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# Bioavailability and speciation of Cadmium in contaminated paddy soil as alleviated by biochar from co-pyrolysis of peanut shells and maize straw

Weijie Xu<sup>1</sup>, Linlin Xiao<sup>1</sup>, Shuzhen Hou<sup>2</sup>, Gul Rukh<sup>3</sup>, Meizhen Xu<sup>4</sup>, Yatian Pan<sup>1</sup>, Jingweng Xu<sup>1</sup>, Wangkaining Lan<sup>1</sup>, Zhongqiang Ruan<sup>1</sup>, Bing Zhong<sup>1</sup> and Dan Liu<sup>1\*</sup>

## Abstract

**Background:** Biochar is an important material for remediation of Cd in contaminated paddy soils. However, different biochars have variable effects on bioavailability of Cd while single biochar cannot properly amend immobilized Cd. Co-production of biochar from peanut shells and maize straw at different mass mixing ratios (1:0, 1:1, 1:2, 1:3). The characteristics, properties and effects of co-pyrolysis biochars on amendments of Cd polluted paddy soil was evaluated.

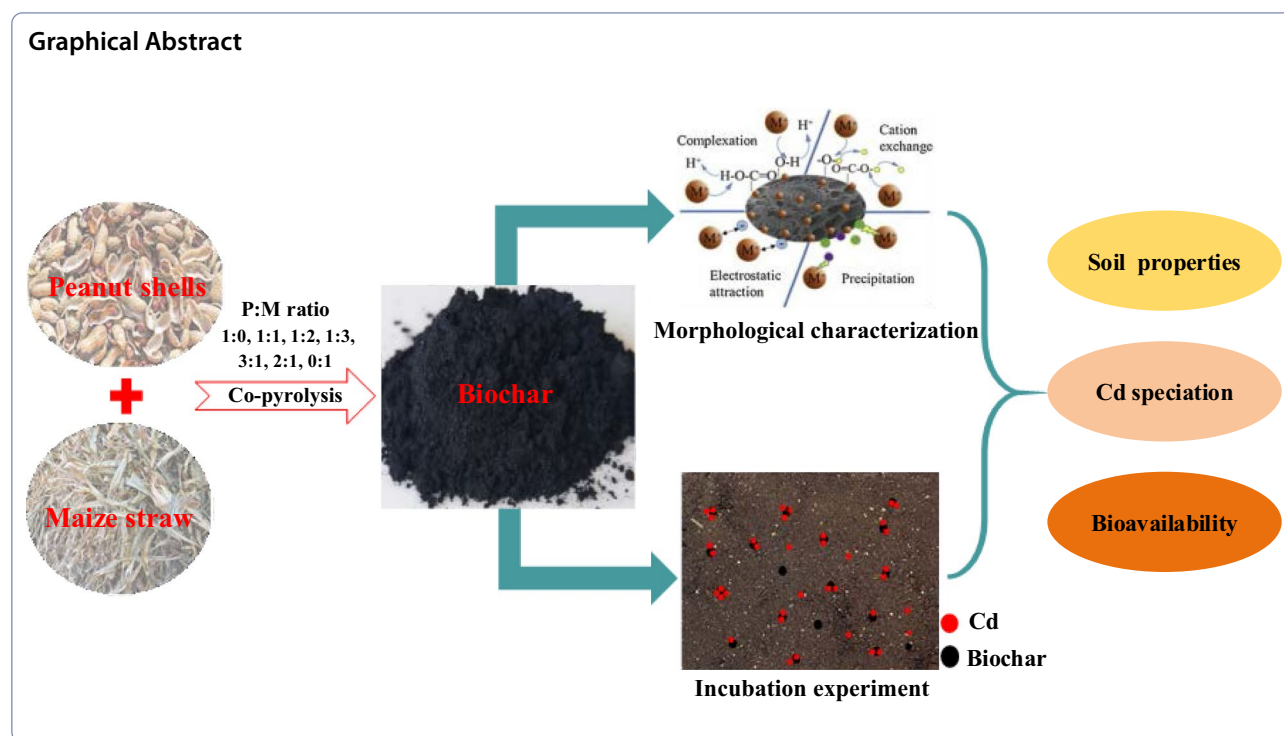
**Results:** Our research revealed that yield, ash, elemental contents and specific surface area of co-pyrolysis biochars have variable amendment effects compared with single biochar. The co-pyrolysis biochars have produced rich oxygen-containing functional groups and crystal structure, especially 1P3M (co-pyrolysis biochar produced from peanut shell and maize straw in mass ratios of 1:3). The addition of biochar has significantly enhanced pH and EC value, however, content of available Cd during incubation was significantly reduced compared with control treatment. The efficiency of biochars have reduced available Cd in order of 1P3M > M > 1P1M > 1P2M > 2P1M > 3P1M > P after incubation. The 1P3M was most effective in reducing CaCl<sub>2</sub>-extractable Cd concentration up to 43.97%. The BCR sequential extraction method has produced lowest exchangeable fraction Cd content and highest residual fraction Cd content in 1P3M among all biochar amended treatments.

