The effect of several activated biochars on Cd immobilization and microbial community composition during in-situ remediation of heavy metal contaminated sediment

Si-jia Liu [a, b], Yun-guo Liu [a, b, *], Xiao-fei Tan [a, b], Guang-ming Zeng [a, b], Ya-hui Zhou [a, b], Shao-bo Liu [c], Zhi-hong Yin [a, b], Lu-hua Jiang [a, b], Mei-fang Li [a, b], Jun Wen [d]

[a] College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, 410082, PR China
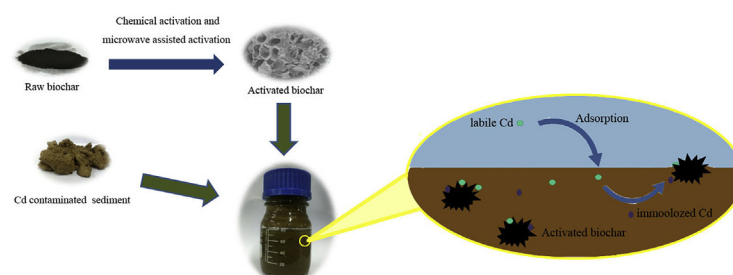[c] School of Metallurgy and Environment, Central South University, Changsha, 410083, PR China
[d] College of Agriculture, Guangxi University, Nanning, 530005, PR China

HIGHLIGHTS

- Activated biochar addition decreased the aqueous concentrations of Cd in sediment.
- Activated biochar showed excellent performance in immobilization of Cd in sediment.
- Activated biochar improved the pH and the CEC of sediment.
- Activated biochar influenced bacterial community diversity.

GRAPHICAL ABSTRACT

ABSTRACT

Chemical activation and microwave assisted activation were adopted to modify biochar. Activated biochars were characterized by SEM, BET, FTIR, XRD and XPS. Raw biochar, activated biochars and commercial activated carbon were compared as remediation strategies for sediment from the Xiangjiang River containing 14.70 mg/kg Cd. After the treatment by activated biochar, the overlying water and pore water concentration of Cd decreased by 71% and 49%, respectively. And the threat of heavy metal along with bioavailability of Cd was depressed. Moreover, the immobilsation of Cd in sediment was related to BET surface area and the content of oxygen containing functional groups of activated biochars. Furthermore, a PCR-DGGE-based experiment was performed for the detection of microbial community. The indigenous microbial community was affected and new microbial community appeared after treat by activated biochar. Activated biochar can be used as an inexpensive and efficient in situ remediation material of sediment containing metal.

© 2018 Published by Elsevier Ltd.

1. Introduction

Cadmium (Cd) is known to be one of the most toxic heavy metals due to its toxicity, persistence, and non-degradability in the environment (Davutluoglu et al., 2011). Cd has a number of adverse

* Corresponding author. College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR China.
E-mail address: liuyunguo_hnu@163.com (Y.-g. Liu).

effects on human health including damage to liver, lungs, bones and can cause cancer as well as other fatal disorders (Khan et al., 2017).

Sediments act as both metal carriers with the primary exchange modes being adsorption or precipitation, and potential sources of contaminants in the river (Yu, 2001; Davutluoglu et al., 2011). Moreover, the heavy metals can be either adsorbed onto sediments or accumulated by benthic organisms to a toxic level (Yu, 2001). In the south of China, non-ferrous metals are found in the middle and lower reaches of the Xiangjiang River (the largest river in Hunan) (Mao et al., 2012), due to the rapid development of metallurgical industry, mining activities and sewage irrigation (Xu et al., 2012). For example, the average Cd in the sediment of Xiangjiang is up to 19.42 mg/kg, which has been affecting around 43 million people in this drainage area (Zhang et al., 2015). Therefore, it is urgent to remove Cd from contaminated sediment.

In situ remediation of sediments polluted by heavy metal using materials with high adsorption capacity has become a common method due to low cost, simple operation, and less impact on natural hydrological conditions (Song et al., 2017b). A large number of advanced materials have shown their advantages for pollution remediation, such as silver nanoparticles (Das et al., 2012), zero-valent iron (Tomašević et al., 2014) and carbonaceous nano-composites (Zhang et al., 2016). However, their high cost and complicated process limited their application.

Biochar is more cost-effective compared to the above materials. Biochar has attracted widespread attention in the remediation of heavy metal pollution in soil and sediment, because of its potential use as a soil amendment to improve soil and sediment quality and immobilization of metal, such as Cu(II), Pb(II) and Cd(II) (Jiang et al., 2012; Sun et al., 2012; Cui et al., 2016). Biochar has been universally applied due to their physical/chemical surface characteristics such as extensive surface area and well-developed pore structure and more environmentally and economically viable (Jiang et al., 2012; Sun et al., 2012; Liu et al., 2017; Zeng et al., 2018). Previous studies showed that biochar had strong sorption to remove Cd. And biochars can contribute to Cd sorption by electrostatic reaction, ion exchange, surface complexation and precipitation (Qi et al., 2017). In addition, recent studies have highlighted that biochar play an important role in immobilizing heavy metals due to their highly porous structure, active functional groups and generally high pH and CEC (Zhang et al., 2013).

Moreover, additional treatment can be used to enhance adsorption ability of biochar (Mahmoud et al., 2012). Chemical activation was applied to activate biochar with chemical reagents such as $ZnCl_2$, KOH, and H_3PO_4, which showed significant improvement in the physicochemical properties of biochar (Tan et al., 2017). Chemical activation could remove of impurities on the surface of biochar to improve the pore properties of biochar, and introduce or increase many functional groups onto the surface of biochar (Mahmoud et al., 2012; Qian and Chen, 2014; Tan et al., 2017). Microwave-assisted heating is an attractive technique that offers internal and volumetric heating as compared to conventional heating, which cause different pore structure and surface area (Ahmed and Billah, 2016). Modified biochar has good application in the removal of pollutants in water, but few researches have been done on using modified biochar for repairing sediment. In this study, we adopted two methods (chemical activation and micro-wave assisted activation) at the same time to gain biochar with more excellent performance in remediation of sediment Cd pollution.

This sediment remediation by different carbonaceous materials aims at improving the stabilization of heavy metals in sediments by reducing their mobility, bioavailability, and toxicity with adsorbents (Song et al., 2017b). The primary principle of the immobilization of heavy metals is to change their form and to make them less available to sediment organisms (Wang et al., 2014). BCR (European Community Bureau of Reference) sequential extraction method was greatly associates with the transportation and mobi-lization of the heavy metals in sediment. Toxicity Characteristic Leaching Procedure (TCLP) (based on USEPA 1311) was also carried out to evaluate the mobility of heavy metals in the specimens (Shen et al., 2017).

A successful immobilization remediation technique must to decrease of the bioavailability of heavy metals. And microbial communities can directly address biological availability and toxicity of heavy metals (Kumpiene et al., 2006). Recent study show that enzymes activities and bacterial community diversity increased during the metal Cd immobilization in contaminated river sedi-ments (Huang et al., 2016). However, some researches indicated that indigenous microbes could be affected by biochar either directly or indirectly via changing the physicochemical properties and heavy metals of sediment (Huang et al., 2017). In this study, we performed 16S rRNA sequencing and polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE) to analyse the bacterial taxonomic composition in sediments.

