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

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Abbreviations

ANC = Acid neutralization capacity

Ba = Soil from Mt Bygalore (Ferrosol, acidic)

CEC = Cation exchange capacity

CL biochar = Chicken litter biochar

EC = Electrical conductivity

Mt = Soil from Mt Shank (Dermosol, alkaline)

PyC = Pyrogenic carbon

TOC = Total organic carbon

WS biochar = Wood shaving biochar

Abstract

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

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

1. Introduction

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

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

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

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

2. Methods

2.1 Incubation of biochar-amended soils

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

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

2.2 Soil and biochar characterization before and after treatment

Soil and biochar pH, electrical conductivity (EC) were determined using 1:5 and 1:10 sample to water ratio, respectively. Soil TOC were determined by combusting oven dried and ground soil samples (<150 µm) at 1100 °C in a CHN Elemental Analyzer (Euro EA 3000 Elemental Analyzer, Eurovector SPA, Milano, Italy) that uses infrared technology to quantify CO_2. Soil pyrogenic carbon (PyC), was measured by a chemo-thermal oxidation (CTO-375) method. Both TOC and PyC analysis were collaborated with a lab in Switzerland where same analytical procedure as Agarwal and Bucheli, (2011) were applied. Soil and biochar total metals was extracted by microwave digestion in aqua regia following USEPA 3051 40

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

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

2.3 Surface charge of soils

Effects of biochars on surface charge properties of soil were assessed by CEC and electrophoretic mobility property of soils. CEC is an indicator of abundance of the negative charge on the surface of a material, which can be balanced by exchangeable cations (Mukherjee et al., 2011; Jiang et al., 2012a; Zhao et al., 2015b; Jiang et al., 2016b). In this study, soil CEC was measured by $BaCl_2/NH_4Cl$ compulsive exchange method descried by Gillman and Sumpter (1986). Electrophoretic mobility property of soil samples, often expressed as zeta potential is another way to evaluate soil surface charge properties. Zeta potential is the electrical potential of a sliding plane which is the interface between the Stern and diffuse layers in the double layer model of colloidal particles (Appel et al., 2003; Jiang et al., 2016b). Its electro-negativity depends on the amount of negative surface charges. Soil and biochar-amended soil samples were ground to <150µm before being dispensed into 0.01M $NaNO_3$ suspension (0.02%, w/v) to guarantee the good suspension of samples. The suspensions were then equilibrated on a rotatory shaker for 24 h. The pH values of suspension were recorded and zeta potential of these suspensions were measured by Zetasizer Nano ZS instrument (Malvern, ZEN3600, UK).

2.4 Cadmium sorption and desorption

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

193 $NaNO_3$ solution containing 0, 30, 150, 300, 600, 900, 1200 and 1500 µM $Cd(NO_3)_2$ on a
194 reciprocating shaker at 200 rpm for 24 h. Solution pH at 0 and 300 µM $Cd(NO_3)_2$ 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 PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-} 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 $NaNO_3$ 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

3. Results and discussions

3.1 Basic soil properties

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

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

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

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

3.2 Surface charges of soils

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

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

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

Surface charge as indicated by zeta potential, the electrical potential of a sliding plane of soil colloids (Zhao et al., 2015b) were negative at original soil pH (0.01M $NaNO_3$) for all soil samples (Fig 1). Hence, all soil samples carried negative surface charge. And the zeta potential values after both biochar amendment were comparable (p>0.05) to that of biochar-free soils. These results were consistent with results from CEC on that both biochar amendment did not noticeably change the surface charge characteristics of the studied soils.

3.3 C sequestration potential

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

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

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

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

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

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

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

3.4 Sorption Properties

3.4.1 Sorption isotherms

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

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

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

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

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

3.4.2 Proportions of specific sorption

Sorption of metal cations are relevant to negative surface charge (Naidu et al., 1994; Naidu et al., 1997a; Chintala et al., 2013). Mechanisms involved in metal ions attraction from soil solutions to soil surfaces include non-specific sorption (outer-sphere complexes) through cation exchange reactions where charge of soils are balanced by sorbed metal ions, specific sorption (inner-sphere complexes) where chemical bonds form between metals and soil surface (Evans, 1989; Naidu et al., 1994; Echeverria et al., 1998; Strawn and Sparks, 2000; Appel and Ma, 2002; Bradl, 2004; Bolan et al., 2014) and co-precipitation. On a relative basis, 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 (150μM), 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 intial Cd
368 concentration (1500μM) 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 μM Cd loading,
370 respectively. Hence, both soils, especially soil Mt, were dorminated 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

