A porous biochar supported nanoscale zero-valent iron highly efficient for the remediation of cadmium and lead contaminated soil

Wei Qian
　Zhongkai University of Agriculture and Engineering

Zeng-Hui Diao（✉ zenghuid86@163.com）
　Zhongkai University of Agriculture and Engineering

Research Article

A porous biochar supported nanoscale zero-valent iron highly efficient for the remediation of cadmium and lead contaminated soil

Wei Qian[1], Zeng-Hui Diao [1,2*]

[1] Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China

[2] Hong Kong Polytechnic University, Hong Kong

* Corresponding author:

E-mail address: zenghuid86@163.com (Z.H. Diao).

Abstract

Risk associated with heavy metals in soil has been received widespread attention. In this study, a porous biochar supported nanoscale zero-valent iron (BC-nZVI) was applied to immobilize cadmium (Cd) and/or lead (Pb) in clayey soil. Experiment results indicated that the immobilization of Cd or Pb by BC-nZVI process was better than that of BC or nZVI process, and about 80 % of heavy metals immobilization was obtained in BC-nZVI process. Addition of BC-nZVI could increase soil pH and organic matter (SOM). Cd or Pb immobilization was inhibited with coexisting organic compound 2,4-dichlorophenol (2,4-DCP), but 2,4-DCP could be removed in a simultaneous manner with Cd or Pb immobilization at low concentration levels. Simultaneous immobilization of Cd and Pb was achieved in BC-nZVI process, and both Cd and Pb availability significantly decreased. Stable Cd species inculding $Cd(OH)_2$, $CdCO_3$ and CdO were formed, whereas stable Pb species such as $PbCO_3$, PbO and $Pb(OH)_2$ were produced with BC-nZVI treatment. Simultaneous immobilization mechanism of Cd and Pb in soil by BC-nZVI was thereby proposed. This study well demonstrates that BC-nZVI has been emerged as a potential technology for the remediation of multiple metals in soil.

Keywords: Cadmium (Cd); Lead (Pb); Biochar; Nano zero valent iron (nZVI); Contaminated soil; Heavy metals.

1. Introduction

Heavy metal contamination in environment is considered as one of the most serious environmental issues worldwide (Arshadi et al, 2014; Ren et al, 2017; Zama et al, 2017; Yang et al, 2018; Wang et al, 2020). Numerous heavy metals (ie., cadmium (Cd), lead (Pb) and chromium (Cr)) are non-biodegradable, and accumulate in living organisms (Zhou et al, 2014; Weng et al, 2016; Qian et al, 2019; Liu et al, 2020; Yang et al, 2020), which are contaminants with high toxicity to both human beings and ecosystem even at low concentration levels (Kumari et al, 2015; Wang et al, 2019). Particularly, both Cd and Pb are widely distributed in water and soil through anthropogenic activities and natural activities (Lee et al, 2009; Diao et al, 2018; Qiu et al, 2020), which are usually used in many industrial applications including storage battery and painting pigment and cause serious water, soil and air pollution (Arshadi et al, 2014; Puga et al, 2015; Ahmad et al, 2016; Awual et al, 2018). They are all listed as human carcinogens according to the US EPA (Tchounwou et al, 2014). Thus, the remediations of Cd and Pb contaminated water and soil are urgent.

Up to date, various kinds of remediation techniques have been developed, such as phytoremediation, electrokinetic remediation, chemical precipitation, ion exchange, adsorption and biosorption processes (Ma et al, 2010; Mahar et al, 2015; Zhu et al, 2016). Among these methods, adsorption has been considered as one of the most effective methods for the remediation of heavy metals due to its low cost and high efficiency in use (Cui et al, 2016; Lyu et al, 2018; Wang et al, 2019). Until now, a great deal of adsorbents have been extensively reported, such as clay minerals,

activated carbons, biochar and nanomaterials (Wang et al, 2014; Qiu et al, 2020). Especially, biochar, a carbon-material produced from pyrolysis of biomass, has been widely applied for heavy metals remediation (Rajapaksha et al, 2016; Ren et al, 2017; Wang et al, 2019). Recently, nano zero valent iron (nZVI) is also considered as one of the most promising remediation materials due to high reactivity (Li et al, 2018; Diao et al, 2020). Numerous studies have well demonstrated that nZVI is effective in remediation of various contaminants in water and soil (Vítkova et al, 2018; Diao et al, 2016; Li et al, 2019). Interestingly, it has been reported that biochar materials are also often used as a support to overcome nZVI aggregation in use (Qian et al, 2017; Liu et al, 2018; Wang et al, 2019), and biochar based iron composites exhibit a superior performance on the remediation of various contaminants (Wang et al, 2019; Zhang et al, 2019).

More recently, a biochar supported zerovalent iron (BC-nZVI) perpared using iron salt and green tea has been reported in our previous work (Liu et al, 2018). But it is still unclear whether Pb and/or Cd in soil could be effictively immobilized using this BC-nZVI. So far, most studies focused on investigating the single heavy metal immobilization by biochar based iron composites (Su et al, 2016; Liu et al, 2020; Mandal et al, 2020), but little studies investigated on the simultaneous immobilization of multiple heavy metals in soil (Bian et al, 2014; Yin et al, 2016; Qiao et al, 2018). Actually, in addition to multiple heavy metals, organic compounds like 2,4-dichlorophenol might also exist in soil (Ma et al, 2020; Diao et al, 2020), and the heavy metal immobilization of biochar based iron composites is significantly

4

74 dependent on different soil properties (Shen et al, 2016; Qiao et al, 2019). Thus it

75 would be more motivated to exam the coexisting effect of organic compound on

76 multiple heavy metals immobilization by this BC-nZVI. Also, the underlying

77 mechanisms of the simultaneous immobilization of Cd and Pb in soil have not been

78 fully explored.

79   Herein, the aims of the present work are to (1) study the immobilization of Cd

80 and/or Pb by BC-nZVI at different conditions; (2) examine the variations of soil

81 properties and heay metals bioavailability; (3) determine transformation products of

82 Cd and Pb in soil during the reaction; (4) illustrate the simultaneous immobilization

83 mechanism of Cd and Pb in soil.

84 2. Materials and methods

85 2.1. Materials and chemicals

86   The chemicals such as $PbCl_2$ and $CdCl_2$ were purchased from Guangzhou

87 Chemical Reagent Company. All chemicals were of the analytical grade or higher.

88 The detail characterizations of BC-nZVI samples were described by our previous

89 study (Liu et al, 2018). Previous results showed that nZVI particles were regularly

90 formed on the surface of BC **(Fig. S1)**. A kind of unpolluted soil sample (farm soil)

91 was collected at 0–20 cm depth from agricultural field in Foshan city, China. The real

92 Cd and Pb contaminated surface soil was collected from a farmland near industrial

93 park site in Qingyuan city, China. All soil samples were dried and filtered through 2

94 mm sieves (Yang et al., 2016), and their main characteristics were shown in **Table S1**.

95 For Cd-spiked soil preparation, $CdCl_2$ solution was added to the uncontaminated soil

96　(2 kg) with the solid-liquid ratio (1:5, w/v), and the mixture continuously stirred for

97　120 h. Then the mixture was air-dried (Yang et al., 2016), Cd concentration of the

98　spiked soil was determined using ICP-MS, and it concentration was 9.86 mg/kg. The

99　prepation procedure of Pb-spiked soil was similar to Cd spiked soil as well as

100　co-spiked soil (ie., Cd/Pb, Cd/2,4-DCP and Pb/2,4-DCP).

101　2.2. Experimental procedure

102　　Batch experiments were conducted with a set of 50 mL centrifuge tubes

103　containing 6 g of Cd and/or Pb spiked soil and 30 mL of BC-nZVI under anaerobic

104　condition. Then these centrifuge tubes was placed on a rotator at 50 rpm to react for

105　16 h. At predetermined time intervals, nearly 100 mg of soil suspension were taken

106　out, and separated by centrifugation for further analysis. Also, the supernatant was

107　further filtered for further analysis. The blank experiments were carried out with the

108　absence of BC-nZVI at equal conditions. Generally, the farm spiked soil was used to

109　explore immobilization of Cd and/or Pb. The reaction conditions were set as

110　following: $[Cd]_0$= 9.86 mg/kg, $[Pb]_0$= 101.32 mg/kg, $[BC\text{-}nZVI]_0$= 2.0 g/L, soil pH=

111　6.54 ± 0.02 and reaction time of 16 h. To compare the immobilization performance of

112　different amendments, BC, nZVI and BC-nZVI were used in this study. The effects of

113　BC-nZVI dosages (0.5-3.0 g/L), coexisting organic compound (2,4-DCP) on Cd

114　and/or Pb immobilization were investigated, respectively.

115　2.3. Analytical methods

116　　The extracted procedures of both Cd and Pb in soil sample were similar to

117　previous study (Qiu et al., 2019). Both Cd and Pb concentrations were determined

according to US EPA method 3050 A (1996), and their five kinds of fractions in soil before and after remediation were determined using sequential extraction procedures (SEP) (Tessier et al, 1979). Total Fe in soil was suffered from acid digestion, and then determined using ICP-MS. The species of elements including Cd, Pb, Fe, O and C on soil surface were analyzed by an X-ray photoelectron spectrometer. The extraction and analysis of 2,4-DCP was similar to our earlier study (Diao et al, 2020). The soil pH was measured by a pH detector using a solid-liquid ratio (1:2.5, w/v). The soil cation exchange capacity (CEC) was measured according to Qiu et al. (2019). Soil organic matter (SOM) was determined according to previous study (Nelson and Sommers, 2001). Soil texture was measured according to Bowman and Hutka (2002). All the analysis was performed in triplicate, and the result was calculated as the average. The statistical analysis was shown in Supplementary Materials.