The objectives of this study were to: 1) review the characteris-tics of different chemical activated biochars to better understand its efficiency in sediment remediation; 2) investigate the effectiveness of properties of activated biochars on Cd concentration in sediment pore waters and sediment overlying water; 3) carry out in situ remediation of sediments contaminated by cadmium with raw biochar, different chemical activated biochars and commercial activated carbon, respectively; 4) study the effect of sediment mi-crobial community abundance by different carbonaceous materials.

2. Materials and methods

2.1. Preparation of adsorbent

The raw rice husk biochar (RHB) used in this study was supplied by Wo le biological technology co., Ltd, Beijing where RHB was produced by fast pyrolysis of 5–10 s at 500 °C. The RHB was oven dried at 80 °C for 24 h and crushed to pass through a 0.3 mm sieve. Commercial activated carbon (AC) was purchased from Sinopharm Chemical Reagent Co. Ltd., China.

Activated biochar was prepared from RHB by a simple process that involved with H_3PO_4, HNO_3, H_2SO_4, H_2O_2 and $ZnCl_2$ treatment followed by microwave-assisted heating, respectively. 5 g of RHB and 20 mL of 2 mol/L activation solution was mixed in a 100 mL Erlenmeyer flask and then it was shaken in a temperature controlled shaker (SHZ-88, Shanghai) at 170 rpm at 25 °C for 24 h. Then, the mixtures were moved into the microwave digestion tank and subjected to microwave treatment under microwave powers of 600 W in the microwave reactor for 10 min. The product was been washed several times with deionized water and was dried in the oven at 80 °C. Activated biochar prepared from different modified reagents were labeled as PAB (H_3PO_4), NAB (HNO_3), SAB (H_2SO_4), OAB (H_2O_2) and ZAB ($ZnCl_2$). The commercial activated carbon (AC) and raw biochar (RHB) were also purchased as adsorbent for comparison.

2.2. Characterization methods

The Brunauer–Emmett–Teller (BET) specific surface area of the samples was characterized by automatic surface analyzer (Quan-tachrome, USA). Scanning electron microscopy (SEM) (Hitachi S-4800, Japan) images were used to determine the structure and morphology of r all biochars we prepared. The Fourier transform

infrared (FTIR) spectra were recorded on a Nicolet 6700 spectro-photometer. The X-ray diffraction (XRD) pattern was performed with a Bruker D8-Advance X-ray diffractometer (Bruker, German). The elemental composition of the samples was examined using an ESCALAB 250X$_i$ X-ray Photoelectron Spectrometer (XPS) (Thermo Fisher, USA). The concentration of Cd was analyzed by ICP-OES (PerkinElmer Optima 5300DV).

2.3. Sediment-activated carbon contact

Xiangjiang River sediment was contacted with the above carbonaceous material dose of 2% dry sediment mass for up to 3 months. Wet sediment, equivalent to 50 g dry mass, was placed in 100 mL screw mouth bottle, followed by and 60 mL of deionized water and standing for 24 h. Then, dose of 2% dry sediment mass (1 g) of RHB, different active biochar (total 5 species) and com-mercial activated carbon added to the bottle, respectively. An identical bottle was prepared without the carbonaceous material. Bottles shook up and were stored in an artificial climate box at 20 °C in the dark to analysis.

2.4. The solid and liquid equilibrium concentration

After biochar sediment cultivating 3 months, the overlying water was obtained from the top of sediment and filtered through a 0.45 μm glass fiber filter. And, the concentration of Cd in overlying water (C_{OW}) was analyzed by ICP-OES. After removing the overlying water, sediment samples were centrifuged at 4000 r/min for 15 min and the pore water was recovered from each sediment sample. The pore water was then filtered to remove particulate matter before being determination of Cd concentration (C_{PW}) by ICP-OES. All centrifuged sediment samples were removed from the bottle and were freeze-dried for 48 h. Then, all dry sediment samples ground to pass through a 60-mesh sieve and were reserved at 4 °C for subsequent analysis.

To determine the amount of Cd of the solid part of sediment, the dry sediment samples were processed by three acids digestion method. 1.0 g dry sediment samples weighed into dried boiling tubes and added in 5 mL HNO$_3$, 5 mL HF and 3 mL HClO$_4$ and the mixture was thermal decomposed by graphite digestion apparatus. The heating procedure was set as following: 90 °C for 40 min, 160 °C for 60 min and 170 °C for 40 min. About 1 mL light green liquid was created when the digestion produce finished and removed the liquid sample after cooling down. Then, the liquid sample was dissolved by 5% HNO$_3$ to a volume of 10 mL for being determination of Cd concentration.

2.5. The sequential extraction procedure

The BCR sequential extraction method was applied for metal partitioning (Jiang et al., 2012). In the procedure, metals were classified into four fractions defined as acid soluble (step1) reduc-ible (step 2), oxidizable (step 3) and residual (not speciated during

the BCR procedure). The exchangeable and acid soluble fraction presents the loosely bound, labile or exchangeable metals that can be released by merely changing the ionic strength of the medium (Davutluoglu et al., 2011). The extractants that used in each step and the sediment fractions targeted are summarized in Table 1. The procedure was conducted by the extraction of 0.5 g of dried sedi-ment sample in 50 mL centrifuge tubes.

Following each extraction, the mixtures were centrifuged at 4000 r/min for 15 min; the supernatant was decanted and stored in clean centrifuge tubes at 4 °C until analysis. The residue from each extraction step was washed with 20 mL deionized water and me-chanically shaken for 15 min at 180 r/min. After shaking, the res-idue was centrifuged at 4000 r/min for 15 min and the supernatant was discarded.

2.6. Toxicity characteristic leaching procedure (TCLP)

The toxicity characteristic leaching procedure (TCLP) was per-formed following U.S. EPA Method 1311 to determine the leach-ability of Cd in the sediment (Shen et al., 2017). The extraction fluid was prepared by diluting 5.7 mL CH$_3$COOH with 500 mL ultrapure water before added 64.3 mL NaOH (1 mol/L) to a volume of 1000 mL, using 1 mol/L HNO$_3$ to achieve pH = 4.93 ± 0.05. Mixed 40 mL extraction fluid with 2 g sediment in a 50 mL centrifuge tube and shook it (190 r/min) for 19 h at 25 °C. Then the tube was centrifuged at 4000 r/min for 15 min, the supernatant was filtered for subsequent analysis.

2.7. Determination of bacterial community

Total genome DNA from samples was extracted using CTAB/SDS method. Then, DNA concentration and purity was monitored on agarose gels. 16S rRNA genes were amplified used the specific primer with the barcode. All PCR reactions were carried out in 30 μL reactions with 15 μL of Phusion® High-Fidelity PCR Master Mix (New England Biolabs); 0.2 μmol/L of forward and reverse primers, and about 10 ng template DNA. Thermal cycling consisted of initial denaturation at 98 °C for 1 min, followed by 30 cycles of denatur-ation at 98 °C for 10 s, annealing at 50 °C for 30 s, and elongation at 72 °C for 30 s. Finally 72 °C for 5 min (Wang et al., 2007).

PCR Products were through quantification, qualification, mixing and purification. Then, Sequencing libraries were generated using TruSeq® DNA PCR-Free Sample Preparation Kit following manu-facturer's recommendations and index codes were added and the library was sequenced on an Illumina HiSeq 2500 and 250 bp paired-end reads were generated (Magoč and Salzberg, 2011).