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

3.4.3.1 Non-specific sorption

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

411 Mg in soil Ba and Mt at both Cd laodings. 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 $Cd(OH)_2$ 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 $Cd(OH)_2$ precipitation can form when
424 solution pH ranges from 8 to 9 (Sun et al., 2014; Zhao et al., 2016), both precipitation of
425 $Cd(OH)_2$ and ion exchange may have occurred in soil Mt system. For soil Ba, $Cd(OH)_2$
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 3450-3475 cm^{-1} (Tsai et al., 2012; Wang et al., 2012), aromatic C=C

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

4. Conclusions and implications

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

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: [a] pH and EC were in 1:5 solid : water ratio. [b] Fe_{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: [a]Molecular ratio of O/C and H/C are ash free base. [b]pH and EC were in 1:10 solid : water ratio. [c]SSA - (BET) specific surface area. [d]ANC - 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: [a]Signifies difference from control is significant (p<0.05 by one-way AVONA anaylsis). [b]pH and EC were in 1:5 solid : water ratio. [c]ANC - acid neutralization capacity. [d]PyC - 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: [a]TOC and PyC were total organic carbon and pyrogenic carbon, respectively.
[b]WS-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

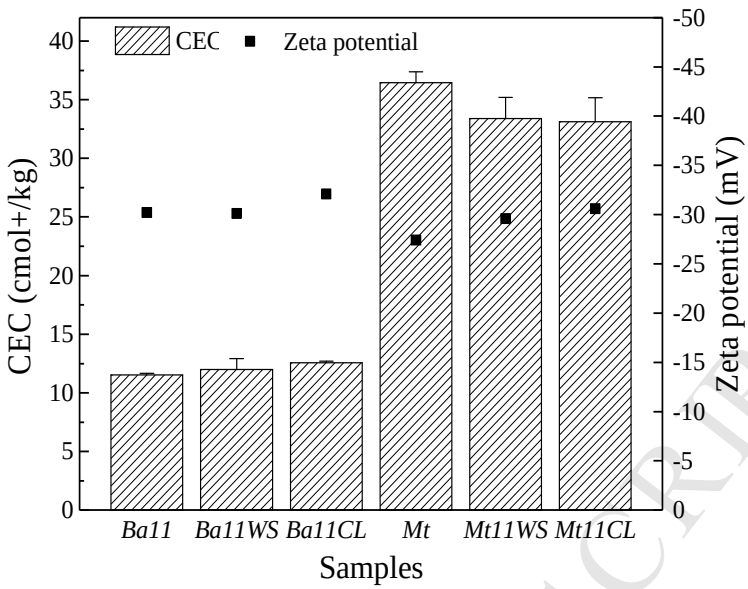

Fig 1. CEC and zeta potential of soil samples

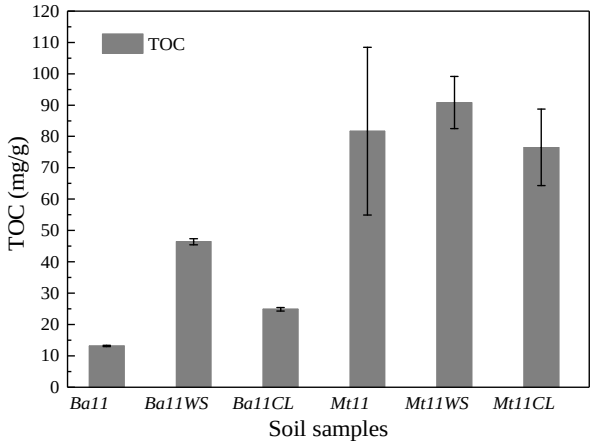

Fig 2a. TOC content of soil samples

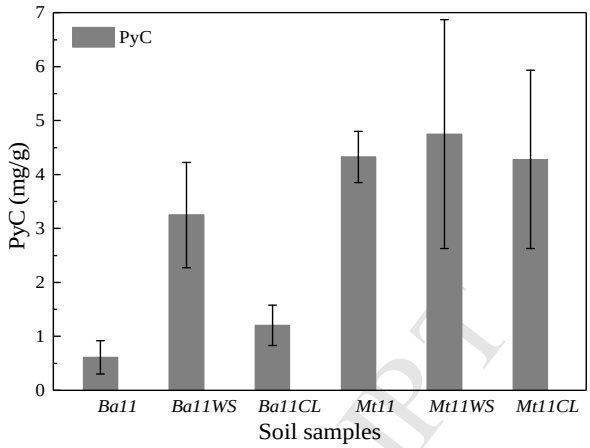

Fig 2b. BC content of soil samples

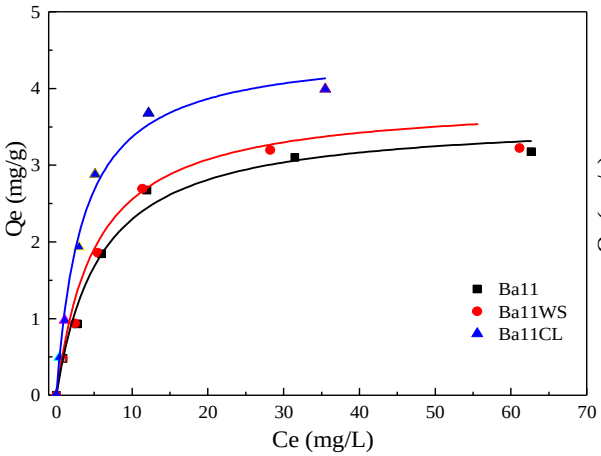

Fig 3a. Sorption isotherm of soil Ba

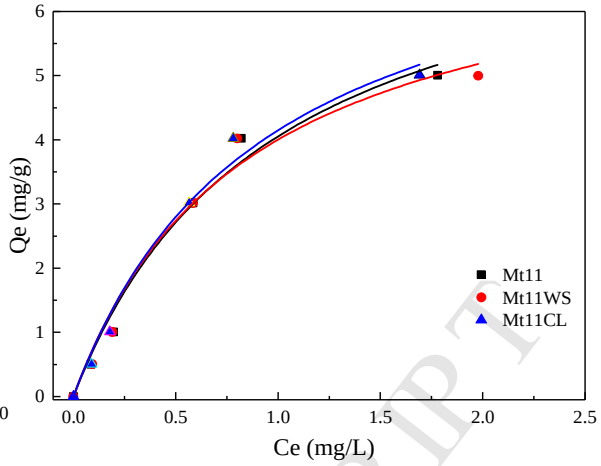

Fig 3b. Sorption isotherm of soil Mt

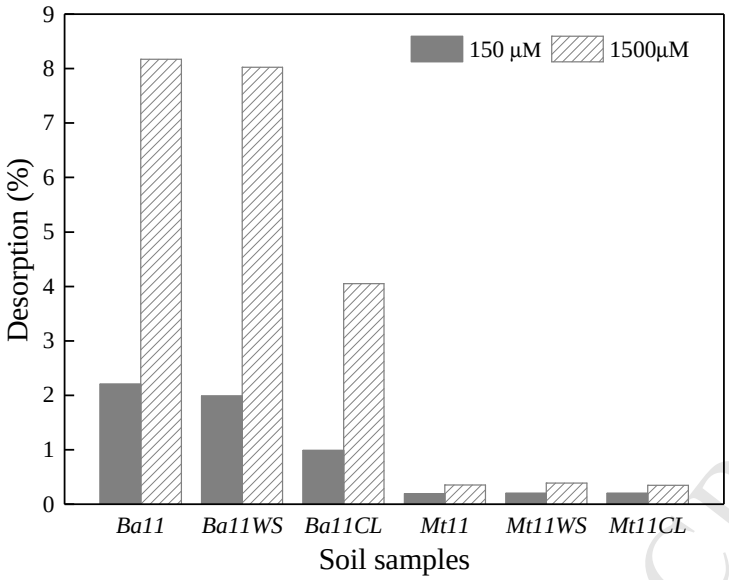

Fig 4. Desorption ratio of Cd of soil Ba and Mt

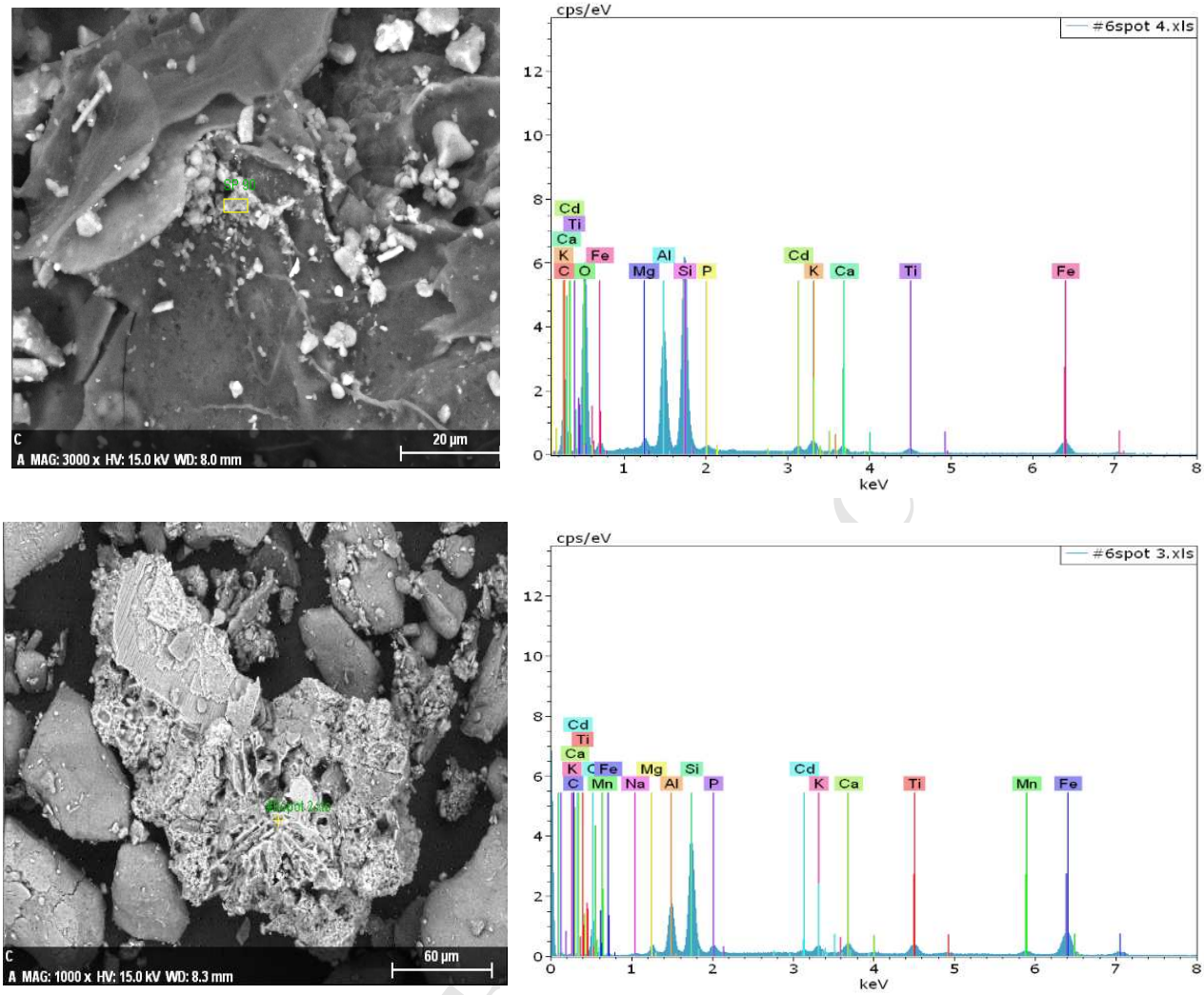

Fig 5. SEM image and EDS spectrum of CL biochar in soil Ba matrix

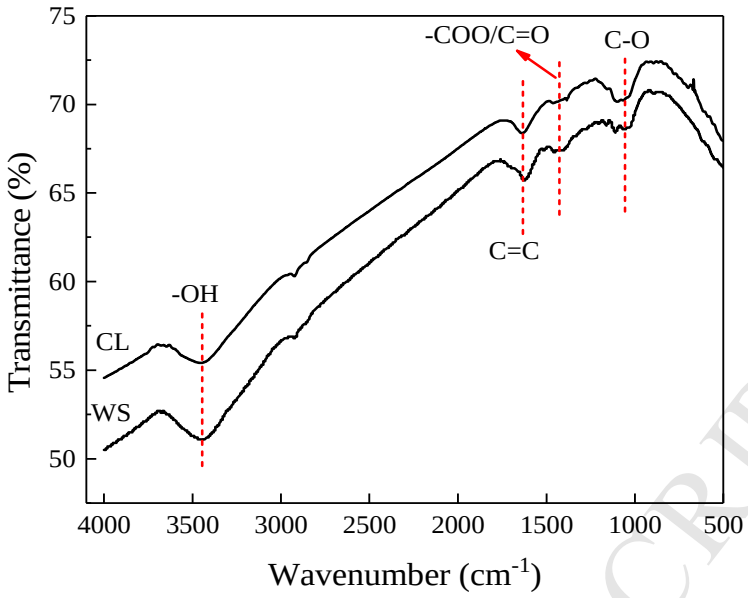

Fig 6. FTIR spectrum of WS and CL biochars

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.