**Conclusions:** It is concluded that 1P3M has a much greater potential to decreased the bioavailability of Cd in contaminated paddy soil. And 1P3M was highly effective for transporting Cd from soluble form to less toxic stable forms in polluted paddy soils.

**Keywords:** Co-pyrolysis biochar, Remediation, Modification, Cd polluted

\*Correspondence: liudan7812@aliyun.com

<sup>1</sup> Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, State Key Laboratory of Subtropical Silviculture, Zhejiang A & F University, Hangzhou, Zhejiang 311300, People's Republic of China  
Full list of author information is available at the end of the article



## Introduction

Paddy soil contamination by heavy metals is a long term dilemma, which poses an impending threat to human health and ecological security [1–3]. Cadmium (Cd) is an extremely toxic heavy metal, has long been identified as major human health hazard [4]. The China's National Investigation of contaminated paddy soils has reported  $5.33 \times 10^6$  ha of Cd-polluted paddy soils in 2014. The Cd have highest standard exceeding ratios of 7.0% in China, for which remediation is necessary [5]. The previous studies have revealed that Cd can cause induced heart disease, and kidney damage etc. at accumulation rate as low as 0.001 mg/L via food due to its high mobility and toxicity. The toxicity of Cd depends on their speciation and bioavailability in contaminated paddy soil. The stabilization of heavy metals reduces bioavailability and mobility of Cd in paddy soil [6]. The several studies have evaluated ecological effect of different heavy metal stabilization, such as bentonite, lime, phosphate rock, sepiolite, etc. [7, 8]. However, investigation of cost-effective and eco-friendly heavy metal stabilization is the biggest challenge.

Biochar is a carbon-rich material which is produced from pyrolysis of agricultural and forestry residues during oxygen deficient environment [9]. The biochars have low cost, high surface area, unique spatial structure, abundant functional groups of oxygen with high cation exchange capacity [10]. The studies have reported that

biochar is an efficient and environmentally friendly stabilization material which can be utilized for immobilization of Cd in polluted paddy soil [11]. Previous studies have reported that 5% (w/w) biochars from variable raw materials can effectively reduce Cd content in Cd contaminated paddy soil. The highest reduction of Cd by 81.9% and 65.5% was observed in peanut shells biochar and maize straw biochar [7]. Zhang revealed that biochar of co-pyrolysis from sewage sludge and rice husk/bamboo sawdust have larger aromatic clusters and provide higher Cd immobilization than biochar derived from pyrolysis of a single feedstock [5].

The biochar derived from the pyrolysis of mixed feedstock (i.e., co-pyrolysis) has significantly improved efficiency of Cd eradication, which may due to improved physicochemical properties, such as content of inorganic mineral particles, carbon, oxygen containing functional groups and surface area produced as synergistic effect of their constituents [12]. China is a large agricultural country, producing  $2 \times 10^8$  tons of residues maize straw and  $3 \times 10^8$  tons of residues peanut shell every year [13]. However, management of huge quantity of residues without causing environmental problems is a challenging task. The biochars produced from peanut shell and maize straw have high effectiveness for immobilization of Cd in polluted paddy soil and may account for up to 79.0% [14]. The preparation of biochar from residues is an appropriate method for remediation of Cd contaminated paddy

soil. However, majority studies have emphasized on Cd remediation mechanism of single biochar, while mechanism of co-pyrolysis biochar was rarely involved. In this experiment, comparison of physicochemical properties of co-pyrolysis biochar (produced from peanut shell and maize straw in variable mass mixture ratios) was studied for evaluation of the effects and alteration of speciation and bioavailability of Cd.

## Materials and methods

### Paddy soil sample collection and biochar preparation

The Cd contaminated paddy soil in this study was collected from a paddy field in Zhejiang province, China. The paddy soil samples were air-dried and passed through 2 mm sieve. The peanut shell and maize straw were used to make co-pyrolysis biochar from a farm in Zhejiang. The peanut shell and maize straw were cleaned with distilled water, oven-dried at 75°C, and milled through 2 mm sieve. The peanut shell and maize straw were mixed for preparation of mass ratios (w/w) of 1:0, 1:1, 1:2, 1:3, 0:1, 2:1 and 3:1. The mixture of raw materials was pyrolyzed in a slow pyrolysis muffle furnace (Shanghai Yi Zhong Electricity Furnace Inc, China). The pyrolysis temperature was raised to 550°C at a heating rate of 20°C/min and was held for 2 h at peak temperature. The pyrolyzed material was cooled to room temperature in an inert atmosphere, and ground with 100-mesh sieve. The seven co-pyrolysis biochar samples produced from peanut shell and maize straw in mass ratios of 1:0, 1:1, 1:2, 1:3, 0:1, 2:1 and 3:1 were respectively labeled as P, 1P1M, 1P2M, 1P3M, M, 2P1M and 3P1M.