3. Results and discussion

3.1. Characterization of adsorbent

The chemical and physicochemical properties of the different activated biochars are shown in Table 2. From Table 2, the hydrogen

Table 1
The modified BCR 3- step sequential extraction procedure.

Step (Fraction)	Reagent(s)	Procedure(s)
1 (acid soluble)	0.11 mol/L CH$_3$COOH	40 mL CH$_3$COOH + 1 g sample shaken at 250 rpm for 16 h
2 (Reducible)	0.5 mol/L NH$_2$OH·HCl and 0.05 mol/L HNO$_3$	40 mL NH$_2$OH·HCl and HNO$_3$ + residue from step1 and shaken at 250 rpm for 16 h
3 (Oxidizable)	8.8 mol/L H$_2$O$_2$ followed by 1.0 mol/L CH3COONH$_4$ (adjusted to pH 2 with HNO$_3$)	10 mL H$_2$O$_2$ + residue from step2 at 85 °C till almost dryness; 25 mL CH$_3$COONH$_4$ shaken at 250 rpm for 16 h
(Residual)[a]	three acid digestion method (HNO$_3$, HF and HClO$_4$)	As described in Pseudo-total metal digestion

[a] Digestion of residual material is not a specification of the BCR protocol.

Table 2
Physico-chemical characteristics of activated biochars.

Biochar	Elemental composition (%, mass based)				Atomic ratios			BET surface area (m2/g)
	C	H	O	N	O/C	H/C	(N + O)/C	
RHB	52.99	3.59	15.08	0.52	0.21	0.81	0.22	1.72
SAB	46.60	3.97	22.23	0.45	0.36	1.02	0.37	22.73
PAB	47.06	3.85	21.48	0.52	0.34	0.98	0.35	45.16
ZAB	44.46	3.66	22.92	0.56	0.39	0.99	0.40	31.30
NAB	41.75	3.31	20.57	1.91	0.37	1.00	0.41	66.00
OAB	44.80	3.66	25.73	0.57	0.43	0.98	0.44	11.50
AC	80.08	2.95	16.06	0.53	0.15	0.44	0.16	1589.97

and nitrogen content of activated biochars did not change significantly comparing to RHB. And the difference of contents of H between activated biochars is not significant. Biochar activated by HNO_3 (NAB) had the highest surface nitrogen content (1.91%), while the other activated biochars did not change significantly. However, the contents of C in activated biochars decreased, which indicated that the carbon in biochar was loosed by reacting with different modified reagents. Moreover, the contents of O in activated biochars were significant increased, which showed that the modification treatment introduced oxygen-containing functional groups and improve the content of functional group in the surface of biochars. This phenomenon was already reported by others researches (Xue et al., 2012; Qian and Chen, 2014).

The modification treatment with different modified reagents also has a greater impact in the specific surface area of the RHB. BET surface areas of activated biochars are dramatically increased compared with the RHB. The specific surface area size of active biochars was in the following order: HNO_3 activated biochar (NAB) > H_3PO_4 activated biochar (PAB) > $ZnCl_2$ activated biochar (ZAB) > H_2SO_4 activated biochar (SAB) > H_2O_2 activated biochar (NAB), increased to 38, 26, 18, 13 and 6 times than the raw rice husk biochar (RHB). Thus, activation of modified reagents can effectively improve the specific surface area of biochar, even contribute to improve the ability of biochar in remediation of sediment pollution.

The textural structure examination can be undertaken by observation of the scanning electron microscopy (SEM) images in Fig. 1. Many new and bigger pore structures were distributed on the surface of activated biochars after modification. The surface of RHB contains a large amount of ash and mineral components, blocking the pores of rice husk biochar, which could make it getting a weak pore structure. Chemical activation modification significantly improves the pore structure of biochar, which was proved by the BET surface areas analyzing. After modification treatment, the impurities blocking the pores of biochar were removed, thus the original pores of biochar were opened. At the same time, these modifiers react with the surface and pores of biochar, make the original pores larger and produce new microporous and mesoporous (Tan et al., 2016).

The FTIR spectra of rice husk biochar and their chemical activated samples are presented in Fig. 1g. Same as rice husk biochar, the absorption bands of all chemical activated samples existed below the absorption peak, which represented the existence of different functional groups: OH ($3426 cm^{-1}$), $-CH2-$ ($2948 cm^{-1}$ and $1434 cm^{-1}$), $C=O$ ($1631 cm^{-1}$), aromatic $CO-$ and phenolic $-OH$ groups ($1270 cm^{-1}$), $C-O$ ($1101 cm^{-1}$) and aromatic CH ($831 cm^{-1}$). The presence of these absorption bands explained that biochar contains a lot of reactive functional groups such as carboxyl and hydroxyl groups. After different modification, there are different levels of enhancement in some band intensities such as: $1270 cm^{-1}$ ($-OH$ groups), $1631 cm^{-1}$ ($C=O$), $1101 cm^{-1}$ ($C-O$) and $1270 cm^{-1}$ (aromatic $CO-$ and phenolic $-OH$ groups). This phenomenon indicated that these activation modifications increase the

oxygen-containing functional groups on the biochar, which can provide more sites for metal binding. The improvement of these surface chemical properties was conducive to biochar to play its role of heavy metal pollution remediation. Among them, the activation of H_2O_2 (OAB) is the most significant, and its treated biochar contains more active functional groups. These effects are similar to previous studies. H_2O_2 was used to modify peanut hull biochar. The results showed that H_2O_2 modification increased the oxygen-containing functional groups on the surface of biochar, particularly carboxyl groups (Xue et al., 2012). HNO_3/H_2SO_4 oxidation introduced carboxyl functional groups on the surface of biochar, which served as additional binding sites for metal (Qian and Chen, 2014).

The XRD patterns of all kinds of materials are shown in Fig. 1h. When biochar was activated by H_2O_2, $ZnCl_2$ and H_3PO_4, the XRD patterns displayed a new diffraction peak at 26.5° corresponding to the (002) planes of graphitic carbon (Hu et al., 2017). However, other activated biochar did not form new obvious crystal structure.

XPS analysis was performed on RHB, AC and all chemical activated biochars, which further confirmed the change in surface properties of biochars with chemical modification. The C1s and O1s spectra are summarized in Table 3. Table 3 showed the binding energy and percentage of the three peaks for RHB, including 90.97% of $C-C$ at 284.8 eV, 6.76% of $O-C-O$ at 286.4 eV and 2.25% of $-COOR$ at 288.7 eV (Qian and Chen, 2014). When RHB was modified by chemical reagent, the percentage of $O-C-O$ and $-COOR$ increased obviously, while the amount of $C-C$ decreased, which suggested that more oxygen-containing functional groups is generated on the surface of activated biochar compared to RHB. Moreover, a new peak appeared at the binding energy at ~285 eV after activation treatment, which can be attributed to $C-O$ (Liu et al., 2017). Three peaks were observed on the binding energy O1s region. According to the XPS database of Thermo Scientific, the binding energy of O1s at 530.8 eV can be assigned to $-OH$, at 531.9 eV to $C=O$, and at 533.2 eV to COO (Li et al., 2017b). After modified, the molar ratio of the COO increased and the $C=O$ reduced. These changes indicated the change trend of oxygen-containing functional groups.

