Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 656−665
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Stabilization of heavy metals in biochar pyrolyzed from phytoremediated giant reed (*Arundo donax*) biomass

Ya-nan LIU, Zhao-hui GUO, Yang SUN, Wei SHI, Zi-yu HAN, Xi-yuan XIAO, Peng ZENG

School of Metallurgy and Environment, Central South University, Changsha 410083, China

Received 28 August 2016; accepted 13 January 2017

Abstract: The pyrolysis of phytoremediated giant reed (*Arundo donax*) biomass could cause secondary pollution of heavy metals. The stabilization of heavy metals in the pyrolysis process with external materials such as Al_2O_3, $CaCO_3$, $FeCl_3$ and NaOH, was studied. The results showed that 37% As and 97% Cd in biochar were stabilized when giant reed powder was pyrolyzed at 250 °C with 5% Al_2O_3 for 2 h. Furthermore, 59% Pb in biochar was stabilized at 400 °C with 5% $CaCO_3$ for 1 h. Under biochar produced in optimized pyrolysis conditions, Cd mainly existed in a residual fraction, while Pb and As mainly existed in oxidizable fraction in BCR analysis. In XRD analysis, As was only found in $Ca_2As_2O_7$; Cd in biochar mainly existed in Cd $(AlCl_4)_2$, $CdPbO_3$ or $CdSO_3$; and Pb mainly existed as $Pb_3O_2SO_4$.

Key words: phytoremediated giant reed; pyrolysis; biochar; heavy metal; stabilization

1 Introduction

Giant reed (*Arundo donax*), a type of perennial rhizomatous grass widely distributed in South China, is used to stabilize heavy metals in metal-contaminated soils [1,2]. Because of its rapid growth and high biomass yield, giant reed has been explored as an option for phytoremediation, particularly, of soils polluted with multiple metals [3]. However, after phytoremediation, a large amount of metal-containing biomass would be produced, resulting in potential secondary pollution of heavy metals.

The biomass has mostly been utilized for composting [4], phytomining [5], combustion [6], and pyrolysis [7]. Pyrolysis is a potential method to dispose the biomass such as sugar cane [8], willow [9], and generate biochar [10]. In contrast with combustion [11], pyrolysis could be more suitable for the disposal of metal-containing biomass because of the lower volatilization of heavy metals [12].

Giant reed consists of 35%−50% cellulose, 25%−30% hemicellulose, and 15%−30% lignin [13]. As an industrial crop, considering its components and large biomass, phytoremediated giant reed was well suited for the pyrolysis to produce biochar [14]. In addition, the pyrolysis characteristics of giant reed biomass conform to a single-step reaction model. The average activation energy of giant reed is 163 kJ/mol [15]. External materials have been studied as catalysts in the pyrolysis process, including Na_2CO_3 [16], Ni [17], and mesoporous zeolite [18], which significantly increase the production and quality of gas and oil [19] instead of altering the characteristics of the solid residue [20]. However, few reseachers have investigated the stabilization of heavy metals during the pyrolysis of giant reed. Therefore, single factor and orthogonal experiments were carried out in the current study with the following goals: 1) determining the yield of giant reed biochar modified by external materials; 2) studying the optimal conditions for the stabilization of heavy metals in the pyrolysis process of giant reed biomass, as well as simultaneous stabilization of heavy metals through weight analysis; and 3) describing the stabilization characteristics and elucidating the stabilization mechanism of heavy metals under the optimal pyrolysis conditions. In this original study, large biomass of phytoremediated giant reed whose heavy metals were stabilized, was disposed efficiently. The stabilization mechanisms of heavy metal in the pyrolysis process were studied, which provided efficient disposal methods for the biomass after phytoremediation.

Foundation item: Projects (21577176, 41271330) supported by the National Natural Science Foundation of China
Corresponding author: Zhao-hui GUO; Tel: +86-731-88879325; E-mail: zhguo@csu.edu.cn
DOI: 10.1016/S1003-6326(17)60073-6

2 Experimental

2.1 Giant reed biomass

Giant reed biomass was collected from a phytoremediation field site contaminated with As, Cd, and Pb in Hunan Province of China [2]. The harvested biomass was washed sequentially with tap water and distilled water, cut into small rectangle pieces with 1−2 cm in size, heated at 105 °C for 30 min, dried to constant mass by heating at 60 °C, and then ground and sieved to a uniform size fraction of 0.5−1.0 mm to produce giant reed powder for the pyrolysis. The percentage of cellulose in giant reed powder was 61.2% and the contents of As, Cd and Pb were 18.72, 17.68, and 63.14 mg/kg, respectively.