### Paddy soil incubation study

The incubation study was conducted in constant temperature unit. The plastic pots were filled with 2.0 kg of prepared Cd polluted paddy soil and thoroughly mixed with 5% ( $W_{\text{biochar}}/W_{\text{soil}}$ ) of each co-pyrolysis biochars (P, 1P1M, 1P2M, 1P3M, M, 2P1M and 3P1M), and the un-amended paddy soil was control (CK). All treatments were arranged in four replicates. The five Chinese cabbage seedlings (purchase from hezhiyuan seeding company) were planted in each pot and incubated at the paddy soil moisture of 60% for 60 days. All treatments were replicated three times. The incubation paddy soil samples were collected from each plastic pots at 0, 10, 20, 30, 40, 50 and 60 days for determination of bioavailability and speciation of Cd. The Chinese cabbage was harvested after 60 days of sowing.

### Sample analysis

The yield of each co-pyrolysis biochar was computed using Eq. (1). The pH of co-pyrolysis biochar was determined at a solid-to-liquid (w:v) ratio 1:20, and measured

with a Mettler-Toledo SevenMulti dual pH/conductivity meter. The total Cd was measured with HCl-HNO<sub>3</sub> (3:1) and analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000, Perkin Elmer Co, USA). The total C, H, O, and N content was determined by an elemental analyzer (Flash EA1112, Thermo Finnigan, Italy). Fourier transformed infrared spectroscopy (FTIR, Spectrum Two, Perkin Elmer, USA), surface area pore analyzer (BET, Quantachrome Instruments, Boynton Beach, USA) and X-ray diffraction (XRD, Bruker D8 Venture, Bruker, Germany).

$$\text{Yield (\%)} = \frac{W_{\text{biochar}}}{W_{\text{feedstock material}}} \times 100\% \quad (1)$$

where,  $W_{\text{biochar}}$  is the weight of co-pyrolysis biochar,  $W_{\text{feedstock material}}$  is the weight of peanut shell and maize straw mixed in different mass ratios.

The physiochemical properties of paddy soil were determined: The pH and electrical conductivities (EC) of the soil were measured with a Mettler-Toledo SevenMulti dual pH/conductivity meter using a ratio of soil/distilled water of 1:2.5 (w/v) for pH and 1:10 (w/v) for EC. Available Cd content (extracted by 0.1 mol/L CaCl<sub>2</sub>, 1:10, w/v). Total Cd (acid digestion with concentrated HNO<sub>3</sub> and HCl=3:1). Cd speciation content (according to BCR sequential extraction method). The number of certified reference material was GBW 07,405(GSS-5). The Cd was measured with Atomic Absorption Spectroscopy (SHIMADZU AA-7000, Japan). The characteristics of co-pyrolysis biochars and soil are presented in Table 1.

The harvested plants were soaked in 20 mmol/L EDTA-Na<sub>2</sub> for 15 min, and rinsed with deionized water for removal of heavy metals attached to plant surface. The plants were oven dried at 105 °C for 2 h, and dried at 75 °C until a constant weight for measured index. The plants were analyzed with Atomic Absorption Spectroscopy (SHIMADZU AA-7000, Japan) by HNO<sub>3</sub> digestion method for concentration of Cd [6], and total

**Table 1** The characteristics of co-pyrolysis biochars and soil

Property	pH	Total Cd (mg/kg)
Soil	5.24	2.25
P	8.14	0.11
1P1M	9.16	0.32
1P2M	9.35	0.21
1P3M	10.73	0.29
M	8.46	0.35
2P1M	8.77	0.14
3P1M	9.19	0.27

digestion was verified with a standard material GBW 07,603(GSV-2).

Additionally, translocation factor (TF), which indicates the ability of plants to translocate Cd from the roots to the shoots, was calculated by the following formula (2):

$$\text{Translocation Factor (TF)} = \frac{\text{Cd concentration in aerial parts}}{\text{Cd concentration in roots}} \quad (2)$$

### Statistical analysis of data

The one-way analysis of variance (ANOVA) and LSD's multiple range tests were conducted by SPSS 17.0 for statistical significance of the effects of co-pyrolysis biochars in Cd contaminated paddy soils (SPSS Inc., Chicago, USA). The values were reported as means and standard error of three independent replicates. The variations were considered statistically significant at  $p < 0.05$ . The results were visualized with Origin Pro 8.0 (Origin Lab Corporation, Northampton, USA).

## Results and discussion

### Physicochemical properties of co-pyrolysis biochars

Table 2 reveals production of all co-pyrolysis biochar in mass ratios (1:0, 1:2, 1:3) mixture between 30.44% (yield of peanut shell biochar) and 34.32% (yield of maize straw biochar). The production and ash content of co-pyrolysis biochar was enhanced from 31.74% and 27.72% (1P1M) to 32.76% and 28.52% (1P2M), 34.12% and 30.27% (1P3M). The production and ash content of co-pyrolysis biochar was improved with increase of maize straw content in mixture raw materials. It has been reported that yield of biochar depend on content of ash [15]. The production of biochar has positive relationship with content of biochar ash [16]. The production and ash content was improved with increase in maize straw content of co-pyrolysis biochar, which may be due to higher inorganic salt and nonvolatile matter content of maize straw than peanut shell [6].