3.2. Cd concentration in sediment water environment

Cd concentration of overlying water (C_{OW}) in sediment remedied by different activated biochars is shown in Fig. 2a. From Fig. 2a, different carbonaceous materials reduced the concentration of Cd in sediment overlying water significantly. Compared to RHB remediation, Cd concentration in overlying water declined in varying degrees after it was removed by different activated biochars. This phenomenon indicated that activated biochars can effectively increase the sediment adsorption ability of heavy metals, sequentially reduce the migration of heavy metals in sediments to overlying water. NAB, OAB and ZAB observably enhanced the ability of sediment to fix Cd compare to PAB and SAB. The
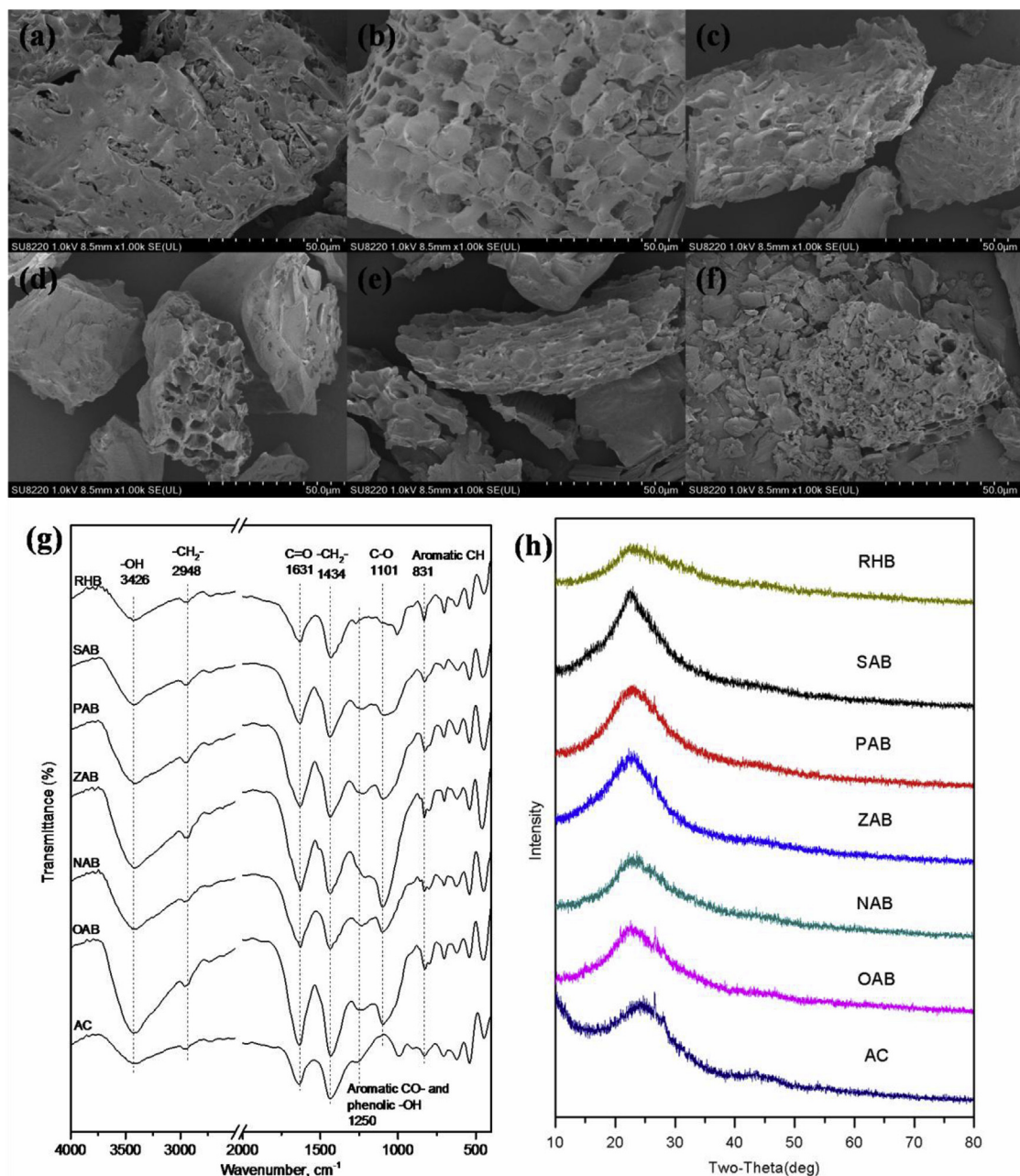
Fig. 1. SEM photograph of different activated biochars: (a) RHB, (b) SAB, (c) PAB, (d) NAB, (e) OAB, and (f) ZAB; (g) FT-IR spectrum and (h) XRD of different activated biochars.

Table 3
Fitted results of C1s and O1s XPS spectra of biochars.

	C1s				O1s		
Assignment (%)	C–C	C–O	O–C–O	–COOR	–OH	C=O	COO
Peak BE (eV)	284.80	285.10	286.40	288.70	530.80	531 .90	533.20
RHB	97.97	0	6.76	2.25	8.66	39.09	52.25
SAB	35.37	38.69	19.87	5.70	19.52	21.09	59.39
PAB	30.94	41.66	20.87	6.52	8.10	25.08	66.81
NAB	35.31	31.85	20.71	12.31	22.07	17.82	60.11
OAB	34.14	37.80	21.44	7.14	5.07	21.66	73.26
ZAB	35.46	37.86	20.61	6.05	5.29	27.03	67.69
AC	44.64	18.91	27.01	9.43	21.39	25.56	53.05

restoration effect of H_2O_2 and $ZnCl_2$ activated biochar was most obvious and Cd concentration in sediment overlying water was reduced by 71% and 58% than that of RHB, respectively. In addition, the concentration of Cd in the overlying water decreased by 66%
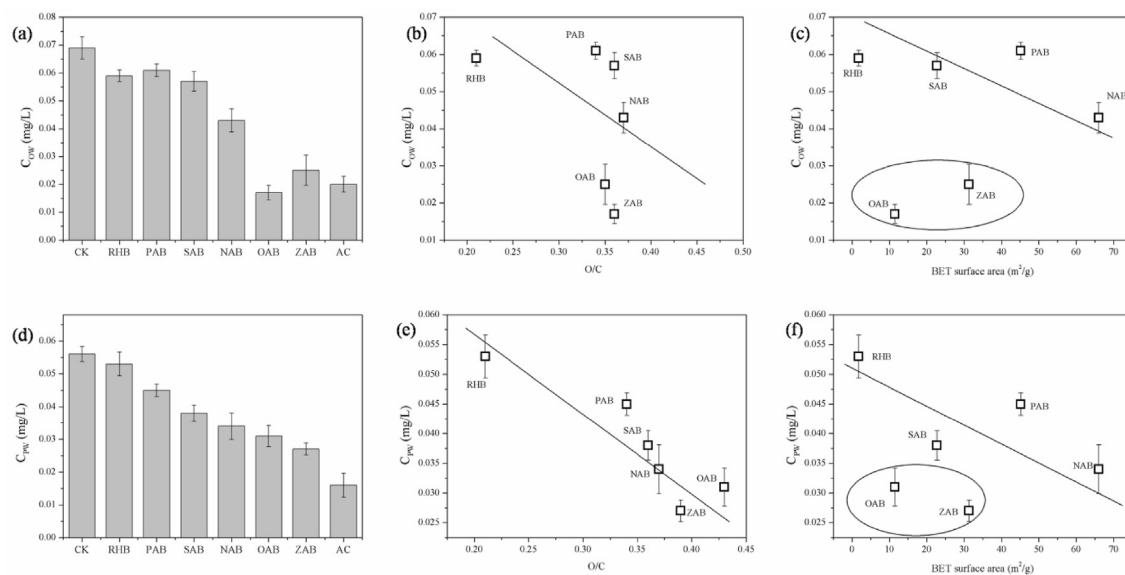
Fig. 2. Cd concentration in overlying water (a) and pore water (d) of sediment under treatment of different activated biochars; (b), (c), (d) and (f) were correlation between heavy metal concentration in aqueous phase of sediment and properties of activated biochars.

under the action of commercial activated carbon (AC), which showed that the restoration effect of OAB and ZAB was equivalent to AC.

