In situ remediation of hexavalent chromium contaminated soil by CMC-stabilized nanoscale zero-valent iron compositied with biochar

Runyuan Zhang, Nuanqin Zhang and Zhanqiang Fang

ABSTRACT

In this study, the remediation experiments were performed outdoors in natural conditions. Carboxymethyl cellulose (CMC)-stabilized nanoscale zero-valent iron (CMC-nZVI), biochar (BC) and CMC-stabilized nanoscale zero-valent iron compositied with biochar (CMC-nZVI/BC) were synthesized and investigated for their effect on the in situ remediation of hexavalent chromium [Cr(VI)] contaminated soil and the concentration of available iron was tested after the remediation, compared with the untreated soil. The results of toxicity characteristic leaching procedure (TCLP) test showed that CMC-nZVI and CMC-nZVI/BC used as remediation materials could obviously improve the remediation rate of Cr contaminated soil and when the ratio of CMC-nZVI to Fe0 was 2.5 g/Kg, the leachability of Cr(VI) and Crtotal can be reduced by 100% and 95.8% simultaneously. Moreover, sequential extraction procedure (SEP) showed that most exchangeable Cr converted to carbonate-bound and Fe-Mn oxides-bound, reducing the availability and leachability of Cr in the soil.

Key words | biochar, Cr(VI)-contaminated soil, in situ remediation, stabilization of nanoscale zero-valent iron

INTRODUCTION

Hexavalent chromium is widely used in metallurgy, electroplating wood processing, leather tanning and other industrial activities (Banks et al. 2006; Xu & Zhao 2007), which easily cause serious soil contamination due to improper disposal of Cr slag or irresponsible treatment of wastewater containing Cr (Chrysochoou et al. 2010; Duan & Tan 2015). Chromium in the contaminated soil not only affects crop yield and quality, but also enters into the human body through the food chain and causes serious diseases (Su et al. 2016a). According to the National Soil Pollution Condition Investigation Communique (EPD & MLR, 2014) published in April 2014, the situation is not optimistic as chromium contamination in China exceeded the standard rate in the national soil sampling points by 1.1% (EPD & MLR 2014). Chromium in soil occurs primarily in two different redox states: the immobile and low toxicity trivalent form, Cr(III), which could exist in alkaline or even weakly acidic environments in the form of Cr(OH)3, and the mobile and highly toxic hexavalent form, Cr(VI) (Franco et al. 2009; Wu et al. 2009). Therefore, reduction of Cr(VI) to Cr(III) and subsequent precipitation of the Cr(III) ion, is the most common method of treating Cr(VI)-contaminated soils to reduce Cr(VI) mobility and toxicity (Reyhani-Tabar et al. 2012). In recent years, nanoscale zero-valent iron applied to in situ remediation of Cr(VI) contaminated soil has received wide attention (Liu et al. 2012). However, nZVI tends to agglomerate rapidly due to its nano-size effects and magnetic interaction, which then lessens its activity and mobility and reduces the remediation efficiency of Cr(VI) contaminated soil (Liu & Zhao 2007). One solution is to stabilize nZVI with modified materials, which prevent the iron from agglomeration and then increase its remediation efficiency, such as starch (Reyhani-Tabar et al. 2012), polyvinylpyrrolidone (PVP) (Fang et al. 2011), sodium carboxymethyl cellulose (CMC) (Liu & Zhao 2007) and so on. Among the modified materials, CMC is cheap and environmentally-friendly; using CMC stabilized nZVI can improve the fluidity and diffusibility of nanoscale zero-valent iron particles, especially for the in-situ remediation of chromium contaminated soil. Moreover, iron amendments can cause soil structure problems such as aggregate cementation and reduce soil porosity, and have

<ref>doi: 10.2166/wst.2018.039</ref>
also been noted to reduce the concentrations of soluble macronutrients such as Mg, P, Ca and S (McBride & Martinez 2000; Kumpiene et al. 2008). Therefore, how to avoid the problems of the application of nanoscale zero-valent iron in the remediation of the contaminated soil effectively is the direction of future research.