The content of C was highest in all co-pyrolysis biochar, followed by O, H and N. Moreover, C, H, O and N

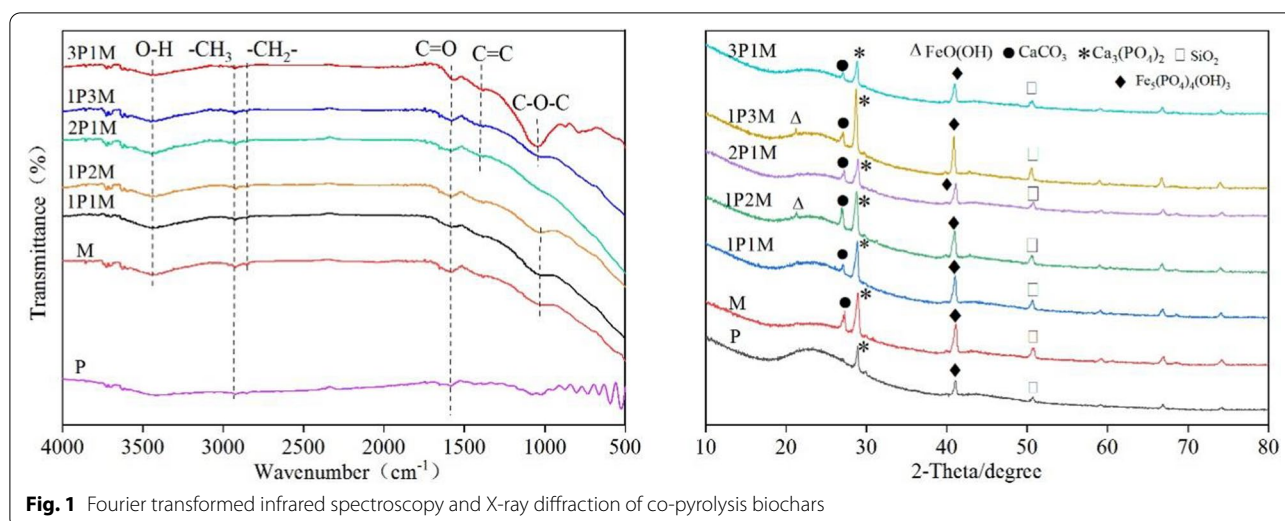
contents of P were higher than M, which were 59.82, 1.77, 12.35, and 0.58%, respectively. The highest O content was observed in 1P3M (up to 17.90%), and O/C ratio showed highest value in 1P3M, which indicated that 1P3M may produce more oxygen containing functional groups during co-pyrolysis process than others co-pyrolysis biochar. In particular, the largest specific surface area was 3.53 m<sup>2</sup>/g in 1P3M. Previous studies reported that number of oxygen-containing functional groups is one of the important factors affecting adsorption of Cd by biochar [17]. The biochar may have high-efficient extraction of Cd due to its large specific surface area [18]. In this study, the 1P3M have highest O/C ratio and largest specific surface area. It has been observed that 1P3M may have higher-efficient extraction of Cd than other co-pyrolysis biochar.

### Morphological characterization

Figure 1. indicates morphological characterization of co-pyrolysis biochar as an important index for adsorption of Cd. The surface functional groups of co-pyrolysis biochar are exhibited in Fig. 1A. The band at 3439 cm<sup>-1</sup> corresponds to stretching and bending vibrations of -OH functional groups due to carboxylic acid on surface of biochar [9, 19]. The peak presence at 3439 cm<sup>-1</sup> of co-pyrolysis biochar was more prominent, broad and stronger than single biochar (M and P). This reveals that co-pyrolysis of peanut shells and maize straw could promote -OH functional groups formation on the surface of biochar [20]. The peaks in the regions of 2936 cm<sup>-1</sup> were assigned to -CH<sub>3</sub> stretching vibration. The band at 2842 cm<sup>-1</sup> was caused by extension of CH<sub>2</sub>- bond [21]. The sharp band 1583 cm<sup>-1</sup> (the stretching vibration of C=O) and 1394 cm<sup>-1</sup> (the stretching vibration of C=C) with higher wave numbers of 1P3M and 3P1M may be attributed to rich oxygen-containing functional groups on their surface [22, 23]. The highly strong and wide peaks at 1035 cm<sup>-1</sup> was originated from stretching vibration of C-O-C in 3P1M [24–26]. The results of FTIR suggested that co-pyrolysis biochar would produce more