From Fig. 2d, Cd concentration in sediment pore water (C_{PW}) was also significantly reduced after the addition of different carbonaceous materials. The Cd concentration in pore water treated by different activated biochars was in the following order: RHB > PAB > SAB > NAB > OAB > ZAB, which indicated that the choice of activated agent was crucial to the performance of biochar. The restoration effect of OAB and ZAB in pore water were most obvious, which was similar to the overlying water. Cd concentration in sediment pore water of OAB and ZAB samples was reduced by 42% and 49% than that of RHB respectively, while that decreased by 70% under the action of commercial activated carbon (AC). The remediation of activated biochar on sediment pore water is slightly lower than AC, but compared to commercial activated carbon, activated biochar has higher economic benefits.

Correlation between Cd concentration in aqueous phase of sediment and properties of activated biochars (O/C mole ratio and BET surface area) was shown in Fig. 2. Fig. 2 illustrates that the O/C molar ratio and the specific surface area of the biochar increase after the activated modification. This phenomenon indicated that the activated modification significantly improved the surface functional group content and the pore structure of the biochar, which was the main reason for improving adsorption capacity of heavy metals on sediment. From Fig. 2b and e, both Cd concentrations in aqueous phase of sediment (overlying water and pore water) decreased significantly with the increase of O/C molar ratio of biochar, indicating that the surface chemical properties of biochar are important factors in sediment remediation. From Fig. 2c and d Cd concentrations in aqueous phase of sediment treated by RHB, SAB, PAB and NAB decreased significantly with the increase of BET surface area of biochar. However, OAB and ZAB samples were not in the trendcy. Both these two kinds of activated biochar have lower BET surface area than other biochar, and the concentrations of Cd in overlying water and pore water are relatively low. This phenomenon was mainly because the higher O/C molar ratio and surface functional group were included by the two biochars. And the surface oxygen-containing functional groups specifically refer

to C=O and COO, from Table 3 and XPS analyzing. The activated biochars introduced oxygen-containing functional groups and improved the content of functional group and the specific surface area of biochar, which were conducive to biochar to remediation of Cd.

3.3. Chemical speciation of Cd in sediment

BCR procedure divides Cd into four species: acid soluble fraction, reducible fraction, oxidizable fraction and residual fraction. Acid soluble fraction and reducible fraction can be easily leached into environment and result in a direct damage to the organisms, while oxidizable fraction showing a potential eco-toxicity to the organisms (Wan et al., 2016). And residual fraction is universally accepted as the most stable fraction and almost unreactive under a wide range of natural conditions (Saeedi et al., 2013). The chemical speciation distribution of Cd estimated by BCR procedure in different activated biochars treated and non-treated sediment were shown in Fig. 3a.

Cd was mainly bound to acid soluble fraction (approximate 74.6%) in the original sediment while the reducible and residual occupied 24.68% and 0.74%, respectively. Oxidizable fraction of Cd in the original sediment accounts for a so small proportion that its content below the minimum detectable line. Acid soluble fraction and reducible fraction, which two were considered to be the most weakly bound fraction of Cd and had direct toxicity to the organisms (Min, 2013), showed decrease after RHB treated sample and all different activated biochars treated samples. As the core structure of biochar was recalcitrant, the complexes that produced by the interaction between heavy metal ions and biochar were expected to be more stable than other complexes that formed with heavy metal and other organic matters (Namgay et al., 2010), resulting in the lower percentage of acid soluble fraction and reducible fraction of Cd in sediment amended with RHB and modified biochar. Additionally, from the comparison between RHB and activated biochars, we can see that all activated biochars treated samples performed better than RHB treated sample. Acid soluble fraction of Cd after different activated biochars treated was sorted by size as follows: RHB > PAB > SAB > NAB > OAB > ZAB, which was almost
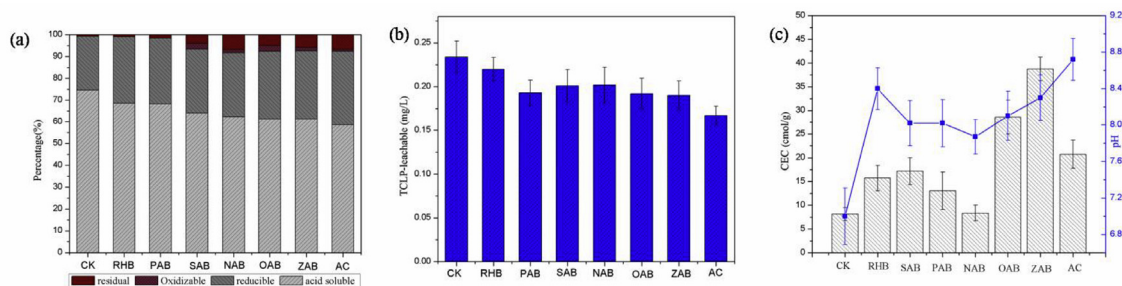
Fig. 3. (a) Fraction of Cd in sediment determined by BCR sequential extraction of sediment after treatment of activated biochars; (b) Cd concentrations in TCLP leachates of sediment after treatment of activated biochars; (c) CEC and pH of sediment after treatment of activated biochars.

same with Cd concentration in pore water. The fixing of Cd in sediment by OAB and ZAB are the most significant.

The content of residual fraction in the original sediment was little and oxidizable fraction of Cd in the original sediment was not detected, which may be caused by the low content of organic matters and weak Cd binding capacity of soil (Wang et al., 2017). The percentages of residual fraction in sediment increased in the groups amended with RHB and different activated biochars. There were plentiful adsorption sites and organic functional groups on the surface of biochar, such as carboxylic and phenolic functional groups that could interact with heavy metals in soil (Cheng et al., 2008). A more sizable increase of residual fraction in sediment was observed in NAB, ZAB and OAB treated samples than RHB treated samples when treated at the same ratio, indicating that activated modification biochar had a better effect on Cd immobilization. This phenomenon can be attributed to that there are more organic functional groups on the surface of NAB, ZAB and OAB than other biochars, which can be demonstrated by their O/C mole ratio in Table 2 and XPS analyzing.

The change of chemical speciation of Cd indicated that there were more acid soluble fraction that was transformed into residual fraction than reducible fraction and oxidizable fraction. Recent research determined that electrostatic reaction was contributed to Cd adsorption of biochars (Namgay et al., 2010) and the mineral components of biochars can work as additional sorption sites for metals through electrostatic reaction and ion exchange (Li et al., 2017a). Cd in acid soluble fraction can be easily released to the environment and converted into free ions, and then the Cd was readily to combine with biochar by electrostatic reaction and subsequently formed the complexes, which caused the reduction of acid soluble fraction and the increase of residual fraction.