3. Results and discussion

3.1. Immobilization efficiency of Cd and Pb using various amendments

As illustrated in **Fig. 1a**, the immobilization efficiency of Cd or Pb was signficantly dependent on different amendments and reaction time. Within 16 h, the immobilization efficiency of Cd or Pb increased as reaction time increased. For Cd, nearly 34 % of Cd immobilization was obtained using BC, which might be the complexation of oxygen-containing functional groups on BC (Wang et al., 2019; Qiu et al., 2020). A slight increase in Cd immobilization was observed from nZVI, and 49.21 % of Cd immobilization was achieved, suggesting that nZVI exhibited a better

7

140   preformance on Cd immobilization than BC. In fact, iron oxide and hydroxide might

141   be formed on nZVI, which was favorable to Cd immobilization (Li et al., 2018).

142   Obviously, compared with BC and nZVI, BC-nZVI exhibited the highest Cd

143   immobilization efficiency (86.49 %). It was clearly demonstrated that a high

144   performance on Cd immobilization by BC-nZVI had been sucessfully obtained. A

145   similar trend was observed in Pb immobilization, and nearly 30, 44 and 80 % of Pb

146   immobilization were obtained in BC, nZVI and BC-nZVI processes, respectively **(Fig.**

147   **1b)**. Also, the highest immobilization efficiency was still obtained from BC-nZVI

148   process, suggesting that oxygen-containing functional groups, iron oxide and iron

149   hydroxide on BC-nZVI contributed to Pb immobilization (Liu and Zhao, 2013). It

150   should be noted that Pb immobilization by all processes were always lower than Cd

151   since Pb concentration was higher than that of Cd. Furthermore, the variations of soil

152   pH and organic matter (SOM) induced by different amendments were also evaluated

153   **(Table S2).** The pH values of all treatments increased when different amendments

154   were added. For Cd case, pH values increased from 6.54 for blank to 6.82, 6.68 and

155   6.79 in the presence of nZVI, BC and BC-nZVI, respectively. This suggests an

156   increase in soil pH by adding BC based material, which was mainly associated with

157   the alkaline nature of BC (Qian et al., 2019). This clearly confirmed that BC-nZVI

158   could retard the soil acidity. For nZVI treatment, nZVI could also increase soil pH,

159   which was mainly attributable to nZVI corrosion. In fact, the hydrolysis of Cd ions

160   increased with the increase of soil pH, which subsequently resulted in the formation

161   of Cd oxyhydroxides precipitates, and eventually reduced its mobility and reactivity.

Similar phenomenon was observed in several pervious studies (Li et al, 2016; Salam et al, 2019). Besides, SOM significantly increased when BC and BC-nZVI were introduced, which could be explained that BC contains a high organic matter (more than 70 %) (Qiao et al, 2017). The increase in SOM was farvable for replanting in soil since SOM is the main source of nutrients (Yang et al, 2016). For Pb case, the variations of pH and SOM in soil was similar to that of Cd. Overall, BC-nZVI treatment was the most efficient method for Cd and Pb immobilization as well as soil pH and SOM increase.

3.2. Effect of BC-nZVI dosage on Cd and Pb immobilization

As shown in **Fig. 2**, the immobilization efficiencies of both Cd and Pb increased when the BC-nZVI dosage increased. Nearly 49, 71, 86 and 90 % of Cd immobilization were found when BC-nZVI dosage were 0.5, 1.0, 2.0 and 3.0 g/L, respectively **(Fig. 2a).** As expected, more BC-nZVI dosage induced increased available reactive sites (Liu et al, 2020). However, Cd immobilization only increased from 86.19 to 90.12% when BC-nZVI dosage increased from 2.0 to 3.0 g/L. Additionally, Pb immobilization significantly increased from 36.35 to 80.14 % when BC-nZVI dosage increased from 0.5 to 2.0 g/L **(Fig. 2b)**. Similarly, further increase BC-nZVI dosage did not induce an obvious increase in Pb immobilization, and about 85 % of Pb immobilization was obtained at 3.0 g/L. This suggests that a high BC-nZVI dosage might be a waste, BC-nZVI dosage of 2.0 g/L might be an optimal reaction condition for both Cd and Pb immobilization. Additionally, the effect of BC dosage on soil pH and SOM were also examed **(Table S3).** As expected, soil pH

184 significantly rose as BC-nZVI dosage increased. pH values increased from 6.54 for

185 the blank to 6.59, 6.67, 6.79 and 6.92 for Cd treatment when BC dosage was 0.5, 1.0,

186 2.0 and 3.0 g/L, whereas the corresponding values increased from 6.56 for the blank

187 to 6.62, 6.71, 6.83 and 6.97 for Pb treatment, respectively. Meanwhile, the SOM also

188 increased with BC-nZVI dosage increased. Actually, BC, a rich biomass, is favorable

189 to the accumulation and formation of SOM (Qiao et al, 2017; Mandal et al, 2020),

190 leading to a significant increase in SOM.

3.3. Variation of Cd and Pb fractions

192   Generally, five fractions of heavy metals such as exchangeable (EX), carbonate

193 (CB)-bound, iron-manganese oxides (OX)-bound, organic material (OM)-bound and

194 residual (RS) fractions exist in soil (Tessier et al, 1979; Lyu et al, 2018). In order to

195 understand the heavy metals availability in soil, SEP analysis was performed to

196 examine the fractions of both Cd and Pb before and after remediation **(Fig. 3)**. For Cd

197 case, Cd species in untreated soil were EX (59.14 %), CB (14.91 %), OX (13.61 %),

198 OM (5.65 %) and RS (6.69 %). The EX was considered as the most predominant

199 bound for Cd with 59.14 % of participation ratio, and the order of Cd fractions was

200 EX>CB>OX>RS>OM, suggesting that a high Cd availability existed in untreated Cd

201 soil. After remediation, the EX fraction significantly deceased to 10.25 %, whereas

202 CB, OX, OM and RS fractions increased to 15.48, 20.84, 8.20 and 45.23 %,

203 respectively. The RS was regardes as the most predominant bound for Cd with 45.23 %

204 of participation ratio. Furthmore, higher participation ratios of both OX and OM were

205 found in treated soil compared with untreated soil, which might be attributed to both

206 sorption and precipitation of Cd on the BC-nZVI surface through oxygen-containing

207 functional groups and iron oxyhydroxides. These results clearly demonstrate a less

208 availability of Cd was achieved after BC-nZVI treatment. This result was well agreed

209 with earlier studies (Qiao et al, 2017; Ren et al, 2017). Furthermore, the variation

210 fractions of Pb during the reaction were similar to that of Cd. Before remediation, Pb

211 species in untreated soil were EX (57.65 %), CB (12.34 %), OX (14.62 %), OM

212 (7.96 %) and RS (7.43 %). However, the EX fraction significantly decreased to

213 12.47 %, whereas CB, OX, OM and RS fractions increased to 16.59, 21.15, 8.90 and

214 40.89 %, respectively, suggesting that Pb availability in soil significantly decreased

215 after BC-nZVI treatment procedure. These results mentioned above confirm that

216 BC-nZVI exhibited a high effectiveness for both Cd and Pb immobilization in soil.

217 3.4. Effect of coexisting organic compound on Cd and Pb
218 immobilization

219   As we all know, heavy metals and organic compounds are always coexist in

220 emvironment (Ma et al, 2010; Liu et al, 2018). In addition to Cd and Pb, organic

221 compounds like 2,4-dichlorophenol (2,4-DCP) might also exist in soil since 2,4-DCP

222 is usually considered as an intermediate of pesticides (Ma et al., 2010; Diao et al.,

223 2020). Thus effect of coexisting 2,4-DCP on Cd or Pb immobilization was examined.

224 For Cd case, an inhibition effect on Cd immobilization when 2,4-DCP was introduced

225 **(Fig. 4a).** The immobilization of Cd decreased from 86.49 for the blank case to 84.12,

226 64.98 and 47.56 % when 2,4-DCP concentrations were 2.56, 6.42 and 12.31 mg/kg,

227 respectively. It was likely that BC-nZVI surface reactive sites were consumed by the

228 added 2,4-DCP, leading to less available reactive sites for Cd immobilization. But it

229 should be worth noting that a negative effect was negligible at low 2,4-DCP

230 concentration, and 83.12 % of Cd immobilization was observed at 2,4-DCP

231 concentration of 2.56 mg/kg. Meanwhile, the removal of 2,4-DCP was also

232 investigated, and nearly 90, 73 and 50 % of 2,4-DCP removal were obtained when its

233 concentrations were 2.56, 6.42 and 12.31 mg/kg, respectively **(Fig. 4b)**. The removal

234 of 2,4-DCP could be mainly due to the adsorption and reduction processes (Jia and

235 Wang, 2012; Diao et al, 2020). This clearly demonstrates that the coexisting 2,4-DCP

236 also could be removed with Cd immobilization. Additionally, a similar trend appeared

237 on Pb immobilization, and Pb immobilization was also inhibited with addition of

238 2,4-DCP **(Fig. 5a)**. The immobilization of Pb decreased from 80.14 for the blank case

239 to 75.41, 50.27 and 30.15 % when 2,4-DCP concentrations were 2.56, 6.42 and 12.31

240 mg/kg, respectively. Also, nearly 82, 53 and 30 % of 2,4-DCP removal were obtained

241 when its concentrations were 2.56, 6.42 and 12.31 mg/kg, respectively **(Fig. 5b)**. It

242 should be pointed out that the negative effect of 2,4-DCP on Pb immobilization was

243 more serious than Cd immobilization.