2.2 Experimental set-up

In the pyrolysis experiment, a covered aluminum box with a diameter of 5 cm and height of 3 cm was filled with giant reed powder to create an oxygen-limited condition. A control experiment, wherein giant reed powder was pyrolyzed without any external materials, was also carried out.

2.2.1 Single factor experiment

Single factor experiments for biochar yield and the stabilization percentage of heavy metals in biochar were carried out under varying conditions of pyrolysis temperature, pyrolysis time, and external materials. The biochar yield experiments were performed at temperatures of 250, 300, 350, 400 and 500 °C, and the heavy metal stabilization experiments were performed at 300, 400, 500 and 600 °C. For both temperature series, temperatures were increased at a rate of 10 °C/min for 2 h in a muffle furnace. The external material series of the biochar yield and heavy metals stabilization experiments were performed with mass fractions of 2% for Al_2O_3, $CaCO_3$, $FeCl_3$, and NaOH, respectively. The pyrolysis time series were performed with durations of 0.5, 1, 1.5, 2 and 3 h at 300 °C and 500 °C with the same rate of temperature increase noted above, respectively. The biochar samples were collected for the analysis after cooling down to ambient temperature.

2.2.2 Orthogonal experiment

Based on the results of single factor experiment, the $L_{16}(4^4)$ orthogonal experiment was designed to optimize the biochar yield and the stabilization percentage of heavy metals (Table 1). Four factors for orthogonal design were considered, including pyrolysis time (0.5, 1, 1.5, 2 h), pyrolysis temperatures (250, 300, 350, 400 °C), external materials (Al_2O_3, $CaCO_3$, $FeCl_3$, NaOH) and the mass fractions of external material to giant reed biomass (0.5%, 1%, 2%, 5%).

2.3 Biochar properties

The stability of heavy metals in biochar was evaluated according to the Solid Waste Toxicity Leaching Method—Level Oscillation (HJ 557−2010). Heavy metals containing in the biochar were extracted using deionized water with low acidity (pH 5.5) and high acidity (pH 2.5 by HCl). The contents of As, Cd and Pb in leachate were analyzed. The heavy metals in biochar were speciated using a modified European Community Bureau of Reference (BCR) sequential extraction procedure [21]. Biomass samples of 1 g were digested with 10 mL HNO_3 and 2 mL $HClO_4$. Biochar and residual samples after BCR sequential extraction were digested using a microwave digester (MDS−8G, Xinyi Company, Shanghai, China). The contents of Cd and Pb in the digested solutions were measured by atomic absorption spectrometry (AAS−6800, Shimadzu, Japan), and the concentration of As was determined by atomic fluorescence spectrometry (AFS−2202E, Haiguang Instrument Company, China).

The specific surface area of biochar was measured by a laser particle analyzer (OMEC LS-POP, China) with a dispersion medium of alcohol and a refractive index of 1.329. The pore structure of biochar was determined using a scanning electron microscope (KYKY2800, Shimadzu, Japan) operated at 20 kV. Thermal stability and heat values of the biochar were analyzed by thermal gravimetric analysis (NETZSCH STA499C, Germany), and the absorption peaks of the surface organic group were measured by Fourier transform infrared spectroscopy (Nicolet IS10, Thermo Electron Corporation, USA) in the wavenumber range from 4000 to 400 cm^{-1}. The XRD patterns were analyzed using an X-ray diffractometer (Rigaku-TTR III, Japan) with the scanning angle (2θ) varying from 10° to 80° at a rate of 5 (°)/min. The biochar yield and stabilization percentage of heavy metals were calculated according Eqs. (1) and (2):

$$\eta_{Biochar}=m_{Biochar}/m_{Biomass}\times 100\% \quad (1)$$

$$\eta_{SM}=(C_{Biochar}m_{Biochar})/(C_{Biomass}m_{Biomass})\times 100\% \quad (2)$$

where $\eta_{Biochar}$ is the biochar yield; $m_{Biochar}$ and $m_{Biomass}$ stand for the masses of the biochar and corresponding giant reed biomass, respectively; η_{SM} is the stabilization percentage of heavy metal; $C_{Biochar}$ and $C_{Biomass}$ stand for the contents of heavy metals in biochar and giant reed biomass, respectively.