In addition, commercial activated carbon (AC) biochar did not show a clear advantage on Cd immobilization compared to activated biochar (OAC and ZAC). Considering the economic benefit, OAB and ZAB can be used as a potential adsorbent to replace commercial activated carbon, used in-situ remediation of heavy metals contaminated sediment.

3.4. TCLP leachability of Cd

The effectiveness of Cd immobilization can be evaluated by determining the availability of Cd based on Toxicity Characteristic Leaching Procedure (TCLP) in a naturally contaminated soil (Lu et al., 2014). TCLP contained extractable Cd in sediment that was removed by different carbon materials is shown in Fig. 3b.

Concentrations of TCLP-extractable Cd in sediment decreased significantly after amended with RHB and different activated biochars. The OAB and ZAB treatment had the greatest decrease in extractable Cd, causing the concentration of TCLP-extractable Cd reduced by 12% and 18%, respectively. The data, which was

amended only across three months, was not excellent compared to other research which had lowered the levels of TCLP extractable Cd to 61.61% after biochar amendment across three years (Li et al., 2016). The phenomenon can be explained by that unlike the fast adsorption of heavy metals by biochar in aqueous solution (Inyang et al., 2016), which was in accordance with the previous research (Shen et al., 2017). The immobilization of heavy metals to sediment by biochar was a slowly developed process, which indicated that activated biochars can get better effect on immobilization Cd in long-time remediation. In addition, commercial activated carbon lowered the levels of TCLP extractable Cd to 23%, which approximately quite effect to immobilization of heavy metals in sediment with ZAB. Therefore, $ZnCl_2$ activated biochar can be used as a potential material in in-situ remediation.

3.5. pH and CEC

The pH value, which is under the influence of organic matter and carbon dioxide in the sediment, is a basic parameter when analyzing the characteristics of sediment (Song et al., 2017a). From Fig. 3c, the pH value was increased after treated by RHB and different activated biochars. The result indicated that biochar was beneficial to immobilization of heavy metals, because higher pH favored metal precipitation and simultaneously decreased the metal solubility (Song et al., 2017a). Moreover, the pH of activated biochars treated sediments was lower than RHB treated sediments. Because alkaline substances in biochar derived from base cations (primarily Ca, Mg, K, Na) in biomass which were transformed into oxides, hydroxides and carbonates (e.g. ash) during pyrolysis (Van Zwieten et al., 2009; Yuan et al., 2011), and the alkaline substances was washed during chemical activated modification.

Higher CEC favors stabilization of heavy metals in soil and sediment (Bache, 1976). Heavy metals can exchange with K^+, Na^+, Ca^{2+}, Mg^{2+}, and other cations, finally being co-precipitated or forming complexes with humic matters (Song et al., 2017a). Fig. 3c showed that the CEC of sediment increased after using different carbonaceous materials as amendments, due to biochars can cause large cation exchange on themselves (Zhang et al., 2014). In addition, the oxidation of surface functional groups on biochar also contributed to the CEC increase of the amended sediment (Atkinson et al., 2010), because oxidation of surface functional groups can increase charge density per unit surface of biochar and surface area for cation adsorption after the oxidation process (Singh et al., 2014). Therefore, the CEC of the sediment treated by RHB was lower than the sediment treated by SAB, OAB and ZAB that content more oxidation of surface functional groups. Moreover, the lower of pH can cause the decrease of negative charges of sediment, subsequently caused nutrients loss and CEC reduction as cations were disproportionately replaced with H^+ (Sharma et al., 2015). Therefore, the CEC of the sediment treated by H_2SO_3, H_3PO_4 and HNO_3

activated biochars was lower than the sediment treated by OAB and ZAB whose value of pH were higher. Besides, it is obvious that the CEC of OAB and ZAB treated sediment is superior to AC treated sediment.

3.6. Effects on indigenous microbial community abundance

To elucidate the effect of different carbon materials on indigenous microbial community abundance, we performed 16S rRNA sequencing to analyse the bacterial taxonomic composition in sediments. In Fig. 4, hierarchical cluster analysis showed the responses of top 35 genera (relative abundance > 0.1%, A) to biochar amendment in the sediment slurries at the end of 3-month experiment.

Fig. 4 shows that *Candidates_Solibacter*, *Bacillus*, *Fonticella*, *Gracilibacter*, *Phenylobacterium*, *Desulfovirga*, *Desulfurispora* and *Lentimicrobium* were the most dominant in the non-treated sediment. After treated by different carbon materials, the original strains of

dominant species disappear and some new dominants were formed. With the AC addition, the *Massilia*, *Sphingomonas*, *Bryobacter* and *Leptospirillum* species became dominant and new genera appear in *Nitrospirae*. Meanwhile, the *Paucimonas*, *Clostridium_sensu_stricto_10*, *Gemmatimonas* and *H16* species became dominant and new genera appear in *Gemmatimonadetes* after treated by ZAB. However, *Symbiobacterium* was the only dominant in sediment treated by OAC, which have the most adverse effects on sediment microbial environment.

The phenomenon indicated that the application of biochar adversely affect the behavior of indigenous microbes, which have been reported by recent study (Huang et al., 2017). Meanwhile, the value of TOC was increased, while the value of pH was decreased after in situ remediation of by materials in Table S2. The non-treated sediment groups showed more abundance and diversity of bacteria than the sediment treated activated biochar, which may be explained by that activated biochars changed the physico-chemical properties of sediment, sequentially affected the
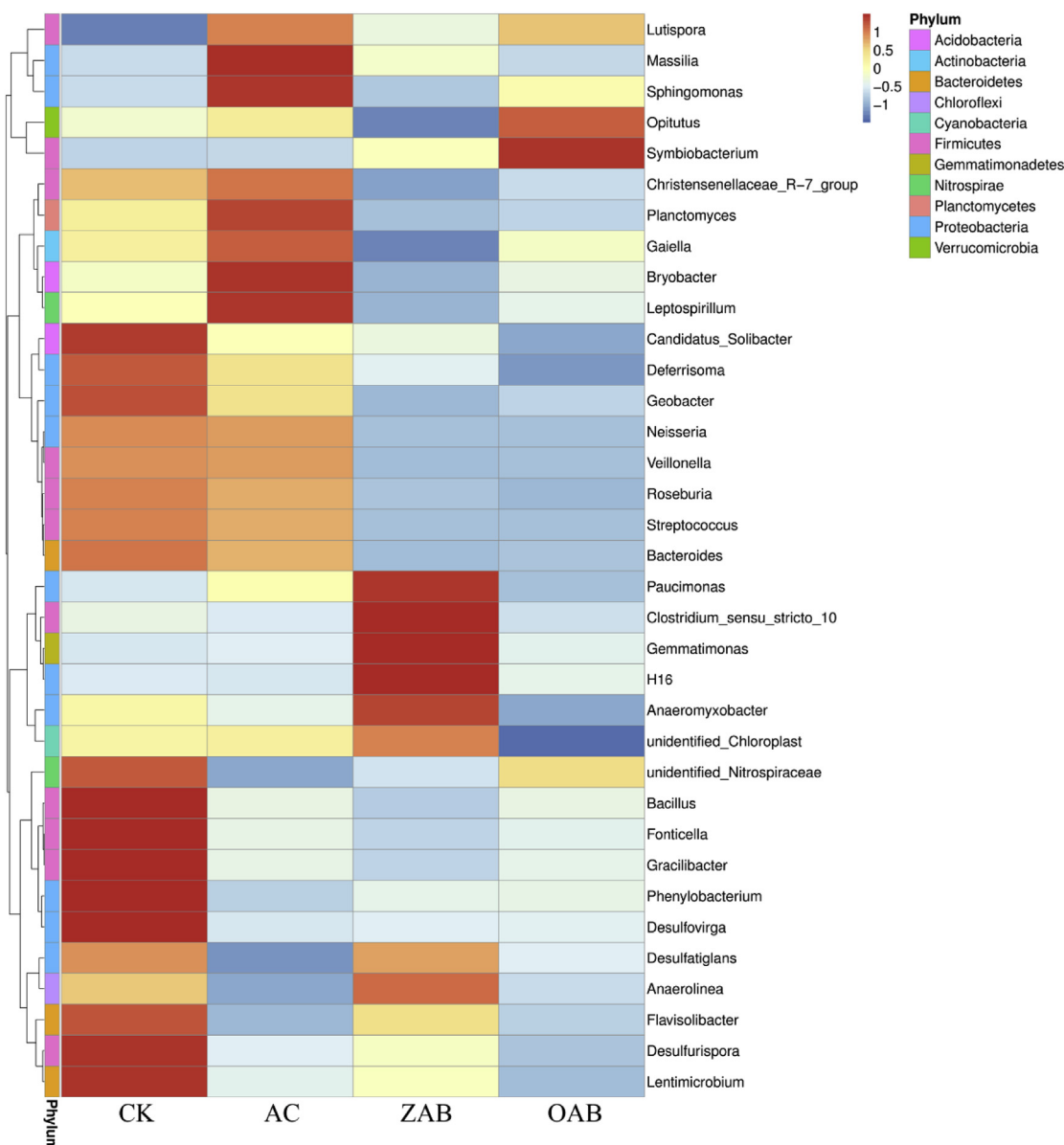