3.5. Simultaneous immobilization of Cd and Pb in soil

245   As described above, BC-nZVI could effectively immobilize Cd or Pb alone in

246 soil, but Cd and Pb might often exist in real contaminated soil (Puga et al, 2015; Li et

247 al, 2018), it was important to investigate the simultaneous immobilization of Cd and

248 Pb by BC-nZVI. The immobilization of Cd decreased with the increase of Pb

249 concentrations (**Fig. 6a**), suggesting that addition of Pb could inhibit Cd

250   immobilization. The immobilization of Cd decreased from 86.49 % for the blank case

251   to 85.54, 66.45, 51.61 and 30.15 % at Pb concentrations of 10.15, 50.27, 104.16 and

252   201.32 mg/kg, respectively. In fact, the decreased Cd immobilization might be due to

253   the occupation of reactive sites when Pb was added. But no obvious difference was

254   found in Cd immobilization at low Pb concentration (10.15 mg/kg), and nearly 86 %

255   of Cd immobilization was also obtained. Meanwhile, the immobilization of Pb was

256   also monitored **(Fig. 6b)**, about 99, 72, 55 and 30 % of Pb immobilization were

257   obtained when Pb concentrations were 10.15, 50.27, 104.16 and 201.32 mg/kg,

258   respectively, suggesting that the simultaneous immobilization of Cd and Pb was

259   obtained in BC-nZVI process under certain conditions. Furthermore, the speciation

260   transformation of both Cd and Pb was also analyzed **(Fig. 7).** After remediation, the

261   EX fraction significantly deceased from 59.14 to 13.52 %, whereas CB, OX, OM and

262   RS increased to 15.12, 18.82, 10.96 and 41.58 % for Cd immobilization, respectively,

263   whereas the EX fraction significantly deceased from 55.04 to 10.07 %, whereas CB,

264   OX, OM and RS increased to 15.42, 18.35, 9.12 and 47.04 % for Pb immobilization,

265   respectively. These results confirmed that both Cd and Pb availability in soil

266   decreased after BC-nZVI treatment.

267   ## 3.6. Transformation products of both Cd and Pb

268   In order to understand the variations of both Cd and Pb transformation products

269   in soil using BC-nZVI, the surface element compositions of both Cd and Pb were

270   analyzed using XPS. For Cd case, four peaks were observed in the Cd ($3d_{5/2}$) region

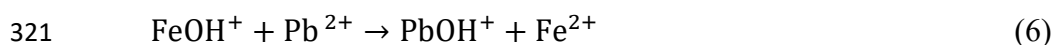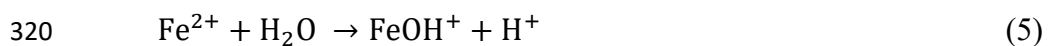271   during the reaction **(Figs. 8a and 8b)**. Four peaks located at 406.50, 405.80, 405.05
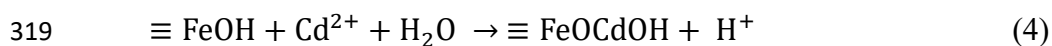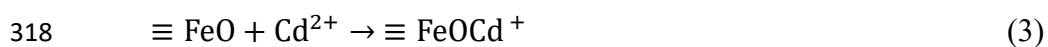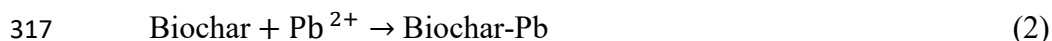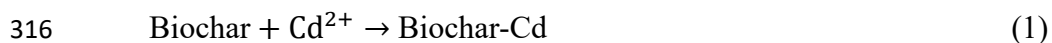
and 404.20 eV corresponding to $CdCl_2$, $CdCO_3$, $Cd(OH)_2$ and CdO were found at 8 h, respectively. Nearly 60 % of the components were assigned to stable Cd species incluling $CdCO_3$, $Cd(OH)_2$ and CdO, but nearly 40 % was still ascribed to free Cd species like $CdCl_2$. After 16 h, there were still four peaks in the Cd ($3d_{5/2}$) region, and peaks located at 406.50, 406.20, 405.80 and 405.05 eV corresponding to $CdCl_2$, $Cd(NO_3)_2$, $CdCO_3$ and $Cd(OH)_2$ were observed, respectively. Nearly 80 % of the components were assigned to stable Cd species incluling $CdCO_3$ and $Cd(OH)_2$, but nearly 20 % was still ascribed to free Cd species such as $CdCl_2$ and $Cd(NO_3)_2$. For Pb case, two peaks were observed in the Pb($4f_{7/2}$) region at 8 h, whereas three peaks were found at 16 h **(Figs. 8c and 8d).** At 8 h, the peak at 139.00 eV was due to free Pb species like $Pb(NO_3)_2$, whereas the peak at 138.40 eV were assigned to stable Pb species such as $PbCO_3$, PbO and $Pb(OH)_2$ (Diao et al, 2018). Only nearly 55 % of the components was still assigned to free Pb species like $Pb(NO_3)_2$, but 45 % was ascribed to stable Pb species. However, about 85 % of the components were assigned to stable Pb species after 16 h. These results mentioned above clearly also confirmed that both Cd and Pb were sucessfully immobilized by BC-nZVI.

3.7. Possible immobilization mechanisms

As mentioned above results, both Cd and Pb could be effectively immobilized by BC-nZVI, and proportion of stable compounds were also high up to 80 % within 16 h. To better understand the immobilization mechanisms of both Cd and Pb by BC-nZVI, the variation of Fe, O and C species in the soil surface during the reaction were also analyzed by XPS technique. As shown in **Fig. 9**, the peaks located at 710.70, 711.40,

713.00, 713.80 and 725.20 eV corresponding to Fe_3O_4, FeOOH, $Fe_2(SO_4)_3$, K_2FeO_4 and Fe_2O_3 were observed from Fe 2p spectrum druing the reaction, respectively (Diao et al, 2018; Liu et al, 2020). It could be explained that nZVI on BC was converted into iron oxide and hydroxide, which plays a quite important role in immobilization of both Cd and Pb. Futhermore, $Cd(OH)_2$, PbO, FeOOH, Fe_3O_4 and OH^- were observed from O 1s spectrum, whereas C=O, C-H and C-C were found from C 1s spectrum (Wang et al, 2019; Liu et al, 2020). These results also suggest these groups on BC surface sinificantly contributed to both Cd and Pb immobilization in soil.

Based on the observation and several previous studies (Yang et al, 2016; Wang et al, 2019), the reaction mechanism for Cd and Pb immobilization in soil by BC-nZVI was thereby proposed in **Fig. 10**. Firstly, BC-nZVI exhibits negative charge through analysis of the Zeta potential (data not shown), free Cd and Pb in cation form can be conveniently adsorbed on the BC-nZVI via the electrostatic attraction process. Also, the oxygen-containing functional groups on the BC-nZVI would complex with free Cd and Pb to form stable species inculding $CdCO_3$, $Cd(OH)_2$, $PbCO_3$ and $Pb(OH)_2$ via the precipitation process. Furthermore, both free Cd and Pb also can be adsorbed on the iron oxide and iron hydroxide on BC-nZVI surface due to their flocculation and precipitation properties. It should be noted that, due to the standard potentials of Cd, Pb and nZVI, the most likely immobilization mechanism of Cd immobilization by BC-nZVI was the adsorption and precipitation, whereas the corresponding mechanism of Pb was the adsorption, reduction and precipitation. The main reaction processes can be described by the following Eqs (1-8).

$$316 \qquad \text{Biochar} + Cd^{2+} \rightarrow \text{Biochar-Cd} \qquad\qquad (1)$$

$$317 \qquad \text{Biochar} + Pb^{2+} \rightarrow \text{Biochar-Pb} \qquad\qquad (2)$$

$$318 \qquad \equiv FeO + Cd^{2+} \rightarrow \equiv FeOCd^{+} \qquad\qquad (3)$$

$$319 \qquad \equiv FeOH + Cd^{2+} + H_2O \rightarrow \equiv FeOCdOH + H^{+} \qquad\qquad (4)$$

$$320 \qquad Fe^{2+} + H_2O \rightarrow FeOH^{+} + H^{+} \qquad\qquad (5)$$

$$321 \qquad FeOH^{+} + Pb^{2+} \rightarrow PbOH^{+} + Fe^{2+} \qquad\qquad (6)$$

$$322 \qquad PbOH^{+} + H_2O \rightarrow Pb(OH)_2 + H^{+} \qquad\qquad (7)$$

$$323 \qquad 2Fe^{0} + 3Pb^{2+} + 4H_2O \rightarrow 3Pb^{0} + 2FeOOH + 2H^{+} \qquad\qquad (8)$$
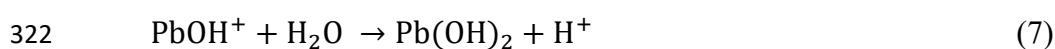
3.8. Application in real Cd and Pb contaminated soil

