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Effects of acidic and neutral biochars on properties and cadmium retention of soils

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24 Abbreviations

25 ANC = Acid neutralization capacity

26 Ba = Soil from Mt Bygalore (Ferrosol, acidic)

27 CEC = Cation exchange capacity

28 CL biochar = Chicken litter biochar

29 EC = Electrical conductivity

30 Mt = Soil from Mt Shank (Dermosol, alkaline)

31 PyC = Pyrogenic carbon

32 TOC = Total organic carbon

33 WS biochar = Wood shaving biochar

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44 **Abstract**

45 In this study, an acidic biochar and a neutral biochar were applied at 5 wt% into two
46 soils for an 11-month incubation experiment. One Ferrosol soil (Ba) was slightly acidic
47 with low organic matter and the other Dermosol soil (Mt) was slightly alkaline with high
48 organic matter. The acidic (pH=3.25) wood shaving (WS) biochar had no marked impact on
49 nutrient levels, cation exchange capacity (CEC), pH and acid neutralisation capacity (ANC)
50 of either soil. By contrast, the neutral (pH=7.00) chicken litter (CL) biochar significantly
51 increased major soluble nutrients, pH, ANC of soil Ba. In terms of C storage, 87.9% and
52 69.5% WS biochar-C can be sequestered as TOC by soil Ba and Mt, respectively, whereas
53 only 24.0% of CL biochar-C stored in soil Ba and negligible amount in Mt as TOC.
54 Biochars did not have significant effects on soil sorption capacity and sorption reversibility
55 except that CL biochar increased sorption of soil Ba by around 25.4% and decreased
56 desorption by around 50.0%. Overall, the studied acidic C rich WS biochar held little
57 agricultural or remedial values but was favourable for C sequestration. The neutral mineral
58 rich CL biochar may provide short-term agricultural benefit and certain sorption capacities
59 of lower sorption capacity soils, but may be unlikely to result in heightened C sequestration
60 in soils. This is the first study comprehensively examining functions of acidic and neutral
61 biochars for their benefits as a soil amendment and suggests the importance of pre-testing
62 biochars for target purposes prior to their large scale production.

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64 **Keyword:** Acidic biochar, neutral biochar, soil, C sequestration, sorption

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69 1. Introduction

70 Biochars are carbon-rich products produced through thermochemical processing of
71 biomass under an oxygen-deficient environment (Cao and Harris, 2010; Venegas et al.,
72 2015). It has been a hot topic of research in recent years due to its versatile role in soil
73 biogeochemical processes. The most important environmental functions of biochar include
74 acting as a long-term carbon sink for climate change mitigation (Lehmann, 2007b;
75 McBeath and Smernik, 2009; Bird et al., 2017), a soil conditioner that increases soil
76 nutrient retention, cation exchange capacity (CEC), soil fertility and crop yield (Liang et al.,
77 2006; Downie et al., 2011; Qu et al., 2016), and an in situ immobilizer for soil heavy metal
78 contaminants (Cao et al., 2009; Uchimiya et al., 2011a; Qian et al., 2013; Lu et al., 2017).
79 Biochars perform in these processes by increasing soil organic carbon and reducing
80 greenhouse gas emission (Lehmann, 2007b), increasing soil pH, acid neutralisation capacity
81 (ANC) and CEC (Glaser et al., 2002; Cheng et al., 2006; Yuan and Xu, 2011; Venegas et
82 al., 2015) as well as increasing soil intrinsic binding sites for soil contaminants (Cao and
83 Harris, 2010; Beesley et al., 2011; Uchimiya et al., 2011c).

84 Biochars are commonly alkaline (Jiang et al., 2012a) which contribute to their
85 liming effects and enhanced sorption of soils for cationic contaminants. However, biochar
86 pH values can range from acidic to alkaline (Chan and Xu, 2009) and lower pH biochars
87 are normally neglected. Biochar pH increases with increasing pyrolysis temperature as
88 more acidic functional groups can be removed at higher temperatures (Ippolito et al., 2016).
89 Biochars produced under low pyrolysis temperatures can be acidic (Novak et al., 2009;
90 Hagner et al., 2016; Zhang et al., 2017). For example, birch (*Betula spp.*) biochar produced
91 at 300 °C and 375 °C were shown to be acidic (pH=5.1 and 5.2, respectively) (Hagner et al.,
92 2016). Pecan shell (350 °C) and switchgrass (250 °C) biochar had a pH of 5.9 and 5.4,
93 respectively (Novak et al., 2009). In limited studies about lower pH biochars, low-

94 temperature (250 and 350 °C) acidic switchgrass biochars were found to lower pH and
95 initially increase plant-available nutrients in aridic calcareous soils (Ippolito et al., 2012;
96 Ippolito et al., 2016). Similarly, neutral biochars may also behave differently from normally
97 available alkaline biochars in environmental processes after being added into soils. From this
98 sense, a more comprehensive examination of potential benefits of acidic and neutral biochar
99 on soil nutrient leaching, C storage and contamination remediation is essential.

100 Cadmium is one of the most hazardous metals and is readily absorbed from soil to
101 plant with a relatively high transfer coefficient and subsequently to animals and human
102 through fodder and food products (Park et al., 2011; Zhao et al., 2015a). In this study, Cd
103 was selected as a model metal to study contaminant retention capacity of soils given its wide
104 presence in agricultural soils due to Cd-rich phosphate fertilizers applications (Naidu et al.,
105 1994; Ali et al., 2013; Muehe et al., 2013). The objectives of this work were to (i) study
106 effects of acidic and neutral biochars on soil properties especially surface charge properties;
107 (ii) examine the C sequestration capacity of acidic and neutral biochars by evaluating soil
108 total organic carbon (TOC) and stable organic carbon (pyrogenic carbon, PyC) content; (iii)
109 explore sorption behaviours and mechanisms of biochar amended soils for Cd.

110

111 **2. Methods**

112 **2.1 Incubation of biochar-amended soils**

113 Two typical Australian soils (0-10 cm) were sampled for this study. One Ferrosol
114 soil from Mt Bygalore (Ba) of New South Wales (S33°39.88', E146°49.07') of Australia
115 that is lower in organic matter content and slightly acidic (pH=6.14, TOC=16.3 mg/g). The
116 other Dermosol soil was sampled from Mt Shank (Mt) of South Australia (S37°56.78',
117 E140°44.59') that is slightly alkaline higher in organic matter soil (pH=7.87, TOC=78.9
118 mg/g). One biochar made from chicken litter (CL, 550 °C) and one from wood shavings

119 (WS, 650 °C) were obtained from commercial producers. The biochars were made by 16-
120 minute slow pyrolysis (8 minutes in the drier, 8 minutes in the pyrolysis chamber) in a
121 Continuous Flow Pyrolyzer. Biochar products were water mist quenched immediately after
122 pyrolysis, then additional water was hosed onto the bulk product. Before use, both biochars
123 were air dried and sieved to pass through a 2-mm stainless steel sieve to represent their
124 typical use as a soil amendment. Biochars were mixed with soils at the ratios 5 wt% on a
125 dry weight base. Soils with/without biochar amendment were incubated at 25 ± 2 °C for 11
126 months in 2L glass jars with holes on the lids. The jars were maintained at 60% water
127 holding capacity (WHC) and weighed for water replenishment every week within the first 3
128 months and every fortnight thereafter. Incubation of all samples were in duplicates. At the
129 end of the 11 months, the soil samples were dried and sieved (<2 mm or <150 μm) for
130 further chemical analysis and the sorption experiment. These soil samples after 11 months
131 incubation were used for following analysis and sorption experiment. Following the way
132 “soil name + months of incubation + biochar types”, the samples were recorded as Ba11,
133 Ba11WS, Ba11CL, Mt11, Mt11WS, Mt11CL, respectively.

