

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

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11 **Abstract**

12 Risk associated with heavy metals in soil has been received widespread attention. In
13 this study, a porous biochar supported nanoscale zero-valent iron (BC-nZVI) was
14 applied to immobilize cadmium (Cd) and/or lead (Pb) in clayey soil. Experiment
15 results indicated that the immobilization of Cd or Pb by BC-nZVI process was better
16 than that of BC or nZVI process, and about 80 % of heavy metals immobilization was
17 obtained in BC-nZVI process. Addition of BC-nZVI could increase soil pH and
18 organic matter (SOM). Cd or Pb immobilization was inhibited with coexisting organic
19 compound 2,4-dichlorophenol (2,4-DCP), but 2,4-DCP could be removed in a
20 simultaneous manner with Cd or Pb immobilization at low concentration levels.
21 Simultaneous immobilization of Cd and Pb was achieved in BC-nZVI process, and
22 both Cd and Pb availability significantly decreased. Stable Cd species including
23 Cd(OH)₂, CdCO₃ and CdO were formed, whereas stable Pb species such as PbCO₃,
24 PbO and Pb(OH)₂ were produced with BC-nZVI treatment. Simultaneous
25 immobilization mechanism of Cd and Pb in soil by BC-nZVI was thereby proposed.
26 This study well demonstrates that BC-nZVI has been emerged as a potential
27 technology for the remediation of multiple metals in soil.

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

30 **1. Introduction**

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

45 Up to date, various kinds of remediation techniques have been developed, such
46 as phytoremediation, electrokinetic remediation, chemical precipitation, ion exchange,
47 adsorption and biosorption processes (Ma et al, 2010; Mahar et al, 2015; Zhu et al,
48 2016). Among these methods, adsorption has been considered as one of the most
49 effective methods for the remediation of heavy metals due to its low cost and high
50 efficiency in use (Cui et al, 2016; Lyu et al, 2018; Wang et al, 2019). Until now, a
51 great deal of adsorbents have been extensively reported, such as clay minerals,

52 activated carbons, biochar and nanomaterials (Wang et al, 2014; Qiu et al, 2020).
53 Especially, biochar, a carbon-material produced from pyrolysis of biomass, has been
54 widely applied for heavy metals remediation (Rajapaksha et al, 2016; Ren et al, 2017;
55 Wang et al, 2019). Recently, nano zero valent iron (nZVI) is also considered as one of
56 the most promising remediation materials due to high reactivity (Li et al, 2018; Diao
57 et al, 2020). Numerous studies have well demonstrated that nZVI is effective in
58 remediation of various contaminants in water and soil (Vítkova et al, 2018; Diao et al,
59 2016; Li et al, 2019). Interestingly, it has been reported that biochar materials are also
60 often used as a support to overcome nZVI aggregation in use (Qian et al, 2017; Liu et
61 al, 2018; Wang et al, 2019), and biochar based iron composites exhibit a superior
62 performance on the remediation of various contaminants (Wang et al, 2019; Zhang et
63 al, 2019).

64 More recently, a biochar supported zerovalent iron (BC-nZVI) prepared using
65 iron salt and green tea has been reported in our previous work (Liu et al, 2018). But it
66 is still unclear whether Pb and/or Cd in soil could be effectively immobilized using
67 this BC-nZVI. So far, most studies focused on investigating the single heavy metal
68 immobilization by biochar based iron composites (Su et al, 2016; Liu et al, 2020;
69 Mandal et al, 2020), but little studies investigated on the simultaneous immobilization
70 of multiple heavy metals in soil (Bian et al, 2014; Yin et al, 2016; Qiao et al, 2018).
71 Actually, in addition to multiple heavy metals, organic compounds like
72 2,4-dichlorophenol might also exist in soil (Ma et al, 2020; Diao et al, 2020), and the
73 heavy metal immobilization of biochar based iron composites is significantly

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 its concentration was 9.86 mg/kg. The
99 preparation 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 were 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: $[Cd]_0 = 9.86 \text{ mg/kg}$, $[Pb]_0 = 101.32 \text{ mg/kg}$, $[BC\text{-}nZVI]_0 = 2.0 \text{ g/L}$, 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