Biochar is generated by the pyrolysis of carbonaceous biomass obtained from a wide range of materials in a low oxygen atmosphere (Jiang et al. 2012a), so it is cheap and easy to produce. Studies show that biochar has a rich porous structure, abundant oxygen-containing functional groups on its microscopic surface and high iron exchange capacity (Bian et al. 2014; Xu & Fang 2015; Yang & Fang 2014), which is greatly useful for absorbing heavy metals and reducing metal availability and leachability (Su et al. 2016b). Therefore, applying biochar in the Cr(VI) contaminated soil composed with CMC-nZVI can not only improve the soil properties such as increasing the soil fertility and improve the soil pH value, but also enhances the immobilization efficiency of CMC-nZVI.

In this study, the remediation experiments were performed outdoors in natural conditions to simulated in situ farmland remediation. The objectives of the study were: (1) prepare and characterise CMC-nZVI, BC and CMC-nZVI/BC; (2) compare the immobilization efficiency among CMC-nZVI, BC and CMC-nZVI/BC in after-amended soil using the TCLP method (EPA Method 1311) (TCLP US EPA 1990); (3) evaluate the changes of Cr speciation in the after-amended soil using the sequential extraction procedure (SEP) method (Tessier et al. 1979).

**MATERIALS AND METHODS**

**Materials and soil**

All chemicals used in this study were of analytical grade or higher and purchased from Tianjin Damao Chemical Agent Factory (Tianjin, China). All the soil samples were collected from 0–20 cm deep in vegetable farmland at Beiting Village in Higher Education Mega Center, Guangzhou, China. The soil is lateritic red earth, which is representative in South China and free of Cr. The main physical and chemical properties of the soil with measuring methods are in Table 1 and the results of soil particle size distribution are in Table 2. Before using, stone, roots and soil organisms were picked up from the soil and then the soil was sieved with a standard 2.00 mm sieve after natural air drying and finally placed in a dryer for storage.

<table>
<thead>
<tr>
<th>Items</th>
<th>Data</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>4.3</td>
<td>NY-1239-1999 (State Forestry Administration 1999a)</td>
</tr>
<tr>
<td>Hydrolyzable nitrogen (mg/kg)</td>
<td>37.5</td>
<td>NY-1229-1999 (State Forestry Administration 1999b)</td>
</tr>
<tr>
<td>Available phosphorus (mg/kg)</td>
<td>10.2</td>
<td>HJ 704-2014 (Ministry of Environmental Protection 2014)</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>1%</td>
<td>HJ 615-2011 (Ministry of Environmental Protection 2011)</td>
</tr>
<tr>
<td>Total chromium (mg/kg)</td>
<td>None</td>
<td>HJ 491-2009 (Ministry of Environmental Protection 2009)</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>1.21</td>
<td>Cutting ring method (Institute of Soil Science 1978)</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.7</td>
<td>Pycnometer method (Institute of Soil Science 1978)</td>
</tr>
<tr>
<td>Field moisture capacity (%)</td>
<td>27.5</td>
<td>Cutting ring method (Institute of Soil Science 1978)</td>
</tr>
</tbody>
</table>

**Table 2 | Particle size distribution in soil (Pipe method, Institute of Soil Science 1978).**

<table>
<thead>
<tr>
<th>Sand (%) (1-0.05 mm)</th>
<th>Silt (%) (0.05-0.001 mm)</th>
<th>Clay (%) (&lt;0.001 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>22.5</td>
<td>18.5</td>
</tr>
</tbody>
</table>

**Soil spiking with Cr(VI)**

The Cr(VI)-spiked soil was prepared using the flowing procedure: a known mass of air-dried soil was first mixed with a solution containing 800 mg/L Cr(VI) and 0.002 M CaCl₂ at a soil-to-solution ratio of 1:1 (kg/L) and then kept under electric stirring for 24 hours to form a slurry. When the slurry was air dried to a constant weight, the soil was ground and then sieved with a standard 2.00 mm sieve, and finally the content of Cr(VI) in the Cr(VI)-spiked soil was 800 mg/kg (w/w) in theory. In this study, totally 20 kg Cr(VI)-spiked soil was prepared, mixed evenly and then stand aging for two weeks before being used.