134

135 **2.2 Soil and biochar characterization before and after treatment**

136 Soil and biochar pH, electrical conductivity (EC) were determined using 1:5 and 1:10
137 sample to water ratio, respectively. Soil TOC were determined by combusting oven dried and
138 ground soil samples (<150 μm) at 1100 °C in a CHN Elemental Analyzer (Euro EA 3000
139 Elemental Analyzer, Eurovector SPA, Milano, Italy) that uses infrared technology to quantify
140 CO₂. Soil pyrogenic carbon (PyC), was measured by a chemo-thermal oxidation (CTO-375)
141 method. Both TOC and PyC analysis were collaborated with a lab in Switzerland where same
142 analytical procedure as Agarwal and Bucheli, (2011) were applied. Soil and biochar total
143 metals was extracted by microwave digestion in aqua regia following USEPA 3051 40

144 method before detecting metals by inductively coupled plasma mass spectrometry (ICP-MS,
145 Agilent 7900, USA). Soil texture was determined by the hydrometer method (Gee et al.,
146 1986). Amorphous Al, Mn and Fe (Al_{oxa} , Mn_{oxa} , Fe_{oxa}) was extracted by 0.2 M ammonium
147 oxalate/oxalic acid following Rayment and Higginson (1992). The contents (wt%) of carbon
148 (C), hydrogen (H), nitrogen (N), sulphur (S) of biochars were measured by a CHNS analyzer
149 (Vario Micro cube, Elementar, Germany). Ash content (%) was measured by heating samples
150 under 800 °C for 4 h in muffle furnace. The weight percent of oxygen was determined by
151 mass difference (Chen et al., 2008; Cheng et al., 2013; Luo et al., 2016). The acid
152 neutralisation capacity (ANC) of the biochar and soil samples is defined as the quantity of
153 acid or base (cmol H^+ /kg) required to shift the initial pH of the material to a pH of 4
154 (Venegas et al., 2015). In this study, we used a 1:200 solid to liquid ratio in 0.01 M NaNO_3
155 for ANC measurement. Specific surface area of char samples (<2mm) were measured with
156 nitrogen adsorption isotherms at liquid nitrogen temperature (-196 °C) by a Surface Area
157 Analyzer (Micromeritics ASAP 2020 M, USA). Biochar samples (=0.2-0.25 g) were
158 outgassed overnight at 60 °C under vacuum at 2 Torr before N_2 adsorption. The molecular
159 surface area of 16.2 Å² for N_2 and the BET (Brunauer-Emmett-Teller) equation (Brunauer et
160 al., 1938) were used to calculate the surface area of the char samples. Fourier Transformed
161 Infrared Spectroscopy (FTIR) (Nicolet IS10, Thermo Fisher, Waltham, MA, USA) spectra
162 were collected to get information on surface functional groups of char samples. This was
163 done by applying dehydrated KBr disc technique, where char samples (150 µm) char sample
164 were mixed with spectroscopic grade KBr at a ratio of 1:50 before scanning to produce
165 sufficient absorbance. Spectra over the 4000-400 cm^{-1} range were obtained by the co-addition
166 of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Surface
167 morphology of the CL biochar in soil Ba matrix were examined under an Environmental

168 Scanning Electron Microscope (SEM) (Zeiss Sigma, Germany) equipped with a Bruker
169 energy dispersive X-ray spectroscopy (EDS) detector

170 **2.3 Surface charge of soils**

171 Effects of biochars on surface charge properties of soil were assessed by CEC and
172 electrophoretic mobility property of soils. CEC is an indicator of abundance of the negative
173 charge on the surface of a material, which can be balanced by exchangeable cations
174 (Mukherjee et al., 2011; Jiang et al., 2012a; Zhao et al., 2015b; Jiang et al., 2016b). In this
175 study, soil CEC was measured by $\text{BaCl}_2/\text{NH}_4\text{Cl}$ compulsive exchange method described by
176 Gillman and Sumpter (1986). Electrophoretic mobility property of soil samples, often
177 expressed as zeta potential is another way to evaluate soil surface charge properties. Zeta
178 potential is the electrical potential of a sliding plane which is the interface between the Stern
179 and diffuse layers in the double layer model of colloidal particles (Appel et al., 2003; Jiang et
180 al., 2016b). Its electro-negativity depends on the amount of negative surface charges. Soil and
181 biochar-amended soil samples were ground to $<150\mu\text{m}$ before being dispensed into 0.01M
182 NaNO_3 suspension (0.02%, w/v) to guarantee the good suspension of samples. The
183 suspensions were then equilibrated on a rotatory shaker for 24 h. The pH values of
184 suspension were recorded and zeta potential of these suspensions were measured by Zetasizer
185 Nano ZS instrument (Malvern, ZEN3600, UK).

186

187 **2.4 Cadmium sorption and desorption**

188 The Cd sorption experiment was performed using a batch equilibration technique. Our
189 preliminary test showed that the two studied biochars did not show noticeable influence to
190 sorption capacities of both soils under $300\mu\text{M}$ Cd. Hence, we increased Cd concentration to
191 $1500\mu\text{M}$ to evaluate the effects of biochars on maximum sorption capacity of the studied
192 soils. Specifically, the sorption was performed by agitating 1g soils in 30 mL of 0.01 M

193 NaNO₃ solution containing 0, 30, 150, 300, 600, 900, 1200 and 1500 μM Cd(NO₃)₂ on a
194 reciprocating shaker at 200 rpm for 24 h. Solution pH at 0 and 300 μM Cd(NO₃)₂ was
195 recorded after equilibrium, and the mixtures were centrifuged, filtered through 0.22μm
196 cellulose acetate syringe filter and acidified prior to major element (Cd, K, Ca, Na, Mg, Al,
197 Fe, Mn) analysis by ICP-MS (Agilent 7900, USA). Metrohm Ion chromatography was used
198 for PO₄³⁻, Cl⁻, NO₃⁻, SO₄²⁻ analysis (790 Personal IC, Switzerland). Dissolved organic
199 carbon (DOC) and dissolved inorganic carbon (DIC) were measured with TOC analyzer
200 (Multi N/C 3100, Analytik Jena, Germany). The amount of Cd sorbed was calculated by
201 subtracting the remaining Cd concentration after sorption from the initial Cd concentration.
202 Subsequently, Cd speciation was conducted by PHREEQC Interactive v3.3.7 software and
203 sorption isotherms were fitted in to Langmuir models to evaluate the sorption properties of
204 soil samples. After removing all solutions from sorption experiment, desorption studies were
205 carried out at a low (150 μM) and high (1500 μM) Cd loading to assess the reversibility of
206 sorption. Specifically, 30 mL 0.01M NaNO₃ was added to the decanted centrifuged tubes
207 following sorption experiment and mixed end over end at 200 rpm for another 24 h.
208 Detection of Cd was performed by ICP-MS (Agilent 7900, USA).