**Table 2** The properties of co-pyrolysis biochars

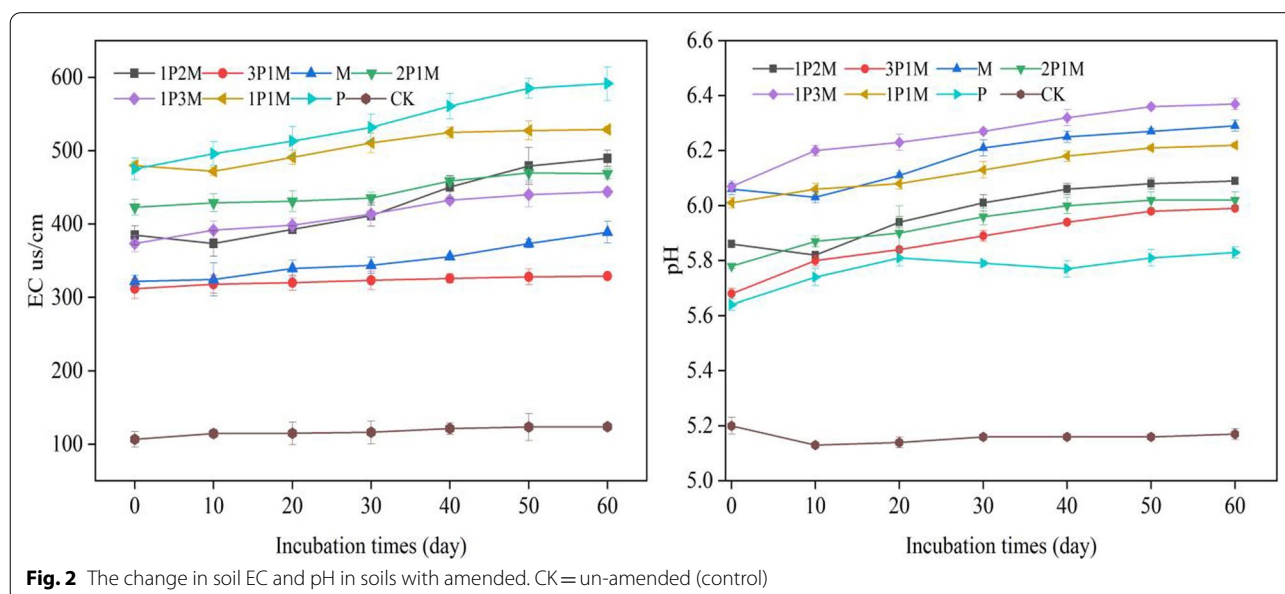
Samples	Yield [%]	Ash content%	N [%]	C [%]	H [%]	O [%]	O/C ratio	H/C ratio	BET [m <sup>2</sup> /g]
P	30.44 ± 1.04	25.32 ± 0.05	0.58 ± 0.08	59.82 ± 2.37	1.77 ± 0.09	12.35 ± 0.19	20.64	2.96	2.24
M	34.32 ± 0.72	31.26 ± 0.07	1.44 ± 0.09	58.49 ± 1.43	1.79 ± 0.06	15.00 ± 0.45	25.64	3.06	2.78
1P1M	31.74 ± 1.49	27.72 ± 0.14	1.12 ± 0.11	60.30 ± 0.46	1.82 ± 0.20	12.70 ± 0.18	21.06	3.02	2.46
1P2M	32.76 ± 0.75	28.52 ± 0.08	1.32 ± 0.14	58.67 ± 1.05	1.79 ± 0.02	14.85 ± 0.31	25.31	3.05	2.37
2P1M	32.89 ± 1.08	29.69 ± 0.11	1.05 ± 0.14	59.23 ± 1.68	1.69 ± 0.06	13.75 ± 0.30	23.21	2.85	1.35
1P3M	34.12 ± 1.07	30.27 ± 0.17	0.61 ± 0.06	60.31 ± 0.85	1.77 ± 0.05	17.90 ± 0.14	29.68	2.93	3.53
3P1M	33.46 ± 0.93	27.54 ± 0.09	0.90 ± 0.12	55.61 ± 0.92	1.80 ± 0.02	12.85 ± 0.06	23.11	3.23	1.19



surface oxygen-containing functional groups than single biochar.

The XRD spectra from biochar was product from co-pyrolysis (Fig. 1B). The diffraction peaks at 27.1°, 29.0°, 40.9° and 50.6° in 2θ degree can be assigned to  $\text{CaCO}_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3$  and  $\text{SiO}_2$ , respectively [27, 28]. The high-intensity peak at 29.0° was observed in 1P3M, which is probably due to high content of  $\text{Ca}_3(\text{PO}_4)_2$  in biochar after co-pyrolysis [29]. The intensities of co-pyrolysis biochar peaks at 40.9° were stronger in 1P3M than others biochar, which means that biochar produced from peanut shell and maize straw in mass ratios of 1:3 could promote  $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3$  formation

compared to other ratios [30]. Additionally, a new 2θ diffraction peaks at 21.3° was observed in 1P3M and 1P2M, which might be attributed to presence of  $\text{FeO}(\text{OH})$  [31]. Similarly, co-pyrolysis biochar has stronger diffraction peaks than single biochar (P and M), and new diffraction peaks appear (at 21.3°), especially 1P3M. The result of XRD spectra indicated that 1P3M has high content of  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  at surface of biochar, which could contribute to immobilization of Cd by precipitation reaction (e.g.  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}_3(\text{PO}_4)_2$ ,  $\text{CdCO}_3$ , etc.) [32]. Primarily, co-pyrolysis biochar could form rich oxygen-containing functional groups and crystal structure.