325   BC-nZVI could effectively immobilize Cd and/or Pb in simulated soil, but the

326   practical applicability in real Cd and Pb contaminated soil is quite important for

327   BC-nZVI in use. Thus, a kind of real Cd and Pb contaminated soil was selected for

328   applicability experiment, which was collected from a farmland near industrial park

329   site in Qingyuan city, China. The main physicochemical properties of real

330   contaminated soil sample were shown in **Table S1**. Accordingly, the concentrations of

331   Cd and Pb were 2.53, 167.12 mg/kg, respectively. Thereby, it was imperative to use

332   this BC-nZVI for the remediation of contaminated soil. Nearly 100 % of Cd

333   immobilization was achieved at the dosage of 1.0 or 3.0 g/L **(Fig. 11a)**, suggesting

334   that an efficient remediation of Cd was obtained at a lower BC-nZVI dosage. For Pb

335   case, nearly 47.25 and 86.02 % of Pb immobilization were observed at the dosage of

336   1.0 and 3.0 g/L, respectively. This suggests that only high BC-nZVI dosage could

induce a higher Pb immobilization in this real contaminated soil. Additionally, the speciation transformation of both Cd and Pb was also investigated **(Fig. 11b).** After remediation, the EX fraction of Cd significantly decreased from 56.85 to 4.59 % at BC-nZVI dosage of 1.0 g/L, whereas the RS fraction increased from 10.23 to 49.29 %, respectively. Meanwhile, the EX fraction of Pb decreased from 55.11 to 10.48 % at BC-nZVI dosage of 3.0 g/L, whereas the RS fraction increased from 8.97 to 40.26 %, respectively. These results clearly demonstrate that both Cd and Pb availability in real contaminated soil significantly decreased after BC-nZVI treatment. Also, both pH and SOM in real contaminated soil increased when BC-nZVI was introduced (**Table S4**), suggesting that the properties of real contaminated soil has been improved. These results confirmed that BC-nZVI also can effectively immobilize both Cd and Pb in real contaminated soil.

3.9. Environmental implications and limitations

The present work well demonstrate that BC-nZVI not only exhibited efficient Cd or/and Pb immobilization performance in simulated soil, but also effectively immobilized Cd and Pb in real contaminated soil in the short term. These findings could provide an insight into the remediation of multiple heavy metals contaminated soil using biochar based iron materials. Also, the treated contaminated soil can meet the revegetation purpose. However, the used soil textures in this work were typically clayey soils, and other environmental conditions such as the soil textures, the rainfall wash cycles and microbial activity might affect Cd and/or Pb immobilization performance. Thus, further studies are needed to exame the immobilization of Cd

and/or Pb in different textures soils as well as the effects of rainfall wash cycles and microbial activity under long-term conditions.

4. Conclusions

In this work, the application of biochar supported nanoscale zero-valent iron (BC-nZVI) as an amendment for the Cd and/or Pb immobilization in soil was systematically invesigated. Results indicated that BC-nZVI process could effectively immobilize Cd or Pb in soil, and the immobilization of Cd and Pb were high up to 86.49 and 80.14 %, respectively. The increased BC-nZVI dosage not only could induce increase of heavy metals immobilization as well as both soil pH and organic matter (SOM), but also could significantly reduce the bioavailability of these metals. A low concentration of 2,4-dichlorophenol (2,4-DCP) could be removed with Cd or Pb immobilization. Simultaneous immobilization of Cd and Pb by BC-nZVI was achieved, and the corresponding bioavailabilies also decreased. Several stable Cd and Pb species such as $CdCO_3$, $Cd(OH)_2$, $PbCO_3$ and $Pb(OH)_2$ were formed after BC-nZVI treatment. Cd immobilization by BC-nZVI was the adsorption and precipitation, whereas Pb immobilization was the adsorption, reduction and precipitation. Overall, our results suggest that BC-nZVI is an efficient amendment to immobilize Cd and Pb in soil and reduce their bioavailability associated with exposure risk.

Author contributions Wei Qian: Investigation, Conceptualization,

391 **References**

392 Awual MR., Khraisheh M, Alharthi NH., Luqman, M, Islamd A, Karim MR, Rahman

393   MM, Khaleque MA (2018) Efficient detection and adsorption of cadmium(II) ions

394   using innovative nano-composite materials. Chem. Eng. J. 343: 118–127.

395 Ahmad M, Ok YS, Kim BY, Ahn JH, Lee YH, Zhang M, Moon DH, AlWabel MI, Lee,

396   SS (2016) Impact of soybean stover- and pine needle-derived biochars on Pb and

397   as mobility, microbial community, and carbon stability in a contaminated

398   agricultural soil. J. Environ. Manag. 166: 131-139.

399 Arshadi M, Soleymanzadeh M, Salvacion JWL, SalimiVahid F (2014) Nanoscale

400   Zero-Valent Iron (NZVI) supported on sineguelas waste for Pb(II) removal from

401   aqueous solution: Kinetics, thermodynamic and mechanism. J. Colloid. Interf. Sci.

402   426: 241–251.

Bian RJ, Joseph S, Cui L, Pan GX, Li LQ, Liu XY, Zhang A, Rutlidge H, Wong SW, Chia C, Marjo C, Gong B, Munroe P, Donne S, (2014) A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment. J. Hazard. Mater. 272: 121–128.

Bowman GM, Hutka J (2002) Soil Physical Measurement and Interpretation for Land Evaluation. Australian Soil and Land Survey Handbooks, CSIRO Publishing, Collingwood, Australia, pp. 224–239.

Cui LQ, Pan GX, Li LQ, Bian RJ, Liu XY, Yan JL, Quan GX, Ding C, Chen TM, Liu Y, Liu YM, Yin CT, Wei CP, Yang, YG., Hussain Q (2016) Continuous immobilization of cadmium and lead in biochar amended contaminated paddy soil: a five-year field experiment. Ecol. Eng. 93: 1–8.

Diao ZH, Du JJ, Jiang D, Kong LJ, Huo WY, Liu CM, Wu QH, Xu XR (2018) Insights into the simultaneous removal of Cr^{6+} and Pb^{2+} by a novel sewage sludgederived biochar immobilized nanoscale zero valent iron: coexistence effects and mechanism. Sci. Total. Environ. 642: 505-515.

Diao ZH, Yan L, Dong FX, Qian W, Deng QH, Kong LJ, Yang JW, Lei ZX, Du JJ, Chu W (2020) Degradation of 2,4-Dichlorophenol by a novel iron based system and its synergism with Cd(II) immobilization in a contaminated soil. Chem. Eng. J. 379: 122313.

Diao ZH, Qian W, Zhang ZW, Jin JC, Chen ZL, Guo PR, Dong FX, Yan L, Kong LJ, Chu W (2020) Removals of Cr(VI) and Cd(II) by a novel nanoscale zero valent iron/peroxydisulfate process and its Fenton-like oxidation of pesticide atrazine:

425   Coexisting effect, products and mechanism. Chem. Eng. J. 397: 125382.

426 Jia HZ, Wang CY (2012) Adsorption and dechlorination of 2,4-dichlorophenol

427   (2,4-DCP) on a multi-functional organo-smectite templated zero-valent iron

428   composite. Chem. Eng. J: 191, 202–209.

429 Kumari M, Pittman Jr CU, Mohan D (2015) Heavy metals [chromium (VI) and lead

430   (II)] removal from water using mesoporous magnetite (Fe_3O_4) nanospheres. J.

431   Colloid. Interf. Sci. 442: 120–132.

432 Li ZT, Wang L, Meng J, Liu XM, Xu JM, Wang F, Brookes P (2018)

433   Zeolite-supported nanoscale zero-valent iron: New findings on simultaneous

434   adsorption of Cd(II), Pb(II), and As(III) in aqueous solution and soil. J. Hazard.

435   Mater. 344: 1–11.

436 Li H, Ye X, Geng Z, Zhou H, Guo X, Zhang Y, Zhao H, Wang G (2016) The influence

437   of biochar type on long-term stabilization for Cd and Cu in contaminated paddy

438   soils. J. Hazard Mater. 304: 40–48.

439 Lee SH, Lee JS, Choi YJ, Kim JG (2009) In situ stabilization of cadmium-, lead-, and

440   zinc-contaminated soil using various amendments, Chemosphere 77: 1069–1075.

441 Lyu HH, Zhao H, Tang JC, Gong YY, Huang Y, Wu QH, Gao B (2018)

442   Immobilization of hexavalent chromium in contaminated soils using biochar

443   supported nanoscale iron sulfide composite. Chemosphere 194: 360-369.

444 Liu L, Liu X, Wang D, Lin H, Huang L (2020) Removal and reduction of Cr(VI) in

445   simulated wastewater using magnetic biochar prepared by co-pyrolysis of

446   nano-zero-valent iron and sewage sludge. J. Clean. Prod. 257: 120562.

447   Liu, XY, Yang L, Zhao HT, Wang W (2020) Pyrolytic production of zerovalent iron

448   nanoparticles supported on rice husk-derived biochar: simple, in situ synthesis

449   and use for remediation of Cr(VI)-polluted soils. Sci. Total Environ. 708:

450   134479.

451   Liu CM, Diao ZH, Huo WY, Kong LJ, Du JJ (2018) Simultaneous removal of Cu^{2+}

452   and bisphenol A by a novel biochar-supported zero valent iron from aqueous

453   solution:synthesis, reactivity and mechanism. Environ. Pollut. 239: 698–705.