209

210 **2.5 Statistical analyses**

211 All analysis was conducted in duplicate and expressed as means of the replicates.
212 One-way analysis of variance (ANOVA) were carried out using SPSS version 19.0 to
213 determine the significance of the differences between treatments. The post-hoc least
214 significant difference (LSD) test was employed. When a significant F-value ($p < 0.05$) were
215 obtained, means of treatments were regarded as significantly different.

216

217 3. Results and discussions

218 3.1 Basic soil properties

219 Pertinent properties of soils, biochars and 11-month incubated soils used in this study
220 are listed in Tables 1, 2 and 3, respectively. The WS biochar contained a higher amount of C
221 (75.6%) and minimal amount of ash (1.65%) while CL biochar contained relatively less
222 carbon (33.7%) but considerable amount of ash (46.2%). High ash contents of biochars can
223 indicate the higher content of inorganic minerals, which could raise pH, EC and CEC of
224 amended soils (Ahmad et al., 2016).

225 WS biochar was strongly acidic (pH=3.27) and CL biochar was neutral (pH=7.00).
226 Both increase and decrease (Mierzwa-Hersztek et al., 2016) as well as no change (Shafiq,
227 2016) of soil pH can occur upon biochar amendment depending on biochar type and dose. In
228 our study, only CL biochar increased the pH of soil Ba markedly ($p<0.05$) by 0.3 units. WS
229 did not noticeably change pH of both soils while CL biochar failed to change pH of soil Mt
230 significantly. Soil Mt held significantly higher intrinsic ANC than soil Ba due may be to its
231 higher CaCO_3 equivalence (23.2%) (Venegas et al., 2015; Jiang et al., 2016b). WS biochar
232 did not change the ANC of both soils whereas CL biochar increased ANC of both soils
233 significantly ($p<0.05$). This suggests the mineral rich CL biochar contained high amounts of
234 pH buffering components like CaCO_3 .

235 The EC values of both soils was significantly ($p<0.05$) increased by CL but ($p<0.05$)
236 markedly reduced by WS biochar (Table 3). For CL biochar, this was because it contained
237 relatively high amounts of soluble cations and anions (Supporting information Table A1). In
238 biochar application, it was suggested that the EC values of the biochars should be
239 characterized to avoid creating unwanted salt effects (Cantrell et al., 2012). In this study, EC
240 values in CL biochar amended soils were below the saline limits of soils (4 dS/m) (Mohamed
241 et al., 2015) and would not cause salt stress to plant growth.

242 The CL biochar increased soluble anions (Cl^- , PO_4^{3-} and SO_4^{2-}) of both soils
243 significantly (Table A1). As for soluble cations (Table A1), CL biochar increased soluble Na
244 of soil Ba by 10 fold and other mineral element Mg, K, Ca, Fe, Al by 1-3 fold. In contrast,
245 CL biochar increased only soluble Na and Ca of soil Mt at a magnitude of 2.2 and 1.7 fold,
246 respectively. Soil Mt had a high initial K, Mg, Fe, Al concentration, hence effects from CL
247 biochar was not significant. These soluble minerals stored in biochar can serve as plant
248 nutrients (fertilizer) during drought or nutrient deficient conditions (Cao et al., 2014; Hagner
249 et al., 2016). Hence, the WS biochar did not provide much fertilizer benefit while CL could
250 potentially be a source of plant nutrients (K, Ca, Mg, P, Fe).

251

252 3.2 Surface charges of soils

253 Adsorption of heavy metals in soil is mainly governed by interactions with negatively
254 charged soil components (Naidu et al., 1997b; Bolan et al., 1999; Chintala et al., 2013). This
255 surface charge of soil samples evaluated by cation exchange capacity (CEC) and zeta
256 potential are shown in Fig 1. Results showed that CEC of soil Mt (33.4 cmol^+/kg) was
257 around three times that of soil Ba (11.6 cmol^+/kg) (Fig. 4). The higher TOC content, CaCO_3
258 equivalence as well as amorphous Mn, Al, Fe oxides of soil Mt than soil Ba (Table 1) can be
259 responsible for higher negative charge of soil Mt. In addition, higher pH of soil Mt can also
260 contribute to its higher CEC (Naidu et al., 1990; Yu, 1997).

261 Both biochars failed to change soil CEC significantly ($p>0.05$). This indicated low
262 CEC values of these two studied biochars. Normally biochars are considered to develop more
263 oxygen-containing functional groups (Bruun et al., 2011; Manyà, 2012) and hence increased
264 CEC and negative charge of soils (Lehmann, 2007a; Maia et al., 2011; Mohamed et al., 2015;
265 Zhang et al., 2017). Our study, however, suggested the increase of soil functional groups
266 caused by biochars was not significant enough to change soil surface charge. Previously,

267 Slavich et al., (2013) observed no effect of a green waste biochar (10 t/ha) on exchangeable
268 cations and CEC of a Ferrosol in a 36-month field experiment. Schulz and Glaser (2012)
269 found biochar (5%) failed to change CEC of an infertile sandy soil in a greenhouse
270 experiment. Given that CEC is the indicator of capacity of soils to retain nutrients, our
271 studied biochars did not increase the ability of studied soils to hold nutrients.

272 Surface charge as indicated by zeta potential, the electrical potential of a sliding plane
273 of soil colloids (Zhao et al., 2015b) were negative at original soil pH (0.01M NaNO₃) for all
274 soil samples (Fig 1). Hence, all soil samples carried negative surface charge. And the zeta
275 potential values after both biochar amendment were comparable ($p>0.05$) to that of biochar-
276 free soils. These results were consistent with results from CEC on that both biochar
277 amendment did not noticeably change the surface charge characteristics of the studied soils.