**Preparation and characterization of remediation materials**

The preparation of 3.5 L CMC-nZVI colloid using the following procedure is taken as an example: 174 g FeSO₄·7H₂O was dissolved into 1,750 mL deionized water previously purged with nitrogen for 15 minutes to remove dissolved oxygen and stirred continuously until dissolution was complete. 70 g sodium CMC was dispersed into ethanol
previously and also purged with nitrogen to remove dissolved oxygen, and then the CMC suspension was added dropwise slowly into the FeSO$_4$ solution with constant stirring for 15 minutes to form Fe$^{2+}$-CMC solution. 80 g sodium borohydride was dissolved into 40% ethanol, and then the sodium borohydride solution was added dropwise slowly into the Fe$^{2+}$-CMC solution with sufficient shaking for 10 minutes. All the procedures were conducted under nitrogen atmosphere in order to prevent the Fe$^0$ from oxidizing, and the final colloid was labeled as CMC-nZVI, the Fe$^0$ concentration was 10 g/L while CMC content was 2% (w/w). The nZVI was prepared by following same procedure but without CMC. The biochar was produced by the pyrolysis of wood chips at a temperature of 600 $^\circ$C for 3 hours under oxygen-limited condition and then sieved with standard 0.30 mm sieve (Jiang et al. 2022a, 2022b; Ding et al. 2014). The specific surface area of the CMC-nZVI was analyzed by a Brunauer-Emmett-Teller analyzer (BET, ASAP2020M, Micromeritics Instrument Corporation, USA), the particles size and surface morphology of the CMC-nZVI and nZVI were characterized by transmission electron microscopy (TEM) analysis (Chen et al. 2022) and the surface morphology of the biochar was characterized by scanning electron microscopy (SEM) analysis (Yang et al. 2016).

### Outdoor remediation

All the samples in this study were divided into three groups in order to compare the effect of remediation on Cr(VI)-contaminated soil among different amended materials and to discuss the changes of treatment effect with different dosage of amended materials and treatment time. The first group of amended materials was CMC-nZVI labeled as S1: the CMC-nZVI colloid was mixed with 1 kg Cr(VI)-contaminated soil uniformly at the ratio of 1 g/kg, 2.5 g/kg, 5 g/kg, respectively, labeled as S1-1, S1-2, S1-3. The second group of amended materials was BC labeled as S2: the BC was mixed with 1 Kg Cr(VI)-contaminated soil uniformly at the ratio of 10 g/kg, 25 g/kg, 50 g/kg, respectively, labeled as S2-1, S2-2, and S2-3. The third group of amended materials was CMC-nZVI/BC labeled as S3: the CMC-nZVI/BC was mixed with 1 kg Cr(VI)-contaminated soil uniformly at the ratio of 1 g/10 g/kg, 2.5 g/25 g/kg, 5 g/50 g/kg, respectively, labeled as S3-1, S3-2, S3-3. All the three groups of samples were mixed completely and placed outdoors and simultaneously kept the field water-holding capacity at 70% for 21 days. The samples were analyzed when the corresponding reaction times were 1 d, 3 d, 7 d, 14 d and 21 d.

### Analysis methods

To estimate the remediation effective of amended materials on Cr(VI)-contaminated soil, toxicity characteristic leaching process (TCLP, EPA Method 1311) was performed by comparing the leachability of Cr in the soil between treated and untreated samples. The immobilization efficiency was calculated to characterize the migration capacity of Cr in soil by Equation (1):

$$\text{Crimmobilization efficiency (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100\%$$  \hspace{1cm} (1)

where c is the concentration (mg/L) of Cr(VI) or Cr$_{\text{total}}$ in the supernatant of the treated soil and c$_0$ is those of the control tests. Moreover, the Tessier SEP was performed to investigate the changes of different forms of chromium in the soil between treated and untreated samples. Finally, 0.1 M hydrochloric acid was used as leaching agent to extract the effective iron (LY/T 1262–1999), because the soil was acidic according to Table 1, to investigate the available iron concentration which can be directly utilized by the plant in the soil after the remediation.

All the determinations in this study were performed with three parallel samples to ensure the reliability of the experimental data. After centrifuging at 2,500 rpm for 5 min, all the extract supernatant was partially filtered with 0.22 $\mu$m hydrophilic membranes and then the Cr$_{\text{total}}$ in the filtrate was analyzed using a flame atomic absorption spectrophotometer (FAAS, TAS-986, Beijing Purkinje General Instrument Co., Ltd, China) while the remaining supernatants were filtered with 0.45 $\mu$m hydrophilic membranes and were processed a color reaction with diphenylcarbazide to determine the Cr(VI) in the filtrate using an ultraviolet-visible spectrophotometer (Model 722S, Shanghai Precision & Scientific Instrument Co., Ltd, China). For comparison, the untreated soil was also extracted and analyzed with the same methods.