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

130 **3. Results and discussion**

131 **3.1. Immobilization efficiency of Cd and Pb using various** 132 **amendments**

133 As illustrated in **Fig. 1a**, the immobilization efficiency of Cd or Pb was
134 significantly dependent on different amendments and reaction time. Within 16 h, the
135 immobilization efficiency of Cd or Pb increased as reaction time increased. For Cd,
136 nearly 34 % of Cd immobilization was obtained using BC, which might be the
137 complexation of oxygen-containing functional groups on BC (Wang et al., 2019; Qiu
138 et al., 2020). A slight increase in Cd immobilization was observed from nZVI, and
139 49.21 % of Cd immobilization was achieved, suggesting that nZVI exhibited a better

140 performance 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 successfully 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.

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

170 **3.2. Effect of BC-nZVI dosage on Cd and Pb immobilization**

171 As shown in **Fig. 2**, the immobilization efficiencies of both Cd and Pb increased
172 when the BC-nZVI dosage increased. Nearly 49, 71, 86 and 90 % of Cd
173 immobilization were found when BC-nZVI dosage were 0.5, 1.0, 2.0 and 3.0 g/L,
174 respectively (**Fig. 2a**). As expected, more BC-nZVI dosage induced increased
175 available reactive sites (Liu et al, 2020). However, Cd immobilization only increased
176 from 86.19 to 90.12% when BC-nZVI dosage increased from 2.0 to 3.0 g/L.
177 Additionally, Pb immobilization significantly increased from 36.35 to 80.14 % when
178 BC-nZVI dosage increased from 0.5 to 2.0 g/L (**Fig. 2b**). Similarly, further increase
179 BC-nZVI dosage did not induce an obvious increase in Pb immobilization, and about
180 85 % of Pb immobilization was obtained at 3.0 g/L. This suggests that a high
181 BC-nZVI dosage might be a waste, BC-nZVI dosage of 2.0 g/L might be an optimal
182 reaction condition for both Cd and Pb immobilization. Additionally, the effect of BC
183 dosage on soil pH and SOM were also examined (**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.

191 **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 decreased to 10.25 %, whereas
202 CB, OX, OM and RS fractions increased to 15.48, 20.84, 8.20 and 45.23 %, respectively.
203 The RS was regarded as the most predominant bound for Cd with 45.23 %
204 of participation ratio. Furthermore, 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 environment (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.

244 **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 decreased 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 decreased 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

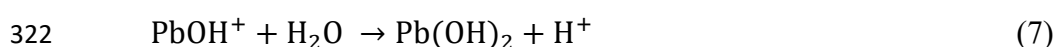
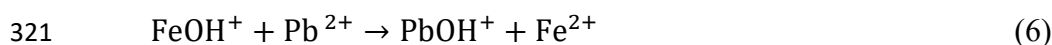
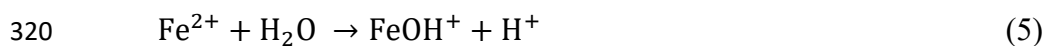
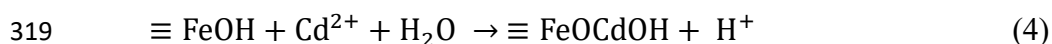
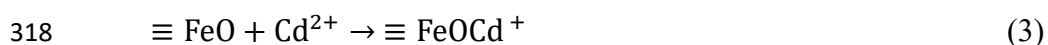
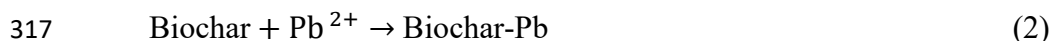
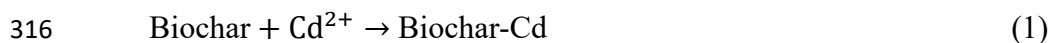
272 and 404.20 eV corresponding to CdCl₂, CdCO₃, Cd(OH)₂ and CdO were found at 8 h,
273 respectively. Nearly 60 % of the components were assigned to stable Cd species
274 including CdCO₃, Cd(OH)₂ and CdO, but nearly 40 % was still ascribed to free Cd
275 species like CdCl₂. After 16 h, there were still four peaks in the Cd (3d_{5/2}) region, and
276 peaks located at 406.50, 406.20, 405.80 and 405.05 eV corresponding to CdCl₂,
277 Cd(NO₃)₂, CdCO₃ and Cd(OH)₂ were observed, respectively. Nearly 80 % of the
278 components were assigned to stable Cd species including CdCO₃ and Cd(OH)₂, but
279 nearly 20 % was still ascribed to free Cd species such as CdCl₂ and Cd(NO₃)₂. For Pb
280 case, two peaks were observed in the Pb(4f_{7/2}) region at 8 h, whereas three peaks were
281 found at 16 h (**Figs. 8c and 8d**). At 8 h, the peak at 139.00 eV was due to free Pb
282 species like Pb(NO₃)₂, whereas the peak at 138.40 eV were assigned to stable Pb
283 species such as PbCO₃, PbO and Pb(OH)₂ (Diao et al, 2018). Only nearly 55 % of the
284 components was still assigned to free Pb species like Pb(NO₃)₂, but 45 % was
285 ascribed to stable Pb species. However, about 85 % of the components were assigned
286 to stable Pb species after 16 h. These results mentioned above clearly also confirmed
287 that both Cd and Pb were successfully immobilized by BC-nZVI.