Statistical analysis was performed using Microsoft Excel 2010 and SPSS 16.0. Analysis of variance (ANOVA) was used to determine significance among the heavy metal contents of biochar under different pyrolysis conditions using probability levels of 0.05 and 0.1. Range analysis of orthogonal experiment was carried out with SPSS 16.0 software to evaluate the degree of influence of the pyrolysis conditions.

3 Results and discussion

3.1 Effects of pyrolysis conditions on biochar yield

3.1.1 Single factor experiment

3.1.1.1 Pyrolysis temperature and pyrolysis time

Biochar yield was significantly affected by pyrolysis temperature and pyrolysis time. Biochar yield was as high as 55.5% at 250 °C, but it was only 12.3% at 500 °C (Fig. 1).

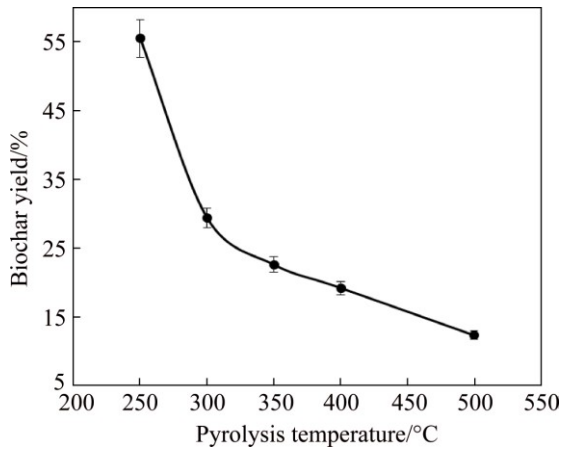

Fig. 1 Effect of pyrolysis temperature on yield of biochar

When the time span of pyrolysis was extented from 0.5 to 3 h, the biochar yield decreased sharply from 35.2% to 23.3% at the pyrolysis temperature of 300 °C, but from 22.3% to 18.7% at 500 °C (Fig. 2).

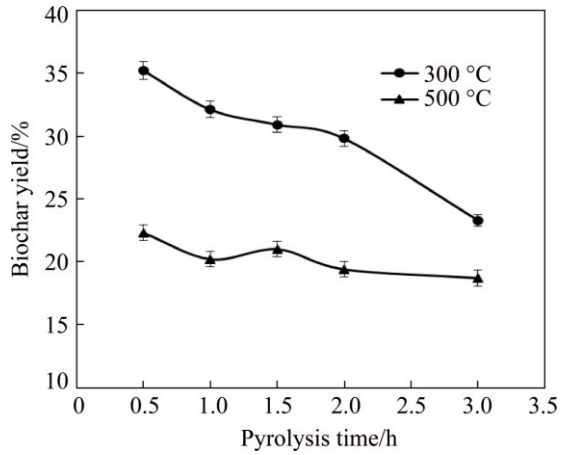

Fig. 2 Effect of pyrolysis time on yield of biochar

The results suggested that biochar yield decreased significantly with increasing pyrolysis temperature and pyrolysis time. The decreased biochar yield was contributed to the releasing of hydroxide compounds in the process [22]. According to the analysis of the FT-IR spectra (Fig. 3), the peaks from 1142 to 1531 cm^{-1} of giant reed powder, standing for C — OH in polysaccharide and phenols, disappeared in biochar.

3.1.1.2 External materials

Biochar yield increased noticeably after the addition of external materials. The carbon yield of char from pure cellulose was increased by external materials such as Ca^{2+} and Cu^{2+} [23,24]. Biochar yield increased more with the addition of external materials compared with the control experiment (Fig. 4).

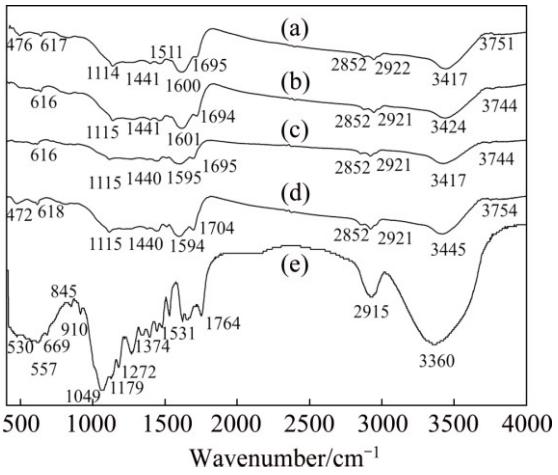

Fig. 3 FT-IR spectra of giant reed powder and biochar produced under optimal orthogonal pyrolysis condition: (a) Biochar produced at 400 °C with 2% Al_2O_3 for 0.5 h; (b) Biochar produced at 400 °C with 5% $CaCO_3$ for 1 h; (c) Biochar produced at 400 °C with 0.5% $FeCl_3$ for 1.5 h; (d) Biochar produced at 400 °C with 1% NaOH for 2 h; (e) Giant reed powder