### RESULTS AND DISCUSSION

#### Characterization of remediation materials

Figure 1(a) and 1(b) show the TEM image of nZVI and CMC-nZVI, respectively. Figure 1(a) found that the fresh nanoparticles grain size ranges from 20 to 40 nm and has a uniform shape with a spherical morphology. Most of the
nanoparticles are connected or clustered together as chain-like structures, which may result from both the effects of static magnetism and surface tension. Figure 1(b) shows that the size of the stabilized nZVI was relatively larger, with a size distribution of 80 to 120 nm and the nanoparticles distributed uniformly rather than as chain-like structures, indicating that CMC can effectively prevent the aggregation of nZVI nanoparticles. Moreover, the BET result indicated that the surface morphology of the CMC-nZVI was $40 \pm 2$ m$^2$/g. Figure 1(c) and 1(d) show the SEM image of biochar, which found that the biochar had a honeycomb-like and highly porous structure that was favorable to the adsorption of heavy metals (Lehmann & Joseph 2009).

**Remediation effect of CMC-nZVI**

Figure 2 shows the remediation effect on Cr(VI)-contaminated soil with three different dosages of CMC-nZVI at the dose of S1-1: 1 g/kg, S1-2: 2.5 g/kg and S1-3: 5 g/kg, respectively. Figure 2(a)–2(c) show the changes of the concentration of Cr(VI) and Cr$_{\text{total}}$ extracted from soil with time under three different dosages of S1-1, S1-2 and S1-3, respectively. Figure 2(d) compares the final remediation effect of three different dosages of CMC-nZVI on Cr(VI)-contaminated soil after 21 d. After remediation, when the dosage of CMC-nZVI was 1 g/kg, the immobilization efficiency of Cr$_{\text{total}}$ and Cr(VI) was 45.4% and 17.9%, respectively, and when the dosage of CMC-nZVI was
increased to 2.5 g/kg and 5 g/kg, the $\text{Cr}_{\text{total}}$ immobilization efficiency reached 72.8% and 95.8%, respectively, while the immobilization efficiencies of Cr(VI) reached 58.6% and 100%. This result showed that the addition of stabilized nZVI can effectively improve the immobilization efficiency of $\text{Cr}_{\text{total}}$ and Cr(VI) and the value of R-squared is 0.974 ($\text{Cr}_{\text{total}}$) and 0.973(Cr(VI)). Similarly, for S1-2 and S1-3, the remediation of Cr-contaminated soil for 1 d can also achieve very desirable results: the $\text{Cr}_{\text{total}}$ immobilization efficiency achieved 67.6% and 92.1%, respectively while the immobilization efficiencies of Cr(VI) were 58.6% and close to 100% (the concentration of Cr(VI) was below the detection limit), respectively. According to EPA Method 1311, the environmental risk threshold of $\text{Cr}_{\text{total}}$ in the TCLP test was 100 mg/kg, so when the dosage of CMC-nZVI was 2.5 g/kg in S1-2 and 5 g/kg in S1-3, the concentration of $\text{Cr}_{\text{total}}$ in soil was lower than the threshold, which showed that CMC-stabilized nZVI achieved a target remediation effect on Cr in the outdoor remediation experiments.

**Remediation effect of BC**

Figure 3 shows the remediation effect on Cr(VI)-contaminated soil with three different dosages of biochar at the dose of S2-1: 10 g/kg, S2-2: 25 g/kg and S2-3: 50 g/kg, respectively. Figure 3(a)–3(c) show the changes of the concentration of Cr(VI) or $\text{Cr}_{\text{total}}$ extracted from soil with time under three different dosages of S2-1, S2-2 and S2-3, respectively. Figure 3(d) compares the final remediation effect of three different dosages of biochar on Cr(VI)-contaminated soil after 21 d. When the dosage of biochar was 10 g/kg, 25 g/kg and 50 g/kg, the immobilization efficiency of $\text{Cr}_{\text{total}}$ was 26.7%, 30.8% and 39.8% respectively, and the value of R-squared is 0.868, which indicates that the addition of biochar can improve the immobilization efficiency of $\text{Cr}_{\text{total}}$. 

![Figure 2](image-url) | Remediation effect of CMC-nZVI on Cr immobilization.