### Effect of co-pyrolysis biochars on pH and EC in paddy soil

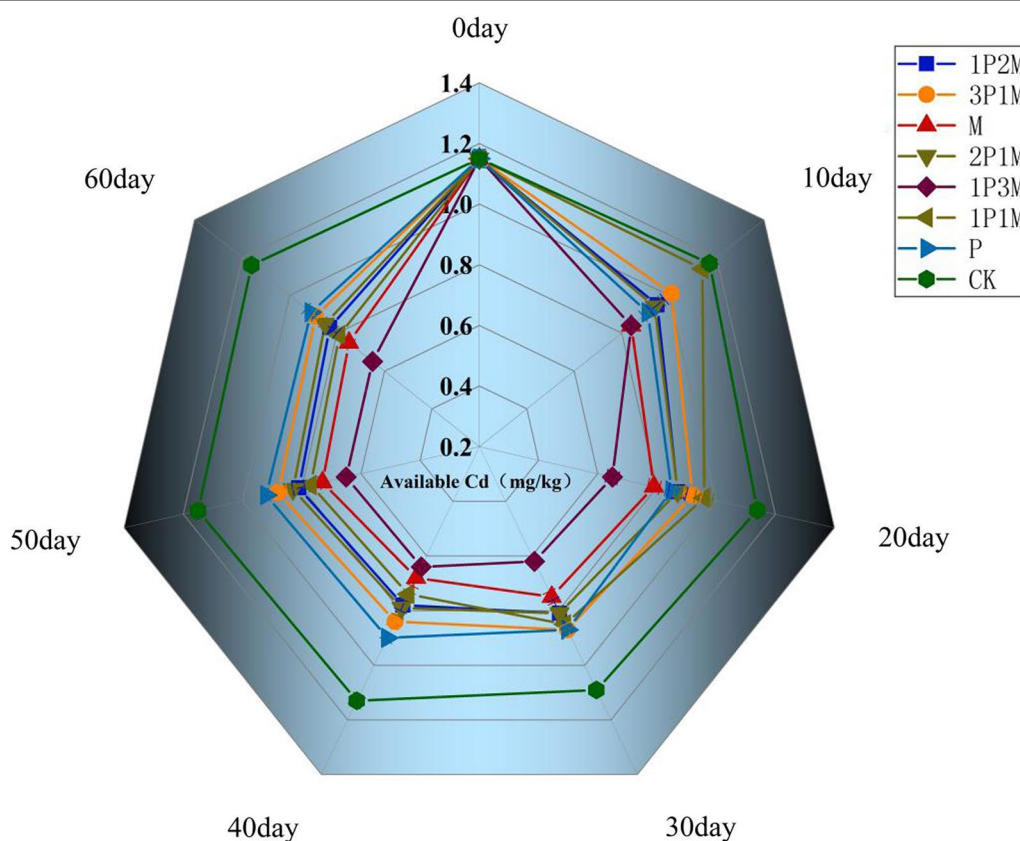
In paddy soil, pH and EC are essential indicators for bio-availability of Cd and plant growth [33]. The changes of pH in contaminated paddy soil amended with co-pyrolysis biochars are displayed in Fig. 2 during incubation. Figure 2 indicates non significant change in pH value during incubation period between 5.13 and 5.20. The pH of soil amended with biochar showed an upward trend during plant growth, and soil pH was increased significantly ( $P < 0.05$ ) compared with control treatment. Moreover, there were sharp increase in soil pH within the first 30 days, which may be caused by strong alkalinity of biochar [12]. The pH of soil was in order of  $1P3M > M > 1P1M > 1P2M > 2P1M > 3P1M > P > CK$  during period of 30 to 60 days of incubation experiment. The amendments of 1P3M, M, 1P1M, 1P2M, 2P1M, 3P1M, P have increased pH by 23.18%, 21.71%, 20.34%, 17.71%, 16.51%, 15.87% and 12.71%, respectively compare with control treatment. The high pH value was recorded from treatment of 1P3M amended within incubation from 6.37 at 60 days, which may be due to richest surface functional groups of 1P3M and content of  $CaCO_3$ ,  $Ca_3(PO_4)_2$  and  $Fe_5(PO_4)_4(OH)_3$  at the surface of biochar. The alkali radical ions were easily

released in soil solution, thereby increasing pH value of soil [34, 35].

The treatments of amendments with biochar have significantly ( $P < 0.05$ ) improved EC in soil from 165.81–377.72% than control treatment (Fig. 2). The highest EC value was observed in treatments of P amended (591.4 us/cm), while lowest EC value was in 3P1M (329.0 us/cm) at 60 days. The improvement of EC in soil was probably attributed to effect of high inorganic salt ion ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  etc.) and ash in biochars [18, 36, 37].