454   Liu RQ, Zhao DY (2013) Synthesis and characterization of a new class of stabilized

455   apatite nanoparticles and applying the particles to in situ Pb immobilization in a

456   fire-range soil. Chemosphere 91: 594–601.

457   Liu JJ, Diao Z.H, Liu CM, Jiang D, Kong LJ, Xu XR (2018) Synergistic reduction of

458   Cu^{2+} and oxidation of norfloxacin over a novel sewage sludge-derived

459   char-based catalyst: performance, fate and mechanism. J. Clean. Prod. 182: 794–

460   804.

461   Mandal S, Pu SY, Wang XK, Ma H, Bai YC (2020) Hierarchical porous structure

462   polysulfide supported nZVI/biochar and efficient immobilization of selenium in

463   the soil. Sci. Total Environ. 708: 134831.

464   Mahar A, Wang P, Li R, Zhang Z (2015) Immobilization of lead and cadmium in

465   contaminated soil using amendments: a review. Pedosphere 25: 555-568.

466   Ma JW, Wang FY, Huang ZH, Wang H (2010) Simultaneous removal of

467   2,4-dichlorophenol and Cd from soils by electrokinetic remediation combined

468   with activated bamboo charcoal. J. Hazard. Mater. 176: 715–720.

Nelson DW, Sommers LE (2001) Total carbon, organic carbon, and organic matter, in: Methods of Soil Analysis. Part 3-Chemical Methods. Soil Science Society of America, Inc., American Society of Agronomy, Inc., Madison, Wisconsin, USA, pp. 961–1010.

Puga AP, Abreu CA, Melo LCA, Beesley L (2015) Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. J. Environ. Manag. 159: 86-93.

Qian TT, Wu P, Qin QY, Huang YN, Wang YJ, Zhou DM (2019) Screening of wheat straw biochars for the remediation of soils polluted with Zn (II) and Cd (II). J. Hazard. Mater. 362: 311–317.

Qian LB, Zhang WY, Yan JC, Han L, Chen Y, Ouyang D, Chen MF (2017) Nanoscale zero-valent iron supported by biochars produced at different temperatures: Synthesis mechanism and effect on Cr(VI) removal. Environ. Pollut. 223: 153–160.

Qiao YX, Wu J, Xu YZ, Fang ZQ, Zheng LC, Cheng W, Tsang EP, Fang JZ, Zhao DY (2017) Remediation of cadmium in soil by biochar-supported iron phosphate nanoparticles. Ecol. Eng. 106: 515–522.

Qiao JT, Liu TX, Wang XQ, Li FB, Lv YH, Cui JH (2018) Simultaneous alleviation of cadmium and arsenic accumulation in rice by applying zerovalent iron and biochar to contaminated paddy soils. Chemosphere 195: 260–271.

Qiu Z, Tang JW, Chen JH, Zhang QZ (2020) Remediation of cadmium-contaminated soil with biochar simultaneously improves biochar's recalcitrance. Environ.

Pollut. 256: 113436.

Ren J, Wang FH, Zhai YB, Zhu Y, Peng C, Wang TF, Li CT, Zeng GM (2017) Effect of sewage sludge hydrochar on soil properties and Cd immobilization in a contaminated soil. Chemosphere 189: 627-633.

Rajapaksha AU, Chen SS, Tsang DCW, Zhang M, Vithanage M, Mandal S, Gao B, Bolan NS, Ok YS (2016) Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148: 276–291.

Su HJ, Fang ZQ, Tsang PE, Zheng LC, Cheng W, Fang JZ, Zhao DY (2016) Remediation of hexavalent chromium contaminated soil by biochar-supported zero-valent iron nanoparticles. J. Hazard. Mater. 318: 533–540.

Shen ZT, McMillan O, Jin F, Al-Tabbaa A (2016) Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a short-term laboratory study. J. Hazard. Mater. 316: 214–220.

Salam A, Bashir S, Khan I, Hu HQ, 2019. Two years impacts of rapeseed residue and rice straw biochar on Pb and Cu immobilization and revegetation of naturally co-contaminated soil. Appl. Geochem. 105: 97–104.

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844-851.

Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2014) Heavy metals toxicity and the environment. PMC 26: 133–164.

Vítkova M, Puschenreiter M, Komarek M (2018) Effect of nano zero-valent iron

24

application on As, Cd, Pb, and Zn availability in the rhizosphere of metal(loid) contaminated soils. Chemosphere 200: 217-226.

Wang AQ, Zheng ZK, Li RQ, Hu D, Lu YR, Luo HX, Yan K (2019) Biomass-derived porous carbon highly efficient for removal of Pb(II) and Cd(II). Green. Energy & Environ. 4: 414-423.

Wang T, Jin XY, Chen ZL, Megharaj M, Naidu R (2014) Simultaneous removal of Pb(II) and Cr(III) by magnetite nanoparticles using various synthesis conditions. J. Ind. Eng. Chem. 20: 3543–3549.

Wang L, Cho DW, Tsang DCW, Cao XD, Hou DY, Shen ZT, Alessi DS Ok YS, Poon CS (2019) Green remediation of As and Pb contaminated soil using cement-free claybased stabilization/solidification. Environ. Int. 126: 336–345.

Weng XL, Jin XY, Lin JJ, Naidu R, Chen ZL (2016) Removal of mixed contaminants Cr(VI) and Cu(II) by green synthesized iron based nanoparticles. Ecol. Eng. 97: 32–39.

Wang SS, Zhao MY, Zhou M, Lia YCC, Wang J, Gao B, Sato S, Feng K, Yin WQ, Deshani Igalavithana A, Oleszczuk P, Wang XZ, Ok YS (2019) Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water: a critical review. J. Hazard. Mater. 373: 820–834.

Wang Y, Wang L, Deng X, Gao H (2020) A facile pyrolysis synthesis of biochar/ZnO passivator: immobilization behavior and mechanisms for Cu(II) in soil. Environ. Sci. Pollut. Res. 27: 1888-1897.

Yin DX, Wang X, Chen C, Peng B, Tan CY, Li HL (2016) Varying effect of biochar

on Cd, Pb and As mobility in a multi-metal contaminated paddy soil. Chemosphere 152: 196–206.

Yang ZM, Fang ZQ, Zheng LC, Cheng W, Tsang PE, Fang JZ, Zhao DY (2016) Remediation of lead contaminated soil by biochar-supported nano-hydroxyapatite. Ecotox. Environ. Safe. 132: 224–230.

Yang Q, Li Z, Lu X, Duan Q, Huang L, Bi J (2018) A review of soil heavy metal pollution from industrial and agricultural regions in China: pollution and risk assessment. Sci. Total Environ. 642: 690-700.

Yang T, Han C, Tang J, Luo Y (2020) Removal performance and mechanisms of Cr(VI) by an in-situ self-improvement of mesoporous biochar derived from chicken bone. Environ. Sci. Pollut. Res. 27: 5018-5029.

Zhu F, Li LW, Ma SY, Shang ZF (2016) Effect factors, kinetics and thermodynamics of remediation in the chromium contaminated soils by nanoscale zero valent Fe/Cu bimetallic Particles. Chem. Eng. J. 302: 663-669.

Zhang S, Lyu HH, Tang JC, Song B, Zhen M, Liu X (2019) A novel biochar supported CMC stabilized nano zero-valent iron composite for hexavalent chromium removal from water. Chemosphere 217: 686–694.

Zhou YM, Gao B, Zimmerman AR, Chen H, Zhang M, Cao XD (2014) Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. Bioresour. Technol. 152: 538–542.