Fig. 4. Hierarchically clustered heat map analysis of the highly represented bacterial taxa (at the genus level) found in the sediment (relative abundance> 1%).

indigenous microbes in sediment (Sigua et al., 2016). Although the immobilization of Cd reduces the toxicity to the sediment microorganisms (Huang et al., 2016), the addition of biochar changes the physicochemical properties of the sediment, which has a negative effect on the sediment microorganisms.

4. Conclusions

Activated biochars showed better surface properties than RHB. In situ remediation with activated biochars distinctly decreased the aqueous concentrations of Cd released from the sediments and reduced environmental risk, which was related to BET surface area and oxygen containing functional groups of activated biochars. Activated biochar also showed more excellent performance in immobilization of Cd in sediment, which was related to electrostatic reaction and oxygen containing functional groups. Activated biochar influenced bacterial community diversity, which was similar to activated carbon. $ZnCl_2$ activated biochar can be used as a cheap and efficient in situ remediation material to replace activated carbon.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.06.023.

References

Ahmed, M., Billah, M.M., 2016. Smart material-actuated flexible tendon-based snake robot. Int. J. Adv. Rob. Syst. 13, 89.

Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant Soil 337, 1–18.

Bache, B.W., 1976. The measurement of cation exchange capacity of soils. J. Sci. Food Agric. 27, 273–280.

Cheng, C.-H., Lehmann, J., Engelhard, M.H., 2008. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. Geochem. Cosmochim. Acta 72, 1598–1610.

Cui, L., Pan, G., Li, L., Bian, R., Liu, X., Yan, J., Quan, G., Ding, C., Chen, T., Liu, Y., Liu, Y., Yin, C., Wei, C., Yang, Y., Hussain, Q., 2016. Continuous immobilization of cadmium and lead in biochar amended contaminated paddy soil: a five-year field experiment. Ecol. Eng. 93, 1–8.

Das, P., Williams, C.J., Fulthorpe, R.R., Hoque, M.E., Metcalfe, C.D., Xenopoulos, M.A., 2012. Changes in bacterial community structure after exposure to silver nanoparticles in natural waters. Environ. Sci. Technol. 46, 9120–9128.

Davutluoglu, O.I., Seckin, G., Ersu, C.B., Yilmaz, T., Sari, B., 2011. Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey. J. Environ. Manag. 92, 2250–2259.

Hu, X., Xu, J., Wu, M., Xing, J., Bi, W., Wang, K., Ma, J., Liu, X.e, 2017. Effects of biomass pre-pyrolysis and pyrolysis temperature on magnetic biochar properties. J. Anal. Appl. Pyrol. 127, 196–202.

Huang, D., Liu, L., Zeng, G., Xu, P., Huang, C., Deng, L., Wang, R., Wan, J., 2017. The effects of rice straw biochar on indigenous microbial community and enzymes activity in heavy metal-contaminated sediment. Chemosphere 174, 545–553.

Huang, D., Xue, W., Zeng, G., Wan, J., Chen, G., Huang, C., Zhang, C., Cheng, M., Xu, P., 2016. Immobilization of Cd in river sediments by sodium alginate modified nanoscale zero-valent iron: impact on enzyme activities and microbial community diversity. Water Res. 106, 15–25.

Inyang, M.I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y.S., Cao, X., 2016. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Crit. Rev. Environ. Sci. Technol. 46, 406–433.

Jiang, J., Xu, R.K., Jiang, T.Y., Li, Z., 2012. Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol.

J. Hazard Mater. 229–230, 145–150.

Khan, M.A., Khan, S., Khan, A., Alam, M., 2017. Soil contamination with cadmium, consequences and remediation using organic amendments. Sci. Total Environ. 601–602, 1591–1605.

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A., Maurice, C., 2006. Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environ. Pollut. 144, 62–69.

Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., Ma, L.Q., 2017a. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. Chemosphere 178, 466–478.

Li, H., Ye, X., Geng, Z., Zhou, H., Guo, X., Zhang, Y., Zhao, H., Wang, G., 2016. The influence of biochar type on long-term stabilization for Cd and Cu in contaminated paddy soils. J. Hazard Mater. 304, 40–48.

Li, M.-f., Liu, Y.-g., Liu, S.-b., Shu, D., Zeng, G.-m., Hu, X.-j., Tan, X.-f., Jiang, L.-h., Yan, Z.-l., Cai, X.-x, 2017b. Cu(II)-influenced adsorption of ciprofloxacin from aqueous solutions by magnetic graphene oxide/nitrilotriacetic acid nanocomposite: competition and enhancement mechanisms. Chem. Eng. J. 319, 219–228.

Liu, S., Xu, W.H., Liu, Y.G., Tan, X.F., Zeng, G.M., Li, X., Liang, J., Zhou, Z., Yan, Z.L., Cai, X.X., 2017. Facile synthesis of Cu(II) impregnated biochar with enhanced adsorption activity for the removal of doxycycline hydrochloride from water. Sci. Total Environ. 592, 546–553.

Lu, K., Yang, X., Shen, J., Robinson, B., Huang, H., Liu, D., Bolan, N., Pei, J., Wang, H., 2014. Effect of bamboo and rice straw biochars on the bioavailability of Cd, Cu, Pb and Zn to Sedum plumbizincicola. Agriculture. Ecosyst. Environ. 191, 124–132.