### Effect of co-pyrolysis biochars on bioavailability of Cd

The available Cd concentration of soil was positively correlated to Cd of plants[38].The application of biochar has significantly ( $P < 0.05$ ) reduced available Cd content in the soil compared with control treatment (Fig. 3). The available Cd in amended soil was significantly decreased in all treatments within first 30 days, and then increased slightly during 30–60 days. This may be due to improvement in pH value after addition of biochar, which contributed to form precipitates between alkali radical ions (such as  $OH^-$ ,  $CO_3^{2-}$  etc.) and Cd in the soil, thereby reducing the mobility of Cd in the soil [28]. The



**Fig.3** The effect of co-pyrolysis biochars on available Cd in contaminated soil. CK=un-amended (control)

oxygen-containing functional groups (including -OH, -COOH, C=O, etc.) on surface of biochar can form a complex with Cd in amended soil, to further reduce bio-availability of Cd [39]. However, as the incubation time is enhanced, the absorbed Cd would be re-released, resulting in a slight raise in available Cd content of the soil at later stage of incubation. The available Cd concentration in the soil was in sequence of  $1P3M < M < 1P1M < 1P2M < 2P1M < 3P1M < P < CK$  at the end of incubation, while available Cd content was decreased in amended soil by 43.97%, 35.34%, 31.90%, 28.45%, 26.72%, 23.28% and 21.55% respectively compared to control treatment. The alteration trend of available Cd was consistent with pH during incubation. Generally, most of co-pyrolysis biochars have highest efficiency for absorption of Cd in soil than single biochar, especially 1P3M. Meanwhile, morphological characterization (XRD and FTIR) revealed that co-pyrolysis biochars (1P3M) would produce more oxygen-containing functional groups and inorganic salt ions than single biochar, which could increase adsorption efficiency of biochar to Cd in the soil [40, 41]. Therefore, the biochar of co-pyrolysis of different material in an appropriate ratio could improve extraction efficiency of Cd.

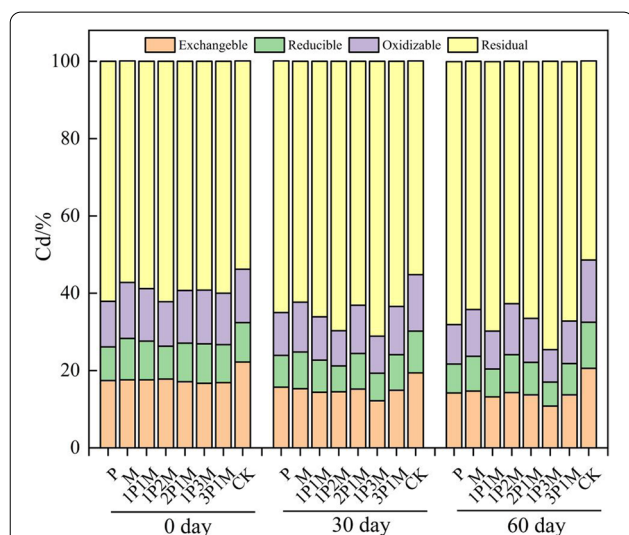
#### Speciation of Cd in soil of co-pyrolysis biochars amended

The speciation of Cd was determined with BCR sequential extraction method, which could be divided into four fractions of exchangeable, reducible, oxidizable and residual [42]. Previous studies have indicated that exchangeable fraction of Cd were easily utilized by plants, however residual fractions were stable and were

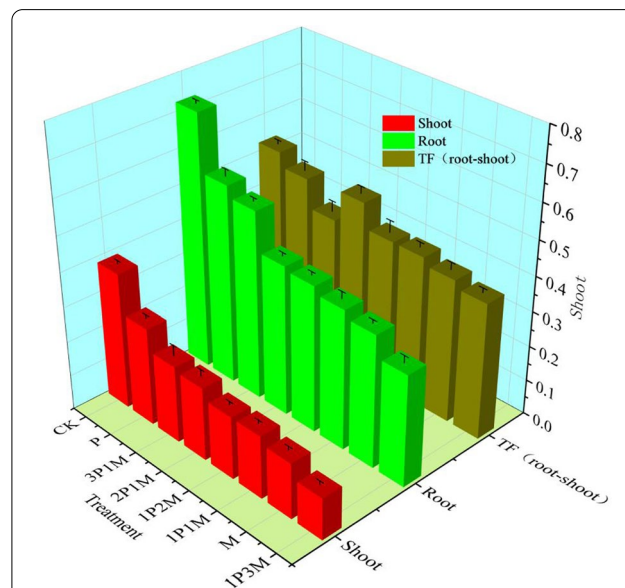
not utilized readily by plants [43]. Figure 4 shows variation in four speciation categories of Cd in soil after biochars amendment. The exchangeable Cd in all treatments was reduced in comparison to CK. The content of residual fraction was enhanced with increase of incubation time, which indicated that biochars could transport Cd from soluble form to less toxic stable form. The biochars applied could enhance soil pH, increase concentration of  $OH^-$  in solution, contribute to formation of hydroxide deposits and can promote combination of mineral components of biochar and Cd ions to form salt deposits [44, 45]. The addition of P, M, 1P1M, 1P2M, 2P1M, 1P3M and 3P1M has decreased exchangeable fraction Cd by 18.39%, 16.29%, 24.77%, 19.66%, 19.88%, 35.61% and 18.93% respectively compared with control at completion of incubation. The proportion of Cd exchangeable fractions has stronger reduction than other treatments in 1P3M, which was reduced from 16.7% to 10.8% during incubation. The concentration of Cd reducible fractions was lowest in 1P3M. The residual fraction of Cd was improved from 59.2% to 74.6% in 1P3M. It is concluded that the 1P3M has greater efficiency for extraction of Cd from exchangeable fractions (easily utilized by plants forms) to residual fractions (less toxic stable forms) than single biochars and other co-pyrolysis biochars.