Figures
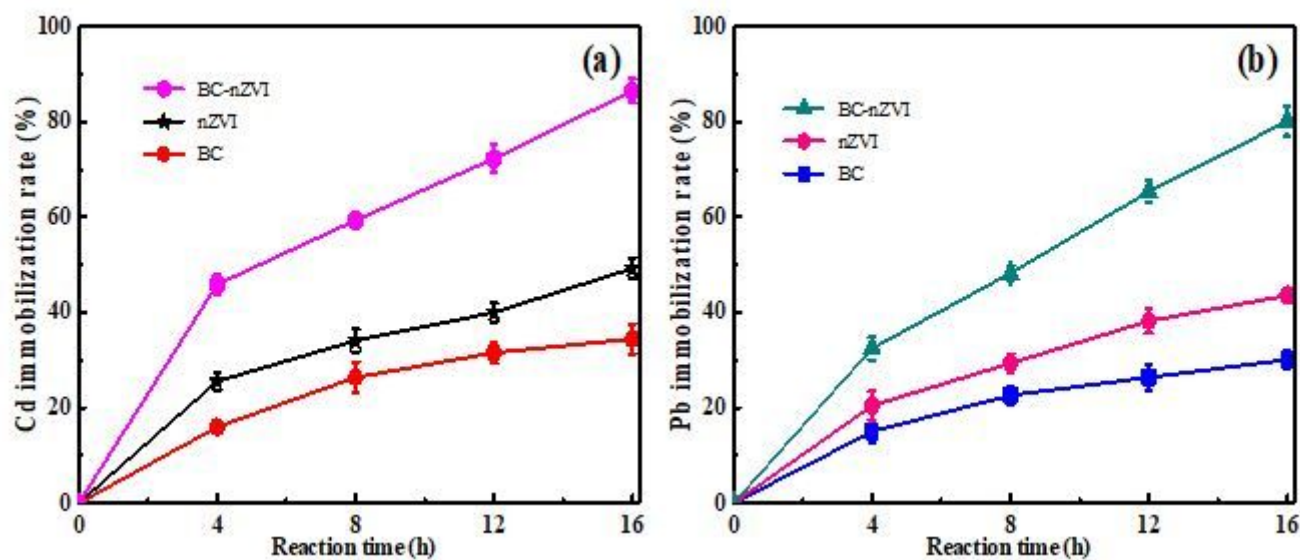
Figure 1

Immobilization efficiency of Cd and Pb by different amendments. Reaction conditions: [Cd]0= 9.86 mg/kg, [Pb]0= 101.32 mg/kg, [BC, nZVI or BC-nZVI]0= 2.0 g/L, pH= 6.54±0.02.
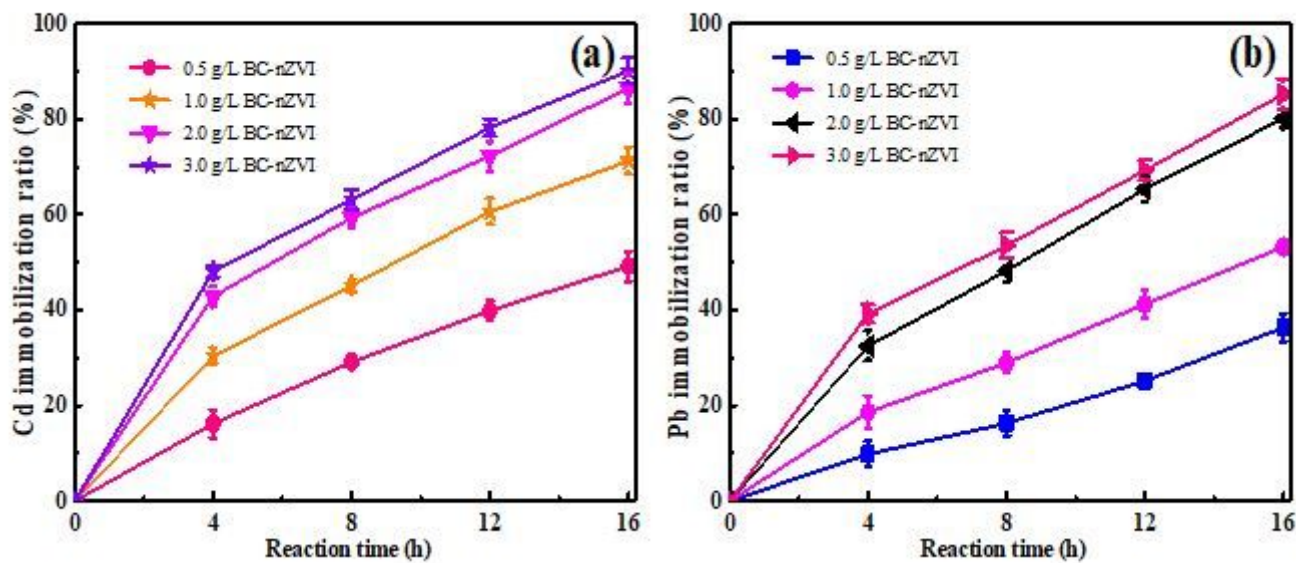
Figure 2

Effect of BC-nZVI dosage on the immobilization of Cd and Pb. Reaction conditions: [Cd]0= 9.86 mg/kg, [Pb]0= 101.32 mg/kg, [BC-nZVI]0= 0.5-3.0 g/L, pH= 6.54±0.02.
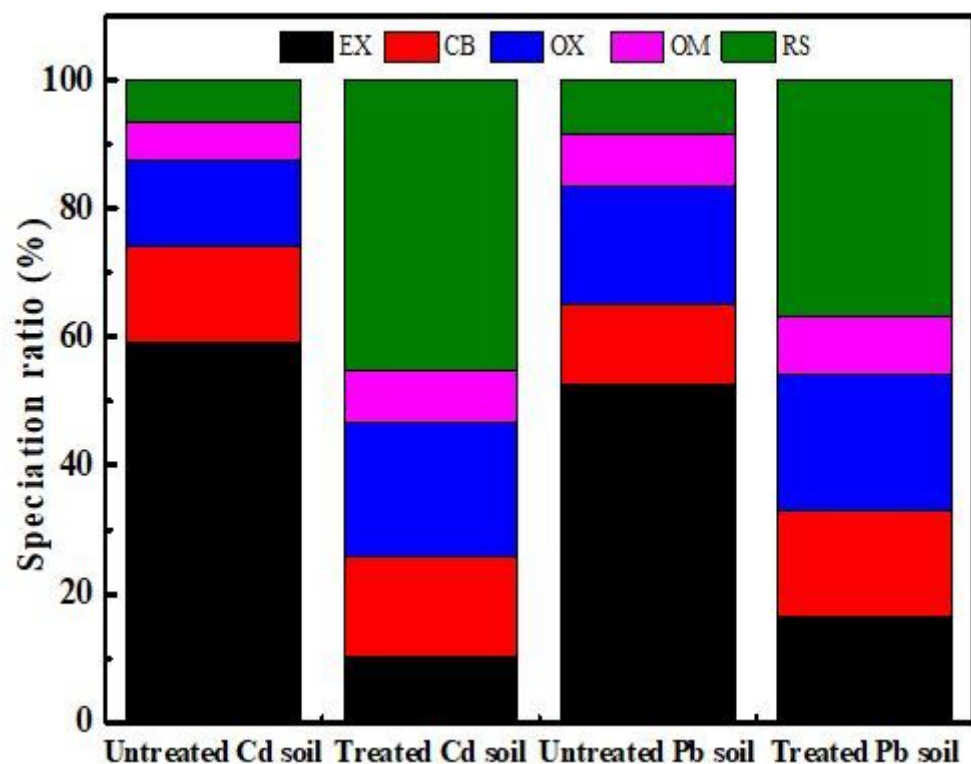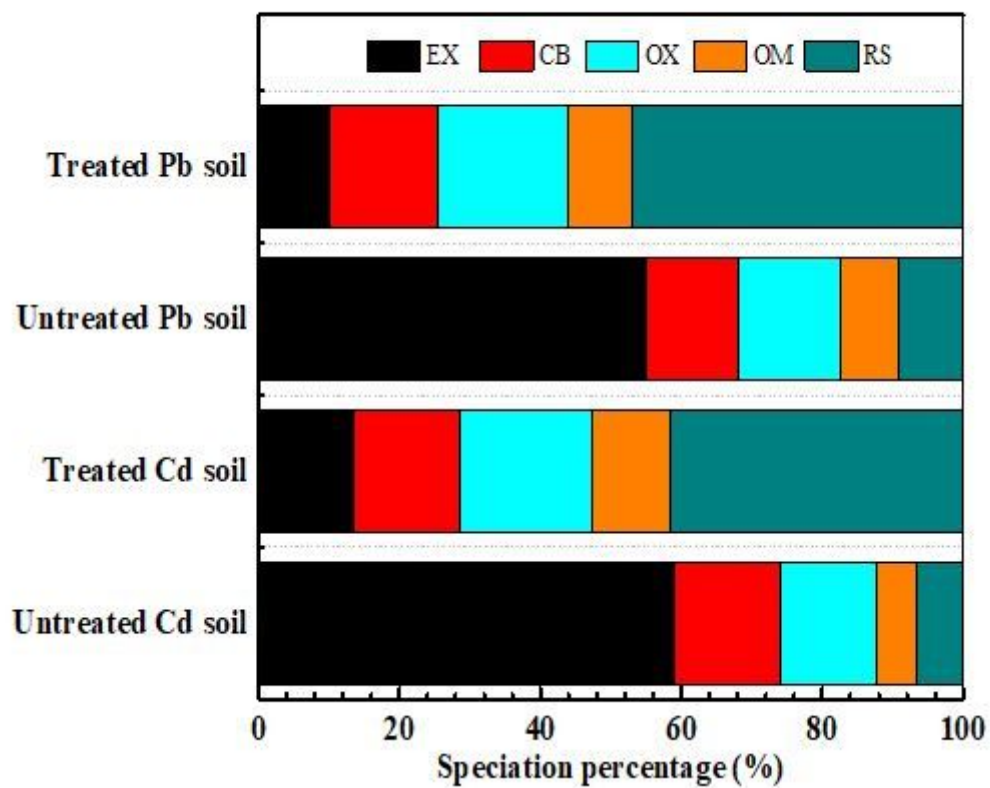
Figure 3