278

279 **3.3 C sequestration potential**

280 Soil PyC is the fraction of TOC that was assumed to be more stable and therefore
281 resistant to thermal oxidation (combustion at 375°C) than other soil organic matter. Table 3,
282 Fig 2a and 2b show the TOC and PyC content in studied soil samples. Results showed that
283 after 11 months, TOC content of soil Ba (13.2 mg/g) increased by 253% ($p<0.05$) due to
284 addition of WS biochar (to 46.4 mg/g) and CL biochar by 88.9% (to 24.9 mg/g), respectively.
285 The PyC content of soil Ba (0.61 mg/g) was increased significantly ($p<0.05$, Table 3) to 3.25
286 mg/g by WS but was not significantly changed by CL biochar. Regarding soil Mt, after 11
287 months, WS biochar increased its TOC (81.7 mg/g) by 11.1% (to 90.8 mg/g) but this increase
288 was not statistically significant ($p>0.05$). Hence, we conclude that both biochars did not show
289 statistically significant change of TOC and PyC level of soil Mt but increased that of soil Ba
290 noticeably.

291 Given that the C content of WS and CL biochar were 75.6% and 33.7%, respectively
 292 (Table 2) and biochar amendment ratio was 5 wt%, the percentage of biochar-C sequestered
 293 as TOC and PyC by each soil were calculated by the following equations:

$$\text{Biochar C sequestered as TOC(\%)} = \frac{(\text{TOC biochar amended soils} - \text{TOC control soils})/\text{gsoil}}{\text{Biochar C/gsoil}} * 100$$

$$\text{Biochar C sequestered as PyC(\%)} = \frac{(\text{PyC biochar amended soils} - \text{PyC control soils})/\text{gsoil}}{\text{Biochar C/gsoil}} * 100$$

294 The calculated percentage (Table 4) showed that, within a time range of 11 months,
 295 87.9% and 69.5% of WS and CL biochar-C was sequestered by soil Ba as TOC. Comparably,
 296 only 24.0% of WS biochar-C was stored as TOC in soil Mt while CL biochar-C totally
 297 degraded in soil Mt. Similarly, soil Ba stored 6.96% and 3.54% of WS and CL biochar-C as
 298 thermally stable OC (PyC), whereas no contribution of biochar-C to PyC of soil Mt was
 299 noted.

300 Hence, overall, both biochars had the capacity to increase total OC of soil Ba but
 301 acidic WS biochar showed a higher capacity within a period of 11 months. This may be due
 302 to the higher C content of WS biochar than CL biochar (Table 2). In addition, WS biochar
 303 had a smaller O/C ratio (0.25) than CL biochar (0.41) (Table 2), suggesting C in WS biochar
 304 may have more stable conjugated aromatic structures (Slavich et al., 2013) that resist
 305 degradation more. Meanwhile, soil Ba displayed a better C sequestration effect than soil Mt.
 306 One of the reasons may be lower pH of soil Ba than soil Mt as lower pH was suggested to
 307 favour C stabilization (Skjemstad et al., 1996; Clough and Skjemstad, 2000). According to
 308 PyC content obtained by CTO-375 method, soil Ba can store only <7% while soil Mt stored
 309 negligible percentage of biochar-C as stable OC in the 11-month period. Our previous study
 310 showed that combustion of biochars (including biochars used in this study) at 375 °C for 24 h
 311 almost oxidized all the C in biochars (data not shown). This was also noted by other studies
 312 (Quénéa et al., 2006; Roth et al., 2012; Kerré et al., 2016). Comparing to other commonly
 313 used methods, the CTO-375 method can remove all of the char PyC and tends to obtain the

314 smallest PyC value that represents highly condensed soot PyC (Hammes et al., 2007; Poot et
315 al., 2009; Qi et al., 2017). Hence, on one hand, the CTO-375 method may have
316 underestimated the PyC introduced from biochar into soils. Better methods to quantify PyC
317 dynamics in biochar-amended soils are needed in the future. On the other hand, the better
318 survival of biochars through CTO-375 combustion in soil Ba matrix than their bare biochar
319 counterparts suggests possible incorporation of biochar-C into soil aggregates which provides
320 physical protection of biochar-C from thermal degradation. This is also one of the most
321 important mechanisms for TOC and PyC to be stabilized into soils.

322

323 3.4 Sorption Properties

324 3.4.1 Sorption isotherms

325 The studied soils and biochars contain very low amounts of heavy metal(loid)s and
326 only negligible amount of Cd (supporting information Table A2). The sorption isotherms of
327 all soils were L type (Limousin et al., 2007) where the ratio of equilibrium solute
328 concentration in solution to that on soils decreased with increasing solute concentration and
329 suggested the soil surfaces were progressively get saturated by Cd. The sorption isotherms of
330 all soil samples were fitted into Langmuir models, with linear form of this model as follows
331 (Yan et al., 2015):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}}$$

332 where C_e (mg/L) and q_e (mg/g) are the equilibrium concentrations of Cd in solution
333 and on soil samples, respectively. Langmuir constants q_{max} (mg/g) and b (L/g) represent
334 maximum sorption capacity and sorption strength, respectively.

335 The Cd sorption isotherms (Fig 3a and 3b) of biochar free and biochar amended soils
336 all followed the Langmuir model ($R^2 = 0.82-0.99$) (Table 5). The amount of Cd sorbed on all

337 soil samples increased with increasing initial Cd concentrations. An assessment of the
338 sorption maxima (q_{\max}) calculated from Langmuir model showed that soil Mt had
339 significantly higher q_{\max} (10.2 mg/g) than soil Ba (3.71 mg/g). This may be due to difference
340 in properties of the two soils. Higher pH and higher capacity to maintain pH (higher ANC) of
341 soil Mt should favour the higher sorption capacity of soil Mt. This is because higher pH
342 affords more negative surface charge (Naidu et al., 1994; Zhou and Wong, 2001; Forján et al.,
343 2016; Jiang et al., 2016a) and more hydrolysis Cd^{2+} that is with higher affinity than free Cd^{2+}
344 ions to sorbent surface (Davis and Leckie, 1978; Naidu et al., 1994; Yu, 1997; Jiang et al.,
345 2016a). Higher TOC and CaCO_3 content (Uchimiya et al., 2011b; Forján et al., 2016; Usman
346 et al., 2016) and Fe, Al and Mn oxides (Yu, 1997; Jiang et al., 2012b) of soil Mt could also
347 drive its high sorption capacity for Cd. WS biochar amendment did not noticeably change
348 sorption capacity of both soils. CL biochar application increased q_{\max} of soil Ba by 25.6%
349 and but showed no effect on sorption capacities of soil Mt. This indicated application of both
350 biochars to alkaline organic matter rich soils may not show its remedial function and acidic
351 biochar would not show remedial effects for both soils.