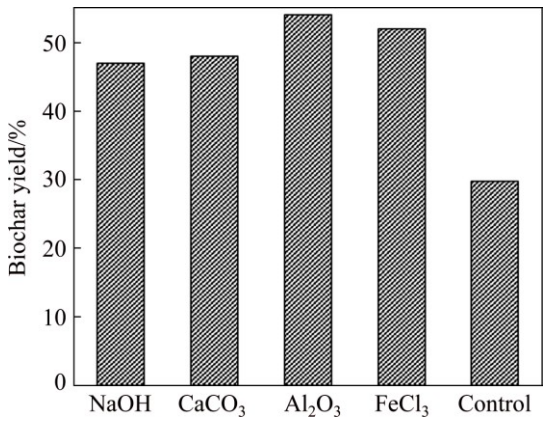

Fig. 4 Effect of external materials on yield of biochar

The external materials enhanced the cracking of the cellulose structure in the biomass [25], blocking off the release of volatiles from biochar [26] and decreasing the adsorbent's surface area [27]. A biochar yield of 54% was obtained at 300 °C with 5% Al_2O_3 for 2 h (Fig. 4). The surface structure of the biochar with Al_2O_3 was more complete than biochar with $CaCO_3$, NaOH or $FeCl_3$, according to the SEM image (Fig. 5).

Biochar with NaOH and $FeCl_3$ reacted with cellulose components and the electromotive force

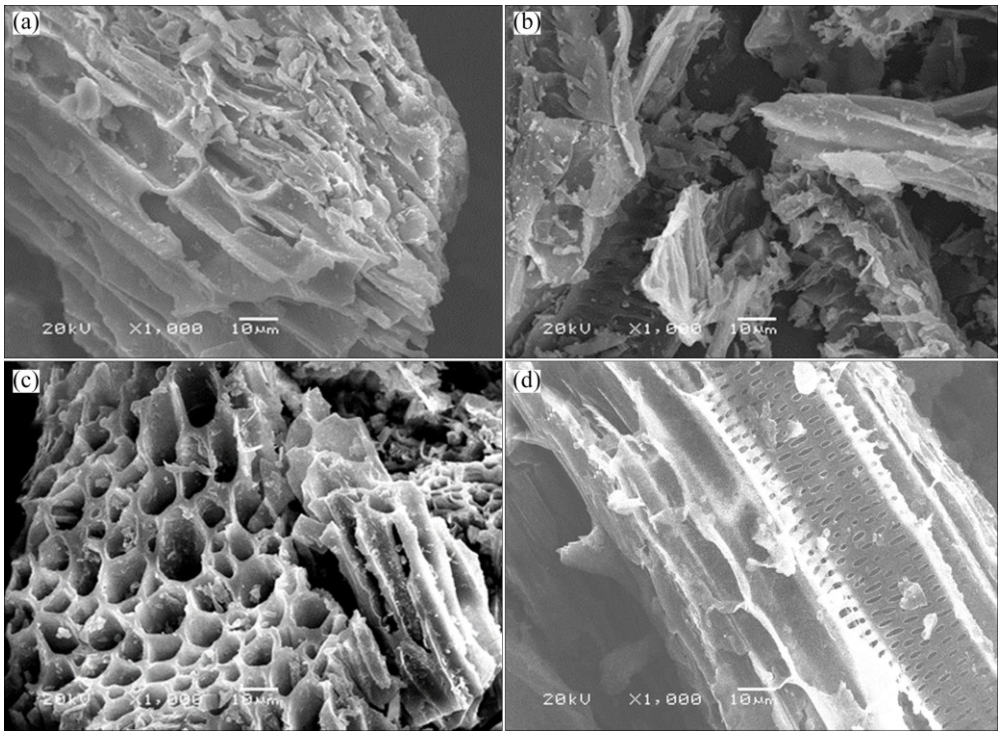

Fig. 5 SEM images of biochar produced under optimal orthogonal pyrolysis condition: (a) Biochar produced at 400 °C with 2% Al_2O_3 for 0.5 h; (b) Biochar produced at 400 °C with 5% $CaCO_3$ for 1 h; (c) Biochar produced at 400 °C with 0.5% $FeCl_3$ for 1.5 h; (d) Biochar produced at 400 °C with 1% NaOH for 2 h