Bioavailability fraction of Cd or Pb in soil before and after remediation. Reaction conditions: [Cd]0= 9.86 mg/kg, [Pb]0= 101.32 mg/kg, [BC-nZVI]0= 2.0 g/L, pH= 5.64±0.02.
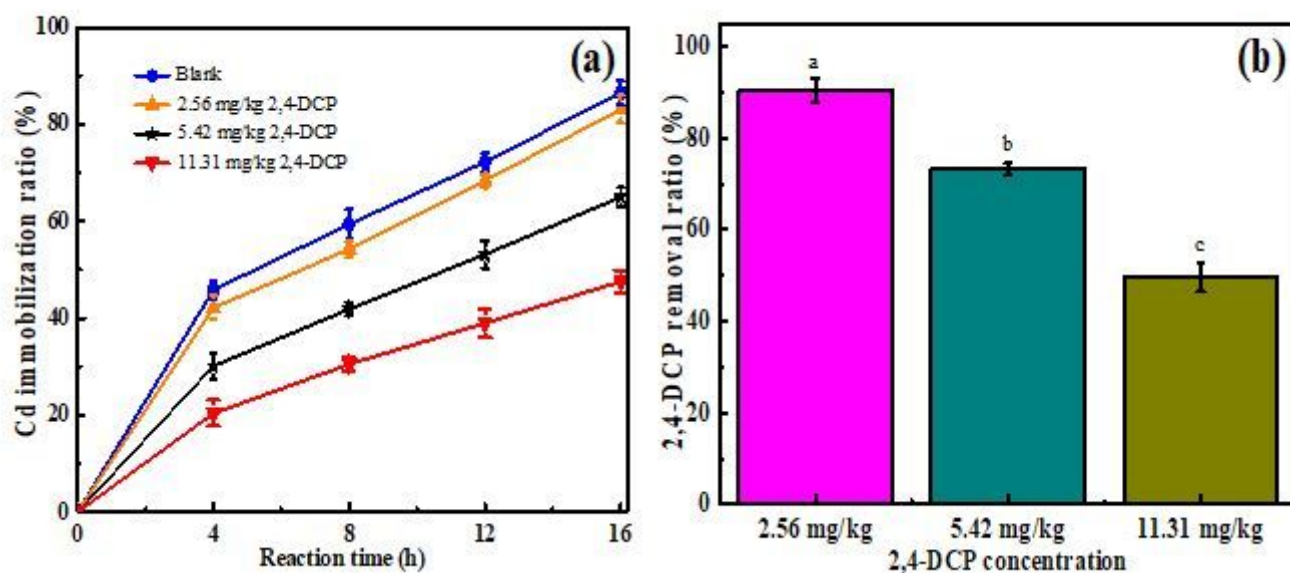
Figure 4

Effect of 2,4-DCP concentrations on Cd immobilization, (a) Cd immobilization; (b) 2,4-DCP removal. Reaction conditions: [Cd]0= 9.86 mg/kg, [2,4-DCP]0= 0-11.31 mg/kg, [BC-nZVI]0= 2.0 g/L, pH= 6.54±0.02.
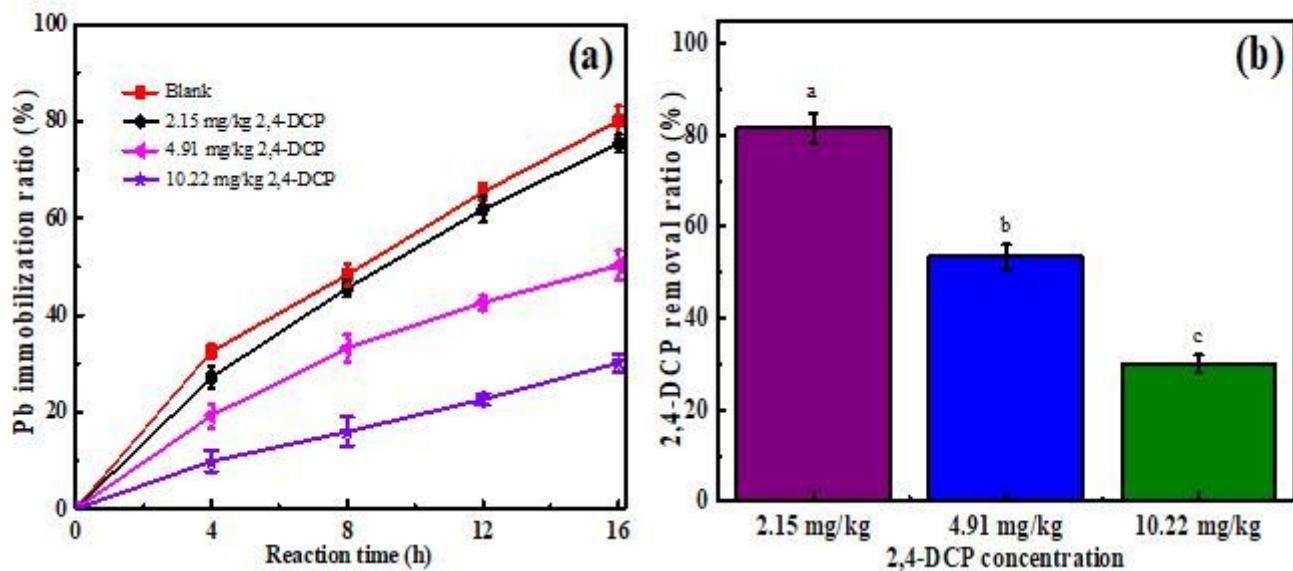
Figure 5

Effect of 2,4-DCP concentrations on Pb immobilization, (a) Pb immobilization; (b) 2,4-DCP removal. Reaction conditions: [Pb]0= 101.32 mg/kg, [2,4-DCP]0= 0-10.22 mg/kg, [BC-nZVI]0= 2.0 g/L, pH= 6.54±0.02.
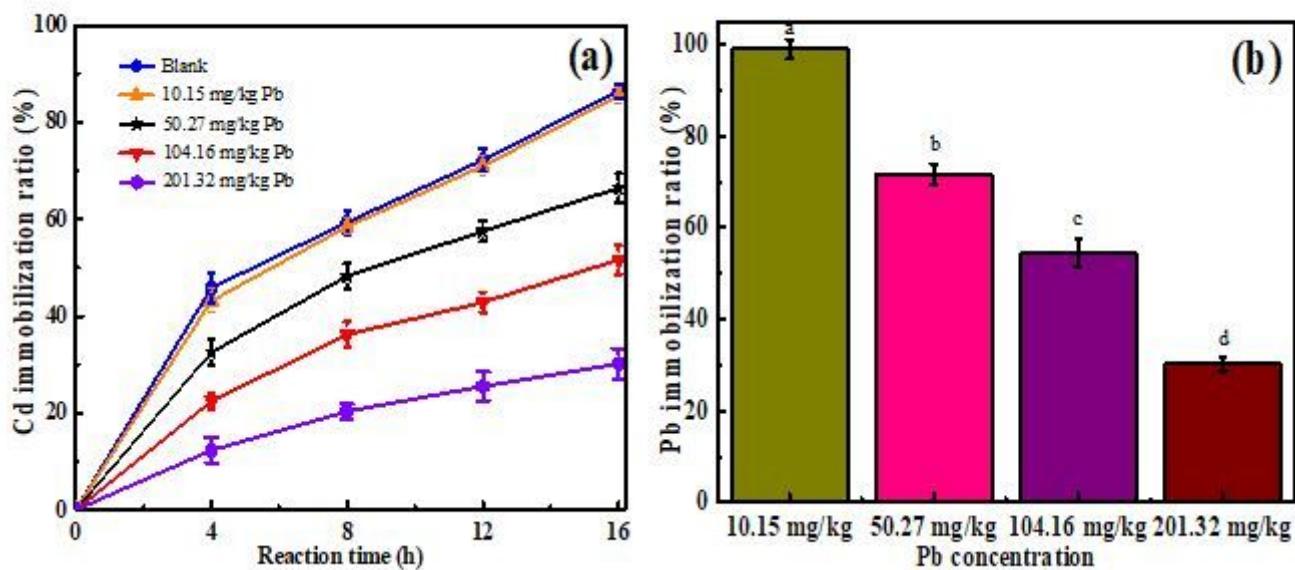
Figure 6

Simultaneous immobilization efficiencies of Cd and Pb in soil. Reaction conditions: [Cd]0= 10.26 mg/kg, [Pb]0= 0-201.32 mg/kg, [BC-nZVI]0= 2.0 g/L, pH= 6.54±0.02.

