pH range. Therefore, combined with the results of

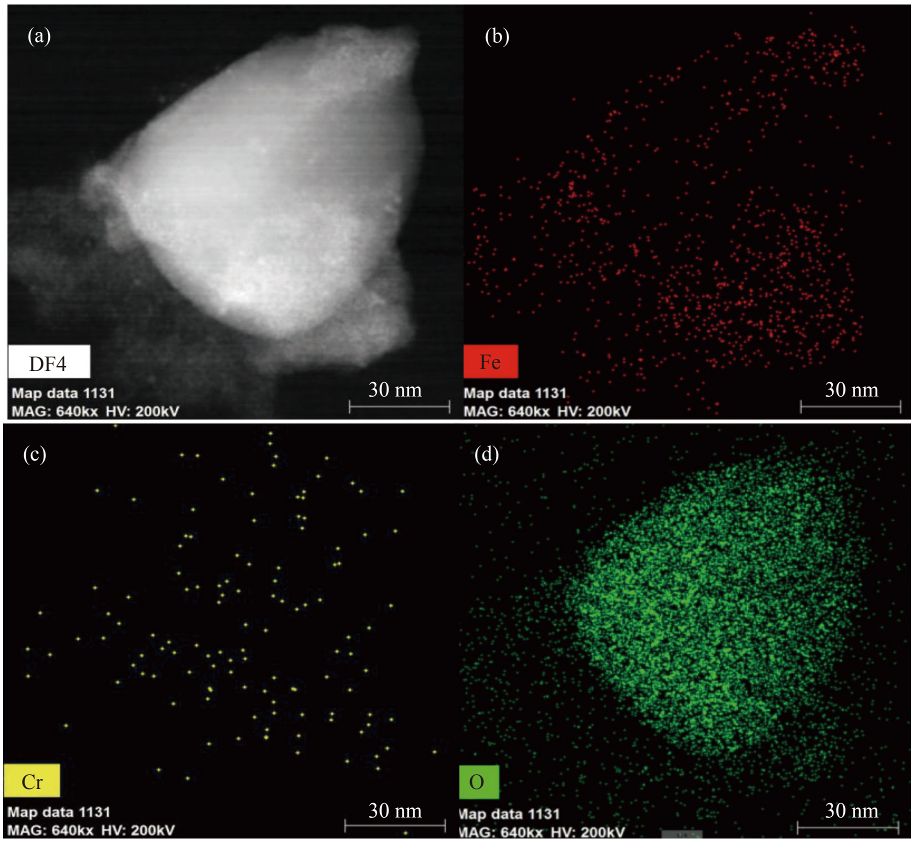

Fig. 12 Cs-corrected STEM image of GT-NZVI and distribution of elements

batch and column tests, it can be inferred that Cr(VI) could be effectively reduced by GT-NZVI and most of Cr(III) co-precipitated with Fe(III) in the form of mixed hydroxides, that was, the reduction reaction was relatively stable and Cr(III) was not easy to be released into the groundwater.

3 Conclusions

(1) GT-NZVI was prepared successfully using green tea extract as a reductant for $FeCl_3$, and the particles were regular spherical with a diameter of 10–20 nm. α-Fe was identified as the key material composition. As a stabilizer, green tea effectively reduced the agglomeration of the particles and increased their dispersity in water.

(2) Cr(VI) in water was removed considerably by GT-NZVI through the process of adsorption and reduction. The removal rate of Cr(VI) reached 94.8%–95.9% and the production rate of Cr(III) was over 80%. pH of reaction solution increased to 2.02 and stabilized at about 1.75, and ORP initially decreased to 289.4 mV and stabilized between 305–310 mV. Chemical reduction was the final mechanism for Cr(VI) removal from water.

(3) GT-NZVI can migrate in natural sand with the size of 0.25–0.5 mm, and the migration efficiency was 71.2%. Cr(VI) contaminated groundwater can be remediated by in-situ reaction zone with GT-NZVI, and outflow concentration of Cr(VI) kept in 0.14–0.32 mg/L within 15 days. The removal efficiency of Cr(VI) by IRZ with GT-NZVI decreased with the increase of particle size of aquifer medium, groundwater flow rate and ionic strength. Most of Cr(III) as reduzate was adsorbed or immobilized on the surface or in the lattice of GT-NZVI, which indicated effective immobilization for chromium.

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