![Figure 3](image-url) | Remediation effect of BC.
The final immobilization efficiency on the 21st day of Cr(VI) on Cr(VI)-contaminated soil with three different dosages of biochar was 16.9%, 19.5% and 19.99% respectively and the value of R-squared is 0.72. This result showed that the difference between the transformation efficiencies of Cr(VI) with three dosages of biochar was not obvious, and all were low. It can be summarized that the remediation of biochar on Cr(VI)-contaminated soil may result from the adsorption mechanism, and the total leaching concentration of Cr\text{total} in the contaminated soil amended with three different dosages of biochar is more than 100 mg/kg, all exceeding the environmental risk threshold of the TCLP method, showing that the biochar applied alone could not achieve the remediation target on Cr(VI)-contaminated soil at the given concentration.

**Remediation effect of CMC-nZVI/BC**

Figure 4 shows the remediation effect on Cr(VI)-contaminated soil with three different dosages of CMC-nZVI/BC (1:10/w:w) at the dose of S3-1: 11 g/kg, S3-2: 27.5 g/kg and S3-3: 55 g/kg, respectively. Figure 4(a)–4(c) show the changes of the concentration of Cr(VI) or Cr\text{total} extracted from soil with time under three different dosages of S3-1, S3-2 and S3-3, respectively. Figure 4(d) compares the final remediation effect of three different dosages of CMC-nZVI/BC on Cr(VI)-contaminated soil after 21 d. When the dosage of CMC-nZVI/BC was 11 g/kg, 27.5 g/kg and 55 g/kg, the immobilization efficiency of Cr\text{total} was 48.6%, 80.2% and 96.7% respectively, and the value of R-squared is 0.95, which indicated that the addition of
CMC-nZVI/BC can significantly improve the immobilization efficiency of $\text{Cr}_{\text{total}}$. The final immobilization efficiency on the 21st day of Cr(VI) on Cr(VI)-contaminated soil with three different dosages of CMC-nZVI/BC was 19.7%, 33.5% and nearly 100% respectively and the value of R-squared is 0.72. This result showed that the addition of CMC-nZVI/BC can effectively improve the immobilization efficiency of Cr$_{\text{total}}$ and Cr(VI). Similarly, for S3-2 and S3-3, the remediation of Cr-contaminated soil for 1 d can also achieve very satisfactory results, the $\text{Cr}_{\text{total}}$ immobilization efficiency achieved 69.5% and 91.8%, respectively, while the immobilization efficiencies of Cr(VI) were 80.2% and 96.7%, respectively. According to EPA Method 1311, the environmental risk threshold of Cr$_{\text{total}}$ in TCLP method was 100 mg/kg so when the dosage of CMC-nZVI/BC was 11 g/kg in S3-1, 27.5 g/kg in S3-2 and 55 g/kg in S3-3, all the concentration of Cr$_{\text{total}}$ in soil was lower than the threshold value, which showed that CMC-nZVI/BC can achieve the target remediation effect on Cr in the outdoor remediation experiments. Moreover, the results of S3-1 and S3-2 showed that Cr(VI) did not decrease significantly in the first day, but gradually decreased with the prolonging of the remediation time. The result of S3-3 was similar to S1-3, which amended with CMC-nZVI so that the concentration of Cr(VI) was lower than the detection limit in the first day. It can be concluded that the addition of biochar with CMC-nZVI would reduce the transformation effectiveness of Cr(VI) slightly, as the biochar could adsorb a little part of CMC-nZVI which reduced the nZVI-Cr effective contact area, but the immobilization efficiency of Cr$_{\text{total}}$ was higher because the reduction reaction prolonged the remediation time.

**Figure 4** | Remediation effect of CMC-nZVI/BC on Cr immobilization.
Speciation of soil-bound Cr

Sequential extraction procedures (SEP) were often used to identify the relative availability or leaching of heavy metals by dividing the speciation of a metal into five fractions. The five species have been defined as exchangeable (EX), carbonate-bound (CB), Fe-Mn oxides-bound (OX), and organic matter-bound (OM) and residual (RS). The relative availability follows the order of EX > CB > OX > OM > RS. Three kinds of samples, S1-2, S2-3 and S3-1, were selected according to the TCLP experiments’ result, as they were the best dosage in each group, and furthermore to explore the morphological transformation of Cr in soils with different amendments. As Figure 5 shows, Cr species in untreated soil mainly existed in exchangeable (EX, 42.0%) and Fe-Mn oxidized-bound (OX, 40.3%) forms. After being amended with CMC-nZVI for 21 d, the EX fraction in S1-3 decreased to 12.0% by 30.0% and was mainly converted to CB, OX and OM, which increased by 20%, 3% and 6.1% respectively. Finally, the Cr species in the soil of S1-3 remediated with CMC-nZVI mainly consisted of carbonate-bound (EX, 32.9%), Fe-Mn oxidized-bound (OX, 51.4%) and organic matter-bound (OM, 9.8%) forms.