Figure 7

Bioavailability fractions of Cd and Pb in soil before and after remediation. Reaction conditions: [Cd]0= 9.86 mg/kg, [Pb]0= 10.15 mg/kg, [BC-nZVI]0= 2.0 g/L, pH= 6.54±0.02.
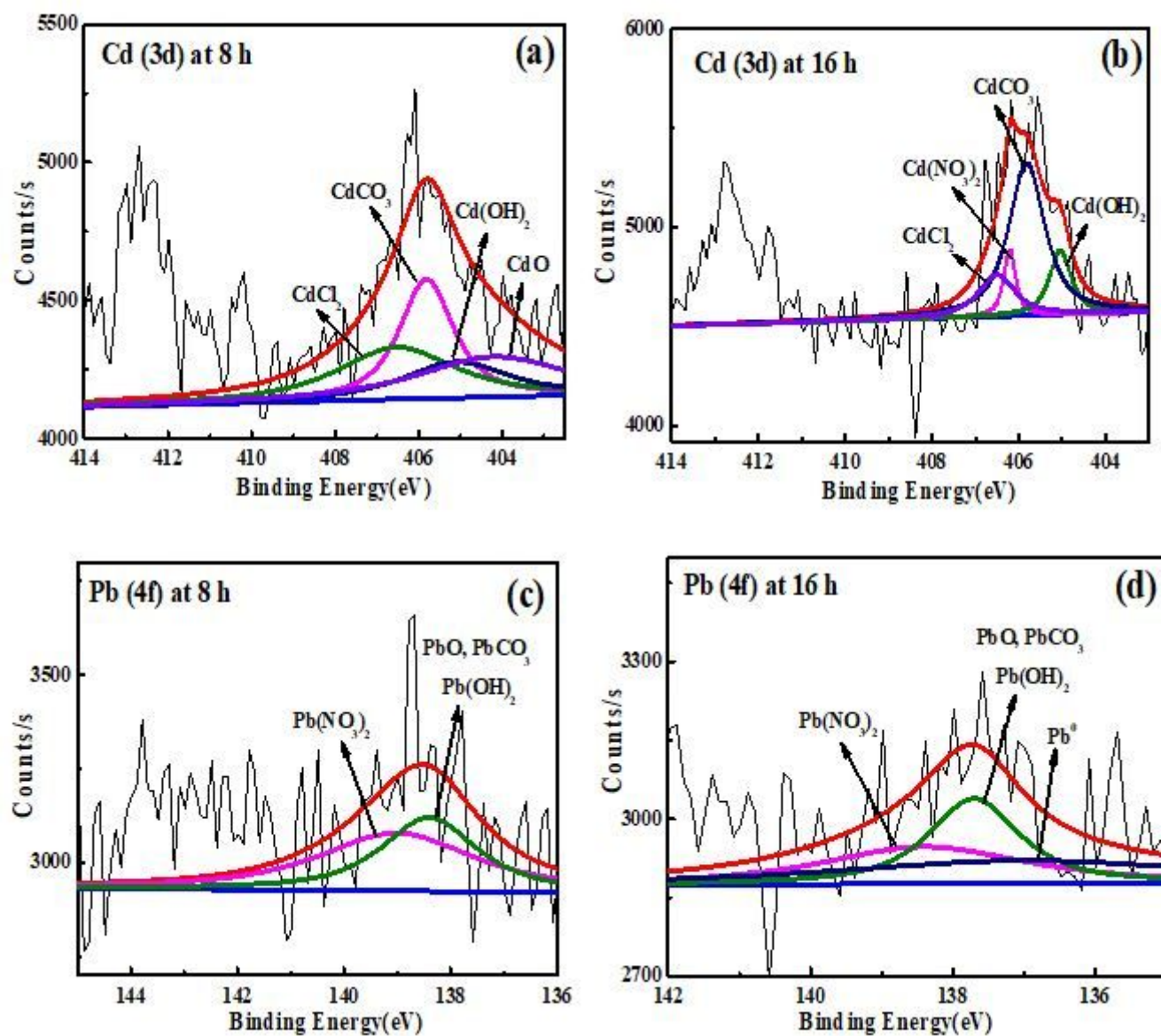
Figure 8

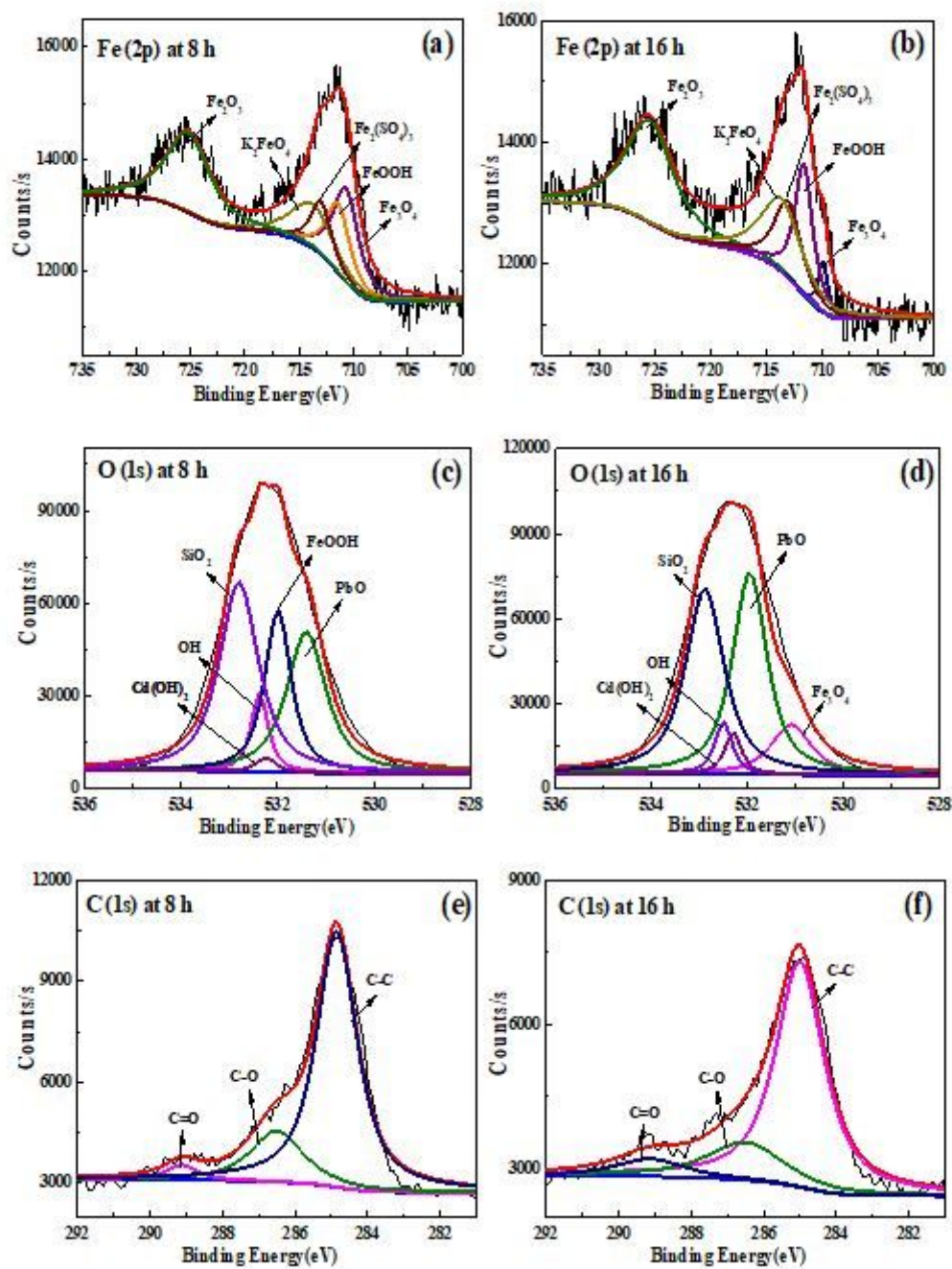XPS spectra variations of Cd(3d) and Pb(4f) during the reaction.

Figure 9

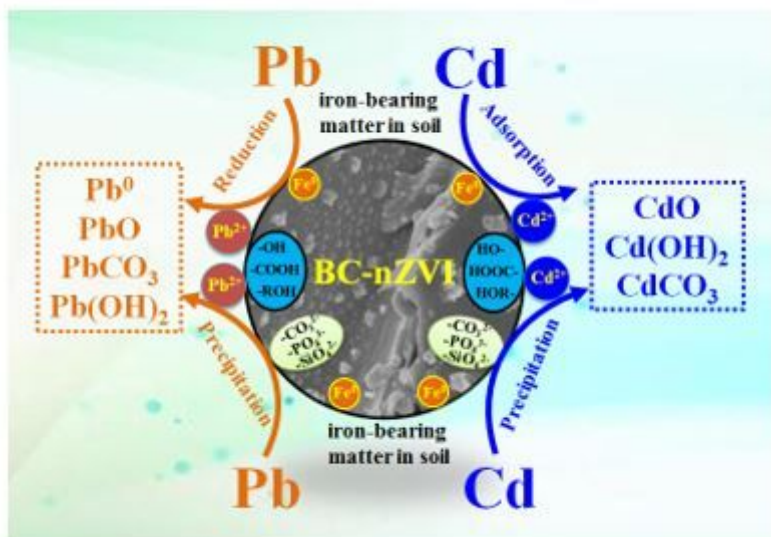XPS spectra variations of Fe(2p), O(1s) and C(1s) during the reaction.

Figure 10

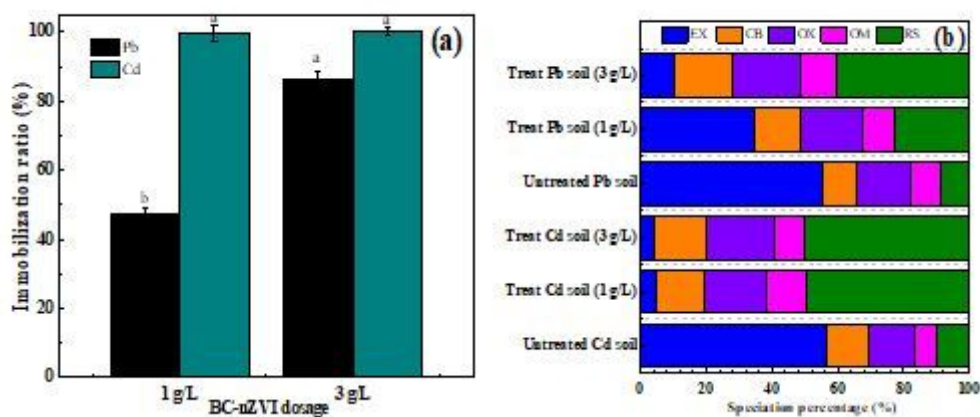The reaction mechanism for Cd and Pb immobilization in soil by BC-Nzvi.

Figure 11

Remediation of Cd and Pb in real contaminated soil by BC-nZVI. Reaction conditions: [Cd]0= 2.53 mg/kg, [Pb]0= 167.12 mg/kg, [BC-nZVI]0= 1.0 and 3.0 g/L, pH= 6.08±0.02.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementaryMaterials0220.docx