between the reactants limited the combustion of carbon [28]. The rigidity of biochar with sodium and chlorine affected the integrity of the carbon chain, which in turn affected the reaction between the cellulose component and external materials.

3.1.2 Orthogonal experiment

The optimal pyrolysis conditions for biochar yield were studied using an orthogonal experiment (Table 1). Based on the range analysis, the contribution percentages of pyrolysis temperature, pyrolysis time, and the mass fraction of external materials all significantly contributed to the stabilization of heavy metals in biochar (P<0.05). The results indicated that the pyrolysis of giant reed was affected more by pyrolysis temperature and time than by external materials. The biochar yield of 86% was achieved at 250 °C with 0.5% NaOH for 0.5 h. Previous research indicated that an appropriate amount of Cu could also increase the yield of tar [24].

3.2 Effects of pyrolysis conditions on heavy metal stabilization

3.2.1 Single factor experiment

3.2.1.1 Pyrolysis temperature and pyrolysis time

The content of heavy metal in biochar was significantly related to pyrolysis temperature. The contents of Cd and Pb in biochar at 400 °C were up to 14.7 and 76.0 mg/kg, respectively (Fig. 6). The results

Table 1 Biochar yield and its range analysis in orthogonal experiment

Test No.	External material	Pyrolysis temperature/ °C	Pyrolysis time/ h	Mass fraction of external material/%	Biochar yield/%
1	NaOH	250	0.5	0.5	86
2	$FeCl_3$	250	1	1	78
3	$CaCO_3$	250	1.5	2	76
4	Al_2O_3	250	2	5	78
5	NaOH	300	1	2	54
6	$FeCl_3$	300	0.5	5	67
7	$CaCO_3$	300	2	0.5	46
8	Al_2O_3	300	1.5	1	47
9	NaOH	350	1.5	5	47
10	$FeCl_3$	350	2	2	43
11	$CaCO_3$	350	0.5	1	45
12	Al_2O_3	350	1	0.5	41
13	NaOH	400	2	1	35
14	$FeCl_3$	400	1.5	0.5	35
15	$CaCO_3$	400	1	5	42
16	Al_2O_3	400	0.5	2	41
R	0.04	0.4125	0.0925	0.0725	
F	6.37	473.4**	25.1*	15.2*	

R and F stand for range and significance, respectively. $F_{0.01}$ (3, 3) =29.5, $F_{0.05}$ (3, 3) =9.23; $^{**}P < 0.01$, $^{*}P < 0.05$

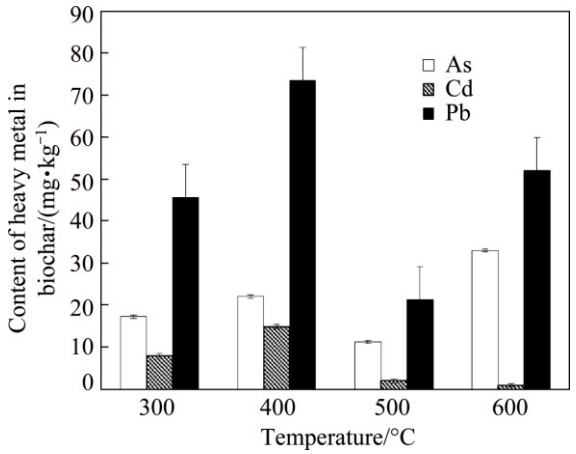

Fig. 6 Effect of pyrolysis temperature on contents of heavy metals in biochar

suggest that the pyrolysis temperature of 400 °C may be optimal for the stabilization of heavy metals in biochar.