#### Effects of co-pyrolysis biochar on cadmium uptake by plants in contaminated paddy soil

The amendment of contaminated paddy soil with co-pyrolysis biochar could reduce Cd contents in Chinese



**Fig.4** Effects of co-pyrolysis biochar on speciation of Cd in contaminated soil at 60 days



**Fig.5** The contents of Cd in shoots and roots of Chinese cabbage grown in Cd contaminated paddy soils amended with co-pyrolysis biochars

cabbage in our study (Fig. 5), which reflected that the co-pyrolysis biochar had a much greater potential to alleviate Cd stress in plant [46, 47]. The results conveyed that the whole co-pyrolysis biochar amended has significantly ( $p < 0.5$ ) reduced Cd contents of shoot (28.2–69.2%) and root (21.1–56.1%) compared to control and single peanut shell biochar treatment. The Cd concentration of Chinese cabbage in all treatments was in the sequence of  $CK > P > 3P1M > 2P1M > 1P2M > 1P1M > M > 1P3M$  in the shoot. And the Cd concentration of the root has also shown a consistent trend. The treatment of 1P3M was the best for reduction of Cd content in shoot and root compared to other treatments, and reduced to 0.12 mg/kg and 0.32 mg/kg, respectively. The Transport Factor (TF) of Cd in Chinese cabbage has indicated that  $TF_{\text{root-shoot}} < 1$  in all treatments. It is concluded that biochar derived from co-pyrolysis of peanut shell with maize straw at a mass ratio of 1:3 could most effectively reduce the bioavailability of Cd in contaminated paddy soil. Previous studies have confirmed that the surface characteristics of biochar (specific surface area, oxygen-containing functional groups, crystal structure, etc.) are one of the main factors affecting its adsorption and fixation of Cd [6, 42]. Besides, this study found that the 1P3M had largest specific surface area, more surface oxygen-containing functional groups (e.g. -OH, -COOH, etc.), and high content of inorganic ions (e.g.  $PO_4^{3-}$ ,  $OH^-$  and  $CO_3^{2-}$ , etc.) at surface of co-pyrolysis biochar. This could contribute to promote the conversion of soil Cd into low toxicity and low mobility substances (e.g.  $Cd(OH)_2$ ,  $CdCO_3$ , etc.) through surface adsorption, precipitation reaction and increasing soil pH value, so as to hinder the absorption and transportation of cadmium by Chinese cabbage [1]. Additionally, co-pyrolysis biochar application could improve the rhizosphere soil environment and promote the stress resistance of Chinese cabbage [48]. In conclusion, among the different co-pyrolysis biochars, results indicated that 1P3M was effectively decreased the bioavailability of Cd in the contaminated paddy soil.

## Conclusions

The co-pyrolysis biochars produced from peanut shell and maize straw have improved content of ash and yield. The co-pyrolysis biochars have generated more surface oxygen-containing functional groups and crystal structure. The co-pyrolysis biochar can significantly enhance pH and EC values, and can reduce available Cd content than control treatment. The 1P3M amended has high efficiency for reduction of available Cd content in soil compared with control and other co-pyrolysis biochar amended treatments. The treatments of biochars can effectively reduce content of Cd exchangeable fraction and can enhance residual fraction concentration,

particularly 1P3M. This study reveals that co-pyrolysis technology can improve efficiency of biochar for immobilization of Cd. And 1P3M has a much greater potential to decrease the bioavailability of Cd in contaminated paddy soil. Overall, the co-pyrolysis biochar produced from peanut shell and maize straw in mass ratios of 1:3 was most efficient for reduction of bioavailable Cd in contaminated soil.

## Abbreviations

The seven co-pyrolysis biochar produced from peanut shell and maize straw in mass ratios of 1:0, 1:1, 1:2, 1:3, 0:1, 2:1 and 3:1 were respectively labeled as P, 1P1M, 1P2M, 1P3M, M, 2P1M and 3P1M.

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## Author contributions

WJX and SHH designed the research and write the research paper. YTP analysis data; GR and BZ check and revised the paper. MZX and LLX determined physicochemical properties of soil and biochar. JWX, WKNL and ZQR collection sample and processing. DL project administration and funding acquisition.

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## Availability of data and materials

The data sets used and/or analyzed during the current study are available from the corresponding author on request.

## Declarations

### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

### Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Author details

<sup>1</sup>Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, State Key Laboratory of Subtropical Silviculture, Zhejiang A & F University, Hangzhou, Zhejiang 311300, People's Republic of China. <sup>2</sup>Zhejiang A & F University Landscape Architecture Institute, Hangzhou, Zhejiang, People's Republic of China. <sup>3</sup>Institute of Chemical Sciences, The University of Peshawar, Peshawar, Pakistan. <sup>4</sup>Chengbang Ecological Environment Co., Ltd, Hangzhou, Zhejiang, People's Republic of China.

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