352

353 **3.4.2 Proportions of specific sorption**

354 Sorption of metal cations are relevant to negative surface charge (Naidu et al., 1994;
355 Naidu et al., 1997a; Chintala et al., 2013). Mechanisms involved in metal ions attraction from
356 soil solutions to soil surfaces include non-specific sorption (outer-sphere complexes) through
357 cation exchange reactions where charge of soils are balanced by sorbed metal ions, specific
358 sorption (inner-sphere complexes) where chemical bonds form between metals and soil
359 surface (Evans, 1989; Naidu et al., 1994; Echeverria et al., 1998; Strawn and Sparks, 2000;
360 Appel and Ma, 2002; Bradl, 2004; Bolan et al., 2014) and co-precipitation. On a relative basis,
361 specific sorption and co-precipitation can retain Cd nearly irreversibly in many cases while

362 nonspecific sorption renders the metals most labile and easily reversible (Appel and Ma,
363 2002).

364 The nonspecifically sorbed metals were estimated by the amount released from
365 desorption process (Jiang et al., 2012b; Dai et al., 2015). Data from Fig 4 shows that at lower
366 Cd loading rate (150 μ M), non-specific sorption accounted for around 0.19% of the total
367 sorption of soil Mt, and this ratio increased to around 0.35% at a higher initial Cd
368 concentration (1500 μ M) but was still minimal. The ratio of non-specific sorption for soil Ba
369 was relatively higher which was around 2.21% and 8.17%, at 150 and 1500 μ M Cd loading,
370 respectively. Hence, both soils, especially soil Mt, were dominated by specific sorption. This
371 specific sorption can be through Cd complexation by multidentate ligands on the surface of
372 particulate organic matter and nonbridging -OH sites of various hydro(oxide)s (Uchimiya et
373 al., 2011c). On the one hand, the large number of functional groups of soil organic matter can
374 retain heavy metal mostly by surface complexation and surface precipitation (Bradl, 2004).
375 On the other, various Fe, Al and Mn oxides could have a good contribution to the specific
376 sorption capacity of metal ions (Yu, 1997) with correlation of specific sorption with free Fe
377 oxides having been reported (Jiang et al., 2012b).

378 Biochar amendments did not noticeably influence the ratio of non-specific sorption
379 of the two soils except a 50.0% reduction caused by CL biochar on that of soil Ba. The P-
380 and Si-related minerals may be responsible for the CL manure biochar to increase the non-
381 electrostatic Cd sorption of soil Ba (Dai et al., 2015). The combination of Cd with Si, Al, P
382 may be supported by the EDS spectrum of CL biochar in soil Ba matrix (Fig 5).

383

384 **3.4.3 Sorption mechanisms**

385 Heavy metal can be removed by biochar through direct electrostatic interactions
386 and cation exchange (nonspecific) as well as surface complexation with functional groups

387 (specific) (Trakal et al., 2014; Inyang et al., 2015; Lu et al., 2017) and co-precipitation.
388 Hence, sorptive mechanisms of biochar-amended soils for Cd will be discussed from non-
389 specific and specific aspects in this section. To make the discussion easy, co-precipitation
390 was included in the specific irreversible sorption.

391 **3.4.3.1 Non-specific sorption**

392 The surface of all soil samples were negatively charged as indicated by negative
393 zeta potential (Table 3 and Fig 1). Hence, the sorption systems were favourable and direct
394 electrostatic interaction can contribute to the sorption of Cd. In addition, given measurable
395 CEC of both soils (Table 3 and Fig 1), Cd can be sorbed on soil constituents by replacing
396 readily exchangeable cations such as Ca^{2+} and Mg^{2+} (Uchimiya et al., 2011b). In this study,
397 Ca and Mg was released after Cd loading (mmol/g, after subtracting the amount released
398 from control sample, 0mM) for both soils, suggesting cation exchange as one of the
399 mechanisms of Cd sorption (Cui et al., 2016; Usman et al., 2016) (Table A3). Both Ca and
400 Mg release were higher at higher initial Cd loading in all soil samples. Soil Ba had more
401 release of Mg while soil Mt had higher release of Ca. Assuming 1 mg/kg Mg or Ca will be
402 released to sorb 1 mg/kg Cd, we calculated the total contribution of Ca + Mg release to Cd
403 retention (R_{exchange}) (Table A3). We can see that R_{exchange} of soil Mt (5.27%) at lower Cd
404 concentration (150 μM) was slightly higher than soil Ba (3.40%), and this may be due to
405 higher CEC of soil Mt. However at higher concentration (1500 μM), R_{exchange} of soil Mt
406 reduced to around 3.30% and that of soil Ba increased to 4.82%. Higher R_{exchange} of soil Ba
407 at higher Cd loading (1500 μM) may be because not all cations were released from soil Ba
408 at 150 μM , while the decrease of R_{exchange} of soil Mt at higher concentration was likely due
409 to a higher increase of Cd sorption than cation release. Overall, WS biochar did not
410 influence the amount of cation release markedly while CL biochar increased the release of

411 Mg in soil Ba and Mt at both Cd loadings. This indicated CL biochar increase the amount
412 of Cd sorbed through increasing Mg exchange in both soils.

413

414 3.4.3.2 Specific sorption

415 As pH can be the governing factor for metal sorption in aqueous systems, we cannot
416 ignore the changes of pH during sorption. The comparison of equilibrium pH of Cd-soil
417 reaction systems at an initial Cd loading of 0 and 300 μM showed that pH drop of soil Mt
418 (0.01-0.14 units) was not as significant as that of soil Ba (0.2-0.35) (Table A4). This drop
419 of pH after metal immobilization in sorption systems suggests either ion exchange of Cd
420 with dissociable proton (proton exchange) (Uchimiya et al., 2010; Inyang et al., 2012) or
421 forming of $\text{Cd}(\text{OH})_2$ precipitants (Dong et al., 2014). For soil Mt, a pH decrease in the soil
422 Mt system may be higher than the obtained value as its high ANC could counter-balanced
423 part of the pH drop (Inyang et al., 2012). Given that $\text{Cd}(\text{OH})_2$ precipitation can form when
424 solution pH ranges from 8 to 9 (Sun et al., 2014; Zhao et al., 2016), both precipitation of
425 $\text{Cd}(\text{OH})_2$ and ion exchange may have occurred in soil Mt system. For soil Ba, $\text{Cd}(\text{OH})_2$
426 may not be likely to form given the equilibrium pH range from 5.6-6.5, hence proton
427 exchange should have caused the pH drop. The precipitation of CdCO_3 in soil Mt was
428 indicated by saturation index calculated by PHREEQC Interactive v3.3.7. Sun et al. (2014)
429 also reported surface precipitation of Cd as carbonate in crop straws and wood shaving
430 biochar sorption systems.