3.2.1.2 External materials

The effect of external materials on the contents of heavy metals in biochar was consistent with the stabilization percentage. The contents of As, Cd, and Pb in biochar without external materials were 6.23, 15.9, and 63.9 mg/kg, respectively. The stabilization percentages of As, Cd and Pb in biochar were 6%, 21% and 50%, respectively. Both of these factors were improved when giant reed powder was pyrolyzed at 300 °C with 5% external materials for 2 h (Fig. 7). The contents of As, Cd and Pb in biochar with NaOH, $FeCl_3$, Al_2O_3 and $CaCO_3$ were up to 36, 33.75, and 137 mg/kg, respectively. The corresponding stabilization percentages of As, Cd, and Pb in biochar were as much as 90.5%, 84.9% and 98.3%, respectively.

3.2.2 Orthogonal experiment

The effects of pyrolysis conditions on the contents of heavy metals in biochar were also studied by the range analysis of orthogonal experiments (Table 2). As content was 16 mg/kg and the stabilization percentage of As was 30% in biochar produced at 400 °C with 1% NaOH for 2 h; Cd content was 182 mg/kg and the stabilization percentage of Cd was 72% at 350 °C with 1% $CaCO_3$ for 0.5 h; Pb content was 861 mg/kg and stabilization percentage of Pb was 33% at 350 °C with 0.5% Al_2O_3 for 1 h.

However, according to the range analysis results of the orthogonal experiments (Table 3), the optimal stabilization percentages of 37% As and 97% Cd in biochar were obtained when giant reed powder was pyrolyzed at 250 °C with 5% Al_2O_3 for 2 h (Table 2). Furthermore, 59% Pb was stabilized at 400 °C with 5% $CaCO_3$ for 1 h. The stabilization of Cd, instead of As and Pb, was significantly affected by pyrolysis conditions (P<0.05).

For the coexistence of As Cd, and Pb in giant reed biomass harvested from soil phytoremediation, a weight analysis of the orthogonal experiment was carried out (Table 4). The weight value under the pyrolysis temperature of 400 °C was 43.83%. Considering the simultaneous stabilization of heavy metals in biochar and the high content of Cd in giant reed biomass, the optimal pyrolysis conditions for giant reed biomass were selected as 400 °C with 1% NaOH for 2 h.

3.3 Stabilization mechanism of heavy metals in biochar produced under optimal orthogonal experiment

3.3.1 Speciation of heavy metals in optimal biochar

The speciation of heavy metals in biochar was significantly affected by the pyrolysis conditions. The oxidizable fraction of heavy metals in biochar increased when the residual fraction decreased significantly with external materials at 400 °C (Fig. 8). The acid-extractable fraction of As in biochar with the addition of external materials decreased significantly compared with the control. Most of the Cd existed in residual fraction and the proportion of acid-extractable Cd fluctuated slightly. Opposed to As, Cd and Pb mainly existed in

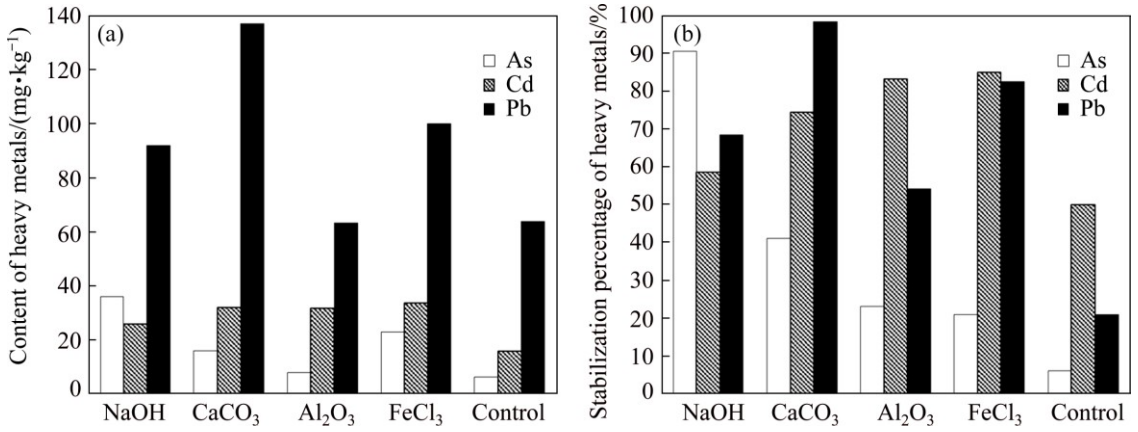

Fig. 7 Effect of external materials on contents (a) and stabilization percentages (b) of heavy metals in biochar