288 **3.7. Possible immobilization mechanisms**

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

294 713.00, 713.80 and 725.20 eV corresponding to Fe_3O_4 , FeOOH , $\text{Fe}_2(\text{SO}_4)_3$, K_2FeO_4
295 and Fe_2O_3 were observed from Fe 2p spectrum during the reaction, respectively (Diao
296 et al, 2018; Liu et al, 2020). It could be explained that nZVI on BC was converted into
297 iron oxide and hydroxide, which plays a quite important role in immobilization of
298 both Cd and Pb. Furthermore, $\text{Cd}(\text{OH})_2$, PbO , FeOOH , Fe_3O_4 and OH^- were observed
299 from O 1s spectrum, whereas C=O, C-H and C-C were found from C 1s spectrum
300 (Wang et al, 2019; Liu et al, 2020). These results also suggest these groups on BC
301 surface significantly contributed to both Cd and Pb immobilization in soil.

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



324 **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

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

349 **3.9. Environmental implications and limitations**

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

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

361 **4. Conclusions**

362 In this work, the application of biochar supported nanoscale zero-valent iron
363 (BC-nZVI) as an amendment for the Cd and/or Pb immobilization in soil was
364 systematically investigated. Results indicated that BC-nZVI process could effectively
365 immobilize Cd or Pb in soil, and the immobilization of Cd and Pb were high up to
366 86.49 and 80.14 %, respectively. The increased BC-nZVI dosage not only could
367 induce increase of heavy metals immobilization as well as both soil pH and organic
368 matter (SOM), but also could significantly reduce the bioavailability of these metals.
369 A low concentration of 2,4-dichlorophenol (2,4-DCP) could be removed with Cd or
370 Pb immobilization. Simultaneous immobilization of Cd and Pb by BC-nZVI was
371 achieved, and the corresponding bioavailabilities also decreased. Several stable Cd
372 and Pb species such as CdCO_3 , $\text{Cd}(\text{OH})_2$, PbCO_3 and $\text{Pb}(\text{OH})_2$ were formed after
373 BC-nZVI treatment. Cd immobilization by BC-nZVI was the adsorption and
374 precipitation, whereas Pb immobilization was the adsorption, reduction and
375 precipitation. Overall, our results suggest that BC-nZVI is an efficient amendment to
376 immobilize Cd and Pb in soil and reduce their bioavailability associated with
377 exposure risk.

378 **Acknowledgements** Prof. Wei Chu for encouragement and enthusiasm during
379 this study.

380 **Author contributions** Wei Qian: Investigation, Conceptualization,

381 Writing-original draft; Zeng-Hui Diao: Writing review & editing, Supervision. All
382 authors read and approved the final manuscript.

383 **Funding** This research was supported by the National Natural Science Foundation
384 of China (No. 21407155) and Guangdong Provincial Key R&D Programme
385 (2020B1111350002).

386 **Data and materials availability** Not applicable

387 **Declarations**

388 **Ethics approval and consent to participate** Not applicable.

389 **Consent for publication** Not applicable.

390 **Competing interests** The authors declare no competing interests.

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