431 Cadmium can be sorbed by complexing with functional groups present on sorbent
432 surface (Sun et al., 2014; Cui et al., 2016). Soil organic matter and various soil hydr(oxide)s
433 contain large number of functional groups (Bradl, 2004; Uchimiya et al., 2011c). FTIR
434 spectrum (Fig 6) confirmed our WS and CL biochar contained phenolic hydroxyl (-OH)
435 groups at around $3450\text{-}3475\text{ cm}^{-1}$ (Tsai et al., 2012; Wang et al., 2012), aromatic C=C

436 functional groups at 1590 - 1641 cm^{-1} (Wang et al., 2011; Zaafour et al., 2016), aliphatic
437 ether C-O stretching at 1085/1110 cm^{-1} (Tsai et al., 2012; Yang and Jiang, 2014) as well as
438 aromatic carbonyl/carboxylic groups (-COO/C=O) at 1427-1463 cm^{-1} with a weaker signal
439 (Yuan et al., 2011; Choppala et al., 2012; Guo and Chen, 2014). Hence, surface
440 complexation should be an important mechanism for Cd sorption to soil Mt and Ba given
441 that around 99.7% and 91.8% of the sorption was specific (Fig 4).

442

443 **4. Conclusions and implications**

444 Chicken litter (CL) biochar had a statistically significant liming effect for the
445 slightly acidic soil Ba as indicated by the significantly increased pH and acid neutralization
446 capacity. Also, CL biochar can serve as short-term nutrient source (increased Mg, Ca, K, P
447 levels) for lower-nutrient soil Ba but cannot improve the capacity of both soils to retain
448 nutrients (no increase in CEC). Acidic wood shaving (WS) biochar held little value in soil
449 liming and soil nutrient supply but it had a higher C sequestration potential (87.9% WS-C
450 in soil Ba and 69.5% WS-C in soil Mt) than CL biochar. The slightly acidic soil Ba could
451 sequester more C from biochars as TOC (87.9% WS-C and 69.5% CL-C) than alkaline soil
452 Mt (24.0% WS-C and -0.27% CL-C). The WS biochar did not change the sorption capacity
453 and sorption reversibility of both soils for Cd while CL biochar improved sorption of the
454 acidic soil Ba by 25.4% and reduced its desorption by around 50.0%. Hence based on the
455 11-month experiment, WS biochar did not offer much value for nutrient supply or remedial
456 aspects of studied soils but can be quite favourable for C sequestration, especially in the
457 acidic soil. In contrast, CL biochar can increase soil nutrient levels and sorption capacity for
458 Cd in soils with lower sorption capacities (like Ba) while offering no C sequestration
459 benefits based on the 11-month experiment. Future longer term experiment will be needed

460 to evaluate these biochars. This study indicates biochars should be properly evaluated
461 before large scale production and application according to the target use.

462

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Table 1. Characteristics of original soil samples

Table 2. Characteristics of biochar samples

Table 3. Characteristics of biochar amended soil

Table 4. C sequestered from biochars as TOC and PyC in soils

Table 5. Langmuir isotherm model parameters

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Table 1. Characteristics of original soil samples

Soils	Soil type	Sand (%)	Silt (%)	Clay (%)	Texture class	TOC (mg/g)	CaCO ₃ equivalence (%)	pH ^a	EC ^a (dS/m)	CEC (cmol+/kg)	Fe _{oxa} ^b (mg/kg)	Al _{oxa} ^b (mg/kg)	Mn _{oxa} ^b (mg/kg)
Ba	Ferrosol	54.9±0.88	30.9±2.17	14.2±1.31	Loam	16.3±0.85	2.00±0.50	6.14±0.05	50.0±0.14	11.6±0.51	4370±37.2	1310±11.8	190±4.93
Mt	Dermosol	50.9±1.17	38.9±2.50	10.1±1.34	Loam	78.9±5.64	23.2±0.67	7.87±0.04	260±50.2	37.8±1.71	14900±858	2290±983	410±19.1

Note: ^apH and EC were in 1:5 solid : water ratio. ^bFe_{oxa}, Al_{oxa}, and Mn_{oxa} - ammonium oxalate/oxalic acid extractable Fe, Al, Mn.

Table 2. Characteristics of biochar samples

Chars	C (%)	H (%)	N (%)	S (%)	O (%)	O/C ^a	H/C ^a	Ash (%)	SSA ^c (m ² /g)	pH ^b	EC ^b (dS/m)	CaCO ₃ equivalence (%)	ANC ^d (cmol H ⁺ /kg)
WS	75.6±0.23	3.23±0.01	0.25±0.00	0.32±0.09	18.9±0.03	0.25	0.04	1.66±0.10	0.81±0.13	3.25±0.07	421±15.0	1.67±0.18	2.00±0.07
CL	33.7±2.33	2.41±0.12	3.81±0.30	0.40±0.04	13.5±2.80	0.40	0.07	46.2±0.00	6.05±0.93	7.00±0.16	9190±439	10.1±0.23	222±12.4

Note: ^aMolecular ratio of O/C and H/C are ash free base. ^bpH and EC were in 1:10 solid : water ratio. ^cSSA - (BET) specific surface area. ^dANC - acid neutralization capacity.

Table 3. Characteristics of biochar amended soil

Soils	pH ^b	EC ^b (dS/m)	CEC (cmol+/kg)	ANC ^c (cmol H+/kg)	zeta potential (mV)	PyC ^d (mg/g)	TOC (mg/g)
Ba11	6.28±0.04	348±3.53	11.5±1.13	6.51±0.72	-30.2±0.14	0.61±0.31	13.2±2.42
Ba11WS	6.20±0.02	3180±2.12 ^a	11.9±0.88	5.50±0.71	-30.1±0.71	3.25±0.98 ^a	46.4±9.46 ^a
Ba11CL	6.58±0.06 ^a	7780±4.95 ^a	12.6±0.85	12.0±1.41 ^a	-32.1±0.99	1.21±0.37	24.9±5.89 ^a
Mt11	7.60±0.00	797±4.24	36.5±0.94	27.0±0.71	-27.4±0.71	4.33±0.47	81.7±26.8
Mt11WS	7.63±0.01	590±14.8 ^a	33.4±1.80	25.0±0.71	-29.6±1.56	4.75±2.12	90.8±8.33
Mt11CL	7.57±0.00	1170±41.7 ^a	33.1±2.05	48.0±1.41 ^a	-30.6±0.57	4.28±1.65	76.5±12.2

Notes: ^aSignifies difference from control is significant ($p < 0.05$ by one-way ANOVA analysis). ^bpH and EC were in 1:5 solid : water ratio.

^cANC - acid neutralization capacity. ^dPyC - pyrogenic carbon.

Table 4. C sequestered from biochars as TOC^a and PyC^a in soils

C sources	Sequestered as TOC in acidic soil Ba (%)	Sequestered as TOC in alkaline soil Mt (%)	Sequestered as PyC in acidic soil Ba (%)	Sequestered as PyC in alkaline soil Mt (%)
WS-C ^b	87.9	24.0	6.96	1.12
CL-C ^b	69.5	-	3.54	-

Note: ^aTOC and PyC were total organic carbon and pyrogenic carbon, respectively.