Table 2 Heavy metal contents and stabilization percentages in biochar produced in orthogonal experiment

Test No.	External material	Pyrolysis Temperature/°C	Pyrolysis time/h	Mass fraction of external material/%	Content/(mg·kg^{-1})			Stabilization percentage/%		
					As	Cd	Pb	As	Cd	Pb
1	NaOH	250	0.5	0.5	1.64	69.8	427	8	96	25
2	$FeCl_3$	250	1	1	2.11	87.8	271	9	90	23
3	$CaCO_3$	250	1.5	2	4.94	118	390	20	93	25
4	Al_2O_3	250	2	5	8.91	106	255	37	97	24
5	NaOH	300	1	2	9.97	65.3	776	29	74	29
6	$FeCl_3$	300	0.5	5	3.32	112	315	12	91	23
7	$CaCO_3$	300	2	0.5	8.39	88.3	226	20	74	29
8	Al_2O_3	300	1.5	1	5.05	97.8	199	13	76	31
9	NaOH	350	1.5	5	3.88	115	212	10	74	29
10	$FeCl_3$	350	2	2	3.93	113	198	9	76	33
11	$CaCO_3$	350	0.5	1	6.11	182	333	15	72	29
12	Al_2O_3	350	1	0.5	5.06	126	861	11	68	33
13	NaOH	400	2	1	16	123	279	30	68	38
14	$FeCl_3$	400	1.5	0.5	5.84	101	210	11	65	37
15	$CaCO_3$	400	1	5	5.33	112	316	12	73	59
16	Al_2O_3	400	0.5	2	6.14	122	289	13	76	44

Table 3 Range analysis for contents and stabilization percentages of heavy metals in biochar based on orthogonal experiment

Item		External material			Pyrolysis temperature			Pyrolysis time			Mass fraction of external material		
		As	Cd	Pb	As	Cd	Pb	As	Cd	Pb	As	Cd	Pb
Content	*R*	4.07	31.8	175	3.93	43.2	128	5.01	23.7	317	1.96	26.4	161
	F	0.89	1.92	0.01	1.06	4.08	0.03	1.59	0.99	0.02	0.29	1.30	0.04
Stabilization percentage	*R*	0.09	0.02	0.07	0.07	0.24	0.20	0.12	0.11	0.06	0.05	1.15	0.04
	F	0.64	0.65	0.71	0.04	68.3**	6.55	0.10	6.99	0.63	0.02	9.20	0.22

$F_{0.01}$ (3, 3)=29.5, $F_{0.05}$ (3, 3) =9.23. $^{**}P < 0.01$, $^{*}P < 0.05$

Table 4 Weight analysis of optimal pyrolysis condition of biochar

Pyrolysis temperature/°C	External material	Stabilization percentage/%			Weight value for different external material at same temperature*	Average weight value
		As	Cd	Pb		
250	NaOH	8	96	25	43.0	43.00
	$FeCl_3$	9	90	23	40.7	
	$CaCO_3$	20	93	25	46.0	
	Al_2O_3	37	97	24	52.7	
300	NaOH	29	74	29	44.0	41.75
	$FeCl_3$	12	91	23	42.0	
	$CaCO_3$	20	74	29	41.0	
	Al_2O_3	13	76	31	40.0	
350	NaOH	10	74	29	37.7	38.25
	$FeCl_3$	9	76	33	39.3	
	$CaCO_3$	15	72	29	38.7	
	Al_2O_3	11	68	33	37.3	
400	NaOH	30	68	38	45.3	43.83
	$FeCl_3$	11	65	37	37.7	
	$CaCO_3$	12	73	59	48.0	
	Al_2O_3	13	76	44	44.3	