The significant change of Cr species in the soil from higher relative availability of EX converted to a lower relative availability of CB and OX may be due to the fact that Cr in the soil is mainly in the form of Cr(OH)₃ or Cr(III)/Fe(III) hydroxide after being amended by nZVI and was immobilized by soil particles as adsorption, which increased the CB-bound and Fe-Mn-bound fractions. Compared with that in untreated soil, a little part of the OX fraction in S2-3 treated with biochar was converted to OM by 7.9% but the EX and CB was almost unchanged, which corresponded to the result that biochar applied alone could not reduce the leachability of Cr in soil significantly. Moreover, compared with that in untreated soil, the EX fraction in S3-1 amended with CMC-nZVI/BC was reduced to 21.4% by 20.6% and was mainly converted to CB by 21.1%. However, compared with that in S1-3 treated with CMC-nZVI, the EX in S3-1 increased respectively by 9.4% while the OX and OM were reduced by 3.5% and 6.0%, which explained that the CMC-nZVI mainly converted from EX to OX and OM.

Change of available Fe in soil

0.1 M hydrochloric acid was used as leaching agent to extract the available iron (LY/T 1262-1999), as the soil was acidic in this study. As Figure 6 shows, the available iron in the untreated soil was 1.8 mg/kg and the maximum value of that in S1, S2 and S3 was 131.9 mg/kg, 15.2 mg/kg and 134.8 mg/kg, respectively. It can be concluded that CMC-nZVI and CMC-nZVI used as amended materials can significantly increase the available iron content in the soil and the maximum can be increased about 73 times. From the above TCLP results, when the Cr(VI) contaminated soil was treated with CMC-nZVI at the dosage of S1-2 or treated with CMC-nZVI at the dosage of S3-1 both can achieve a desirable remediation effect on Cr in the simulated outdoor condition. Furthermore, in order to avoid the stress of plant growth caused by the excessively high iron content in the soil and reduce the cost, the dosage of S3-1 should be used as in situ amended materials for hexavalent chromium contaminated soil.
CONCLUSION

In this study, the feasibility of the application of CMC-nZVI, BC and CMC-nZVI/BC for the in situ remediation of Cr(VI)-contaminated soil performed outdoors in natural conditions was investigated. The remediation effect of three kinds of amended materials on Cr(VI)-contaminated soil was proportional to the remediation time and the dosage of amended materials. The application of biochar alone cannot effectively remediate the Cr(VI)-contaminated soil at the given concentrations of Cr(VI) in this experiment, while the CMC-nZVI or CMC-nZVI/BC can reduce the leachability of Cr\text{total} or Cr(VI) in the Cr(VI)-contamination soil significantly by over 95% and converted the Cr species in the soil from the higher relative availability of EX to a lower relative availability of CB and OX. The ratio of CMC-nZVI/BC to Cr(VI)-contaminated soil should be 11 g/kg as the best sample in order to achieve the desirable remediation target and save cost. The ecological toxicity of the stabilized nanoscale zero-valent iron was further investigated before the farmland application.

ACKNOWLEDGEMENTS

This research was supported by the Guangdong Technology Research Centre for Ecological Management and Remediation of Urban Water Systems, the National College Students Innovation and Entrepreneurship Training Program, the Guangzhou External Science and Technology Cooperation Project (2016201604030002) and the Guangdong Provincial Science and Technology Project (2016A02021029). Runyuan Zhang, the first author, is now at South China University of Technology for further study.

REFERENCES


Ministry of Environmental Protection of P.R. China 2009 HJ 491-2009 Determination of total chromium-Flame atomic absorption spectrometry.


Ministry of Environmental Protection of P.R. China 2014 HJ 704-2014 Determination of available phosphorus-sodium.
hydrogen carbonate solution-Mo-Sb anti spectrophotometric method.
State Forestry Administration of P.R. China. 1999 LY/T 1239-1999a Determination of pH value in forest soil.

First received 22 March 2017; accepted in revised form 13 January 2018. Available online 1 February 2018