^bWS-C and CL-C were C of wood shaving and chicken litter biochar, respectively.

- indicate decrease of soil TOC and PyC by biochar were negligible.

Table 5. Langmuir isotherm model parameters

Samples	q_{\max} (mg/g)	b (L/mg)	R^2
B11	3.50	0.19	0.99
B11WS	3.53	0.21	0.99
B11CL	4.39	0.31	0.99
M11	9.55	0.69	0.89
M11WS	8.69	0.78	0.90
M11CL	9.87	0.69	0.88

Fig 1. CEC and zeta potential of soil samples

Fig 2. TOC and PyC content of soil samples

Fig 3. Sorption isotherm of soil samples

Fig 4. Desorption ratio of Cd of soil Ba and Mt

Fig 5. SEM image and EDS spectrum of CL biochar in soil Ba matrix

Fig 6. FTIR spectrum of WS and CL biochars

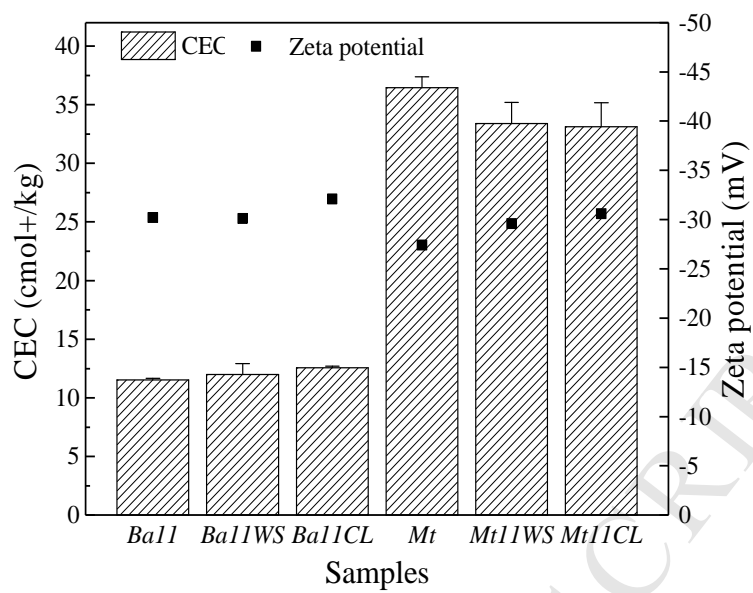
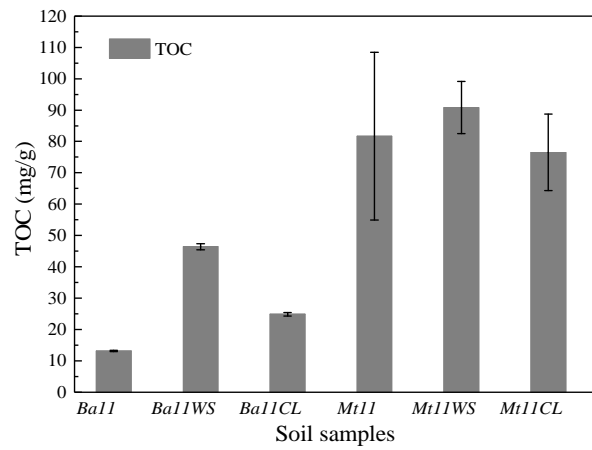
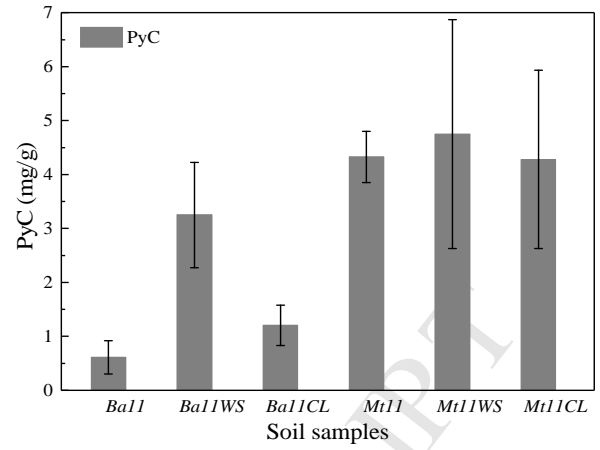