Magoč, T., Salzberg, S.L., 2011. FLASH: fast length adjustment of short reads to improve genome assemblies. Bioinformatics 27, 2957–2963.

Mahmoud, D.K., Salleh, M.A.M., Karim, W.A.W.A., Idris, A., Abidin, Z.Z., 2012. Batch adsorption of basic dye using acid treated kenaf fibre char: equilibrium, kinetic and thermodynamic studies. Chem. Eng. J. 181–182, 449–457.

Mao, L., Mo, D., Guo, Y., Fu, Q., Yang, J., Jia, Y., 2012. Multivariate analysis of heavy metals in surface sediments from lower reaches of the Xiangjiang River, southern China. Environ. Earth Sci. 69, 765–771.

Min, J., 2013. Assessment of heavy metal contamination in the surrounding soils and surface sediments in Xiawangang River, Qingshuitang District. PLoS One 8.

Namgay, T., Singh, B., Singh, B.P., 2010. Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (Zea mays L.). Soil Res. 48, 638–647.

Qi, F., Yan, Y., Lamb, D., Naidu, R., Bolan, N.S., Liu, Y., Ok, Y.S., Donne, S.W., Semple, K.T., 2017. Thermal stability of biochar and its effects on cadmium sorption capacity. Bioresour. Technol. 246, 48–56.

Qian, L., Chen, B., 2014. Interactions of aluminum with biochars and oxidized biochars: implications for the biochar aging process. J. Agric. Food Chem. 62, 373–380.

Saeedi, M., Li, L.Y., Karbassi, A.R., Zanjani, A.J., 2013. Sorbed metals fractionation and risk assessment of release in river sediment and particulate matter. Environ. Monit. Assess. 185, 1737–1754.

Sharma, A., Weindorf, D.C., Wang, D., Chakraborty, S., 2015. Characterizing soils via portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). Geoderma 239, 130–134.

Shen, Z., Hou, D., Zhao, B., Xu, W., Ok, Y.S., Bolan, N.S., Alessi, D.S., 2017. Stability of heavy metals in soil washing residue with and without biochar addition under accelerated ageing. Sci. Total Environ. 619–620, 185–193.

Sigua, G.C., Novak, J.M., Watts, D.W., 2016. Ameliorating soil chemical properties of a hard setting subsoil layer in Coastal Plain USA with different designer biochars. Chemosphere 142, 168–175.

Singh, B., Fang, Y., Cowie, B.C., Thomsen, L., 2014. NEXAFS and XPS characterisation of carbon functional groups of fresh and aged biochars. Org. Geochem. 77, 1–10.

Song, B., Zeng, G., Gong, J., Liang, J., Xu, P., Liu, Z., Zhang, Y., Zhang, C., Cheng, M., Liu, Y., Ye, S., Yi, H., Ren, X., 2017a. Evaluation methods for assessing effectiveness of in situ remediation of soil and sediment contaminated with organic pollutants and heavy metals. Environ. Int. 105, 43–55.

Song, B., Zeng, G., Gong, J., Zhang, P., Deng, J., Deng, C., Yan, J., Xu, P., Lai, C., Zhang, C., Cheng, M., 2017b. Effect of multi-walled carbon nanotubes on phytotoxicity of sediments contaminated by phenanthrene and cadmium. Chemosphere 172, 449–458.

Sun, K., Gao, B., Ro, K.S., Novak, J.M., Wang, Z., Herbert, S., Xing, B., 2012. Assessment of herbicide sorption by biochars and organic matter associated with soil and sediment. Environ. Pollut. 163, 167–173.

Tan, X.-f., Liu, S.-b., Liu, Y.-g., Gu, Y.-l., Zeng, G.-m., Hu, X.-j., Wang, X., Liu, S.-h., Jiang, L.-h., 2016. Biochar as Potential Sustainable Precursors for Activated Carbon Production: Multiple Applications in Environmental Protection and Energy Storage. Bioresource technology.

Tan, X.F., Liu, S.B., Liu, Y.G., Gu, Y.L., Zeng, G.M., Hu, X.J., Wang, X., Liu, S.H., Jiang, L.H., 2017. Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage. Bioresour. Technol. 227, 359–372.

Tomašević, D., Kozma, G., Kerkez, D.V., Dalmacija, B., Dalmacija, M., Bečelić-Tomin, M., Kukovecz, Á., Kónya, Z., Rončević, S., 2014. Toxic metal immobilization in contaminated sediment using bentonite-and kaolinite-supported nano zero-valent iron. J. Nanoparticle Res. 16, 2548.

Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A., 2009. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327, 235–246.

Wan, J., Zhang, C., Zeng, G., Huang, D., Hu, L., Huang, C., Wu, H., Wang, L., 2016. Synthesis and evaluation of a new class of stabilized nano-chlorapatite for Pb immobilization in sediment. J. Hazard Mater. 320, 278–288.

Wang, Q., Garrity, G.M., Tiedje, J.M., Cole, J.R., 2007. Naive Bayesian classifier for rapid assignment of rRNA sequences into the new bacterial taxonomy. Appl. Environ. Microbiol. 73, 5261–5267.

Wang, T., Sun, H., Jiang, C., Mao, H., Zhang, Y., 2014. Immobilization of Cd in soil and changes of soil microbial community by bioaugmentation of UV-mutated Bacillus subtilis 38 assisted by biostimulation. Eur. J. Soil Biol. 65, 62–69.

Wang, Y., Xu, Y., Li, D., Tang, B., Man, S., Jia, Y., Xu, H., 2017. Vermicompost and biochar as bio-conditioners to immobilize heavy metal and improve soil fertility on cadmium contaminated soil under acid rain stress. Sci. Total Environ. 621, 1057–1065.

Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., Liu, Z.F., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. Sci. Total Environ. 424, 1–10.

Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R., Ro, K.S., 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests. Chem. Eng. J. 200–202, 673–680.

Yu, K.-c., 2001. Correlation analyses on binding behavior of heavy metals with sediment matrices. Water Res. 35, 2417–2428.

Yuan, J.-H., Xu, R.-K., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour. Technol. 102, 3488–3497.

Zeng, Z., Tan, X., Liu, Y., Tian, S., Zeng, G., Jiang, L., Liu, S., Li, J., Liu, N., Yin, Z., 2018. Comprehensive adsorption studies of doxycycline and ciprofloxacin antibiotics by biochars prepared at different temperatures. Front. Chem. 6.

Zhang, C., Lai, C., Zeng, G., Huang, D., Yang, C., Wang, Y., Zhou, Y., Cheng, M., 2016. Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. Water Res. 95, 103–112.

Zhang, C., Zeng, G., Huang, D., Lai, C., Huang, C., Li, N., Xu, P., Cheng, M., Zhou, Y., Tang, W., 2014. Combined removal of di (2-ethylhexyl) phthalate (DEHP) and Pb (II) by using a cutinase loaded nanoporous gold-polyethyleneimine adsorbent. RSC Adv. 4, 55511–55518.

Zhang, F., Wang, X., Yin, D., Peng, B., Tan, C., Liu, Y., Tan, X., Wu, S., 2015. Efficiency and mechanisms of Cd removal from aqueous solution by biochar derived from water hyacinth (Eichornia crassipes). J. Environ. Manag. 153, 68–73.

Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Bolan, N.S., Pei, J., Huang, H., 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ. Sci. Pollut. Control Ser. 20, 8472–8483.