Fig 1. CEC and zeta potential of soil samples

**Fig 2a. TOC content of soil samples****Fig 2b. BC content of soil samples**

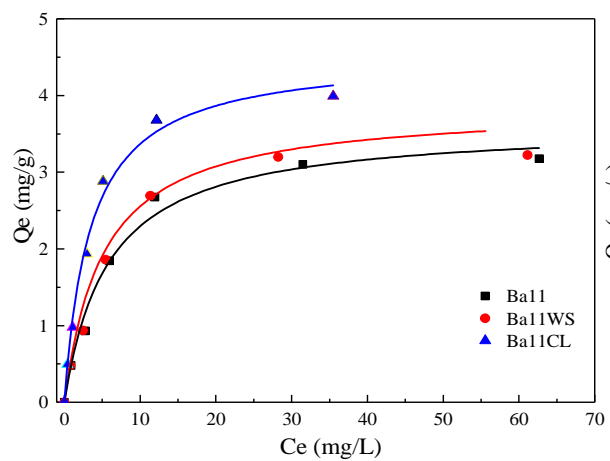


Fig 3a. Sorption isotherm of soil Ba

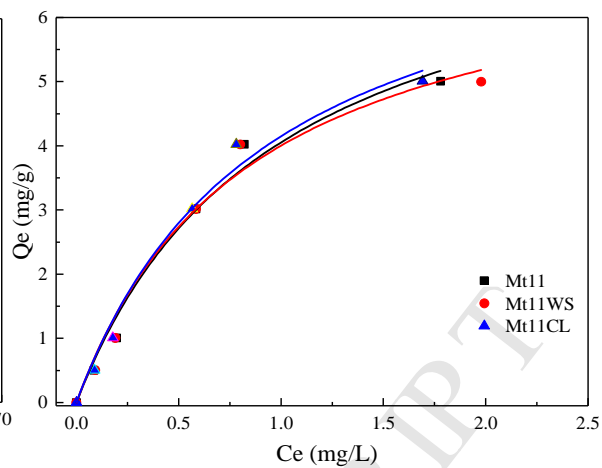


Fig 3b. Sorption isotherm of soil Mt

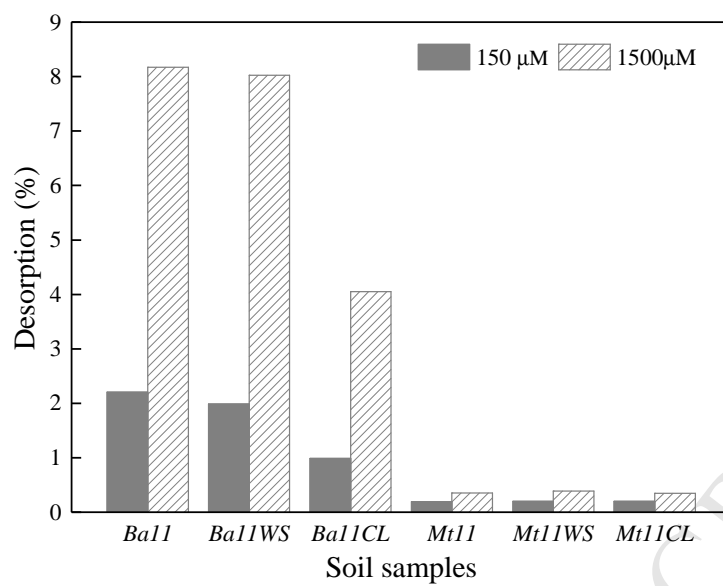


Fig 4. Desorption ratio of Cd of soil Ba and Mt

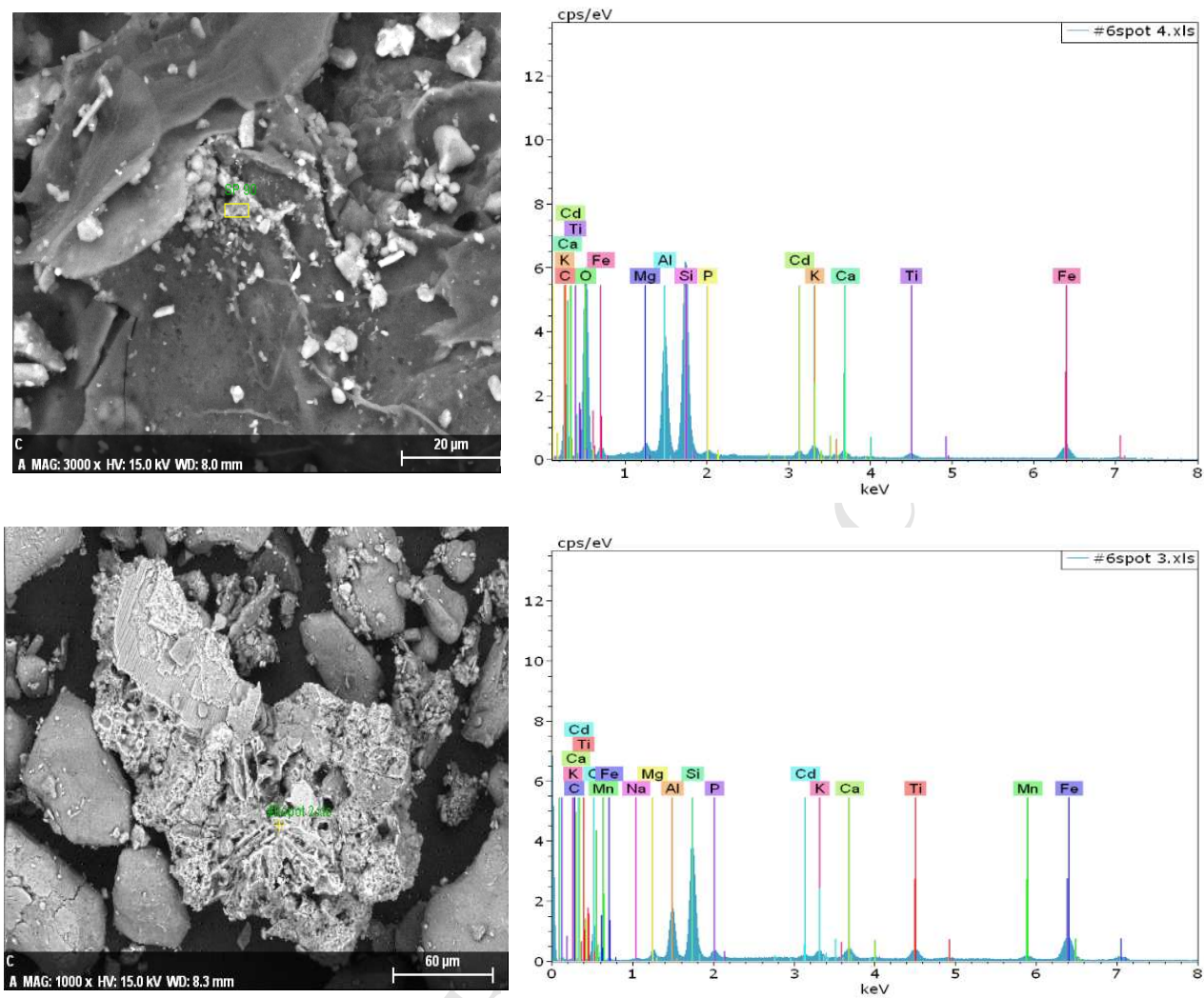


Fig 5. SEM image and EDS spectrum of CL biochar in soil Ba matrix

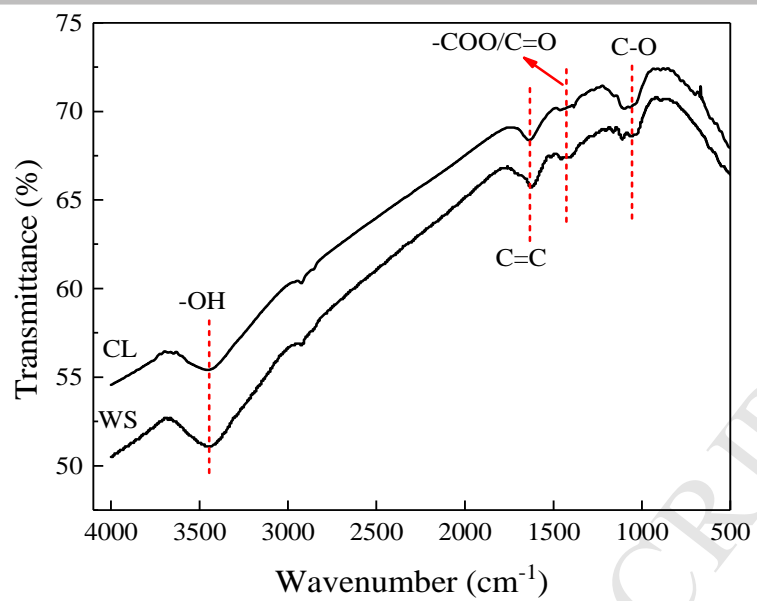


Fig 6. FTIR spectrum of WS and CL biochars

Highlights

- The C rich acidic biochar did not work for nutrients supply or Cd retention but helped in storing C.
- The neutral mineral rich biochar enhanced nutrient and sorption for some soils.
- Neutral mineral rich biochar hardly increased soil C after 11 months.