* Weight value of all heavy metals and external material was considered as 1

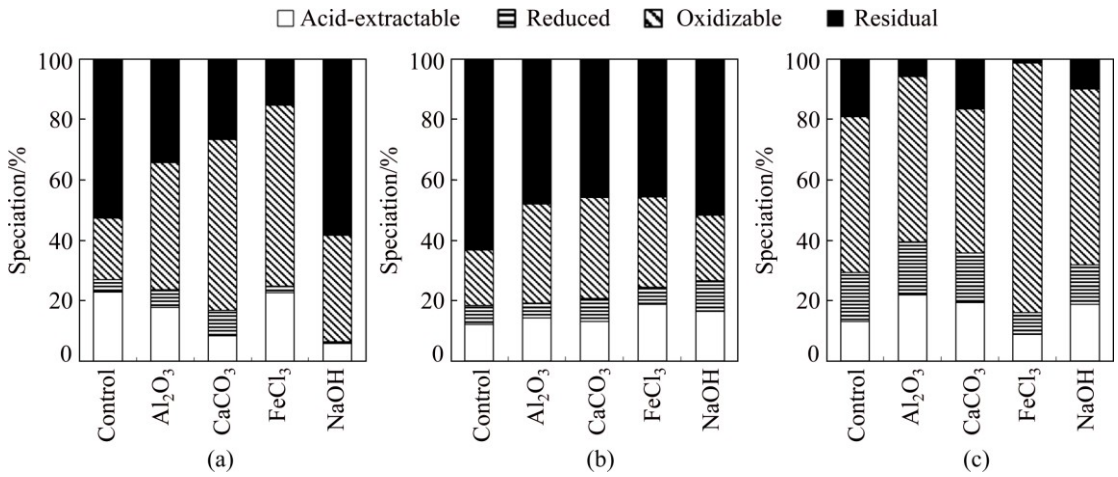

Fig. 8 Speciation of heavy metals in biochar produced under optimal orthogonal pyrolysis condition: (a) As; (b) Cd; (c) Pb

oxidizable fraction, especially in the biochar produced by adding $FeCl_3$. Considering the increased oxidizable fraction of heavy metals in biochar, it was suggested that heavy metals were more likely to combine with organic groups of biochar with the addition of external materials [29].

3.3.2 Leaching potential of heavy metals in biochar

The stability of metals in biochar produced at 400 °C in the orthogonal experiment was assessed through a leaching experiment following the Solid Waste Toxicity Leaching Method-Level Oscillation (HJ 557−2010) Protocol. According to the results in Table 5, the amount of all the metal elements in leachates was less than the level of the Identification Standard for Hazardous Wastes — Identification for Extraction Toxicity (GB 5085.3−2007). The results indicated that it was difficult to leach heavy metals under neutral and acidic conditions, corresponding to heavy metal speciation in biochar. The acid-extractable fraction of heavy metals in biochar was small, which suggested that biochar with the addition of external materials was useful in stabilizing heavy metals [30].

Table 5 Concentrations of heavy metals in TCLP leachate

External material	ρ(As)/(mg·L^{-1})		ρ(As)/(mg·L^{-1})		ρ(As)/(mg·L^{-1})	
	pH=2.5	pH=5.5	pH=2.5	pH=5.5	pH=2.5	pH=5.5
NaOH	1.61	0.67	0.0064	ND	0.049	0.014
$CaCO_3$	1.22	0.70	0.0135	ND	0.023	0.0098
Al_2O_3	2.43	0.71	0.0306	ND	0.048	0.036
$FeCl_3$	1.70	0.59	0.0101	ND	0.042	0.0034
Control	0.89	0.28	ND	ND	0.027	ND

3.3.3 Surface microcellular structure of biochar

The surface characteristics of biochar were significantly affected by external materials. The specific surface areas of biochar with 5% $FeCl_3$, 5% NaOH, 5% Al_2O_3 and 5% $CaCO_3$ were up to 0.31, 0.29, 0.21 and 0.13 m^2/g, respectively. According to the SEM analysis (Fig. 5), a large number of pores with different diameters were discovered in biochar with the addition of external materials. Therefore, the pores were produced by the breaking of cellulose polymer chains [31]. Regular rectangle pores perpendicular to cellulose were generated on the surface of biochar modified with NaOH, which expressed the fracture mode of cellulose polymer chains in the pyrolysis progress.

3.3.4 FT-IR and XRD analysis of optimal biochar

Based on the FT-IR analysis (Fig. 3), the peaks from 1531 to 1610 cm^{-1} in giant reed powder were changed into characteristic peaks at 1600 and 1700 cm^{-1} in biochar. The benzene ring in giant reed powder was cracked into aliphatic cyclics, providing more binding sites for heavy metals. The peak at 618 cm^{-1} for SO_4^{2-} was useful to generate stable sulfide compounds with heavy metal elements. The peak at 1441 cm^{-1} for CO_3^{2-} was useful to produce stable carbonate compounds with heavy metal elements. Moreover, the absorption peaks at 1114 and 3417 cm^{-1} for C—O—C and alcohol hydroxyl reflected the decreased oxygen content. Similar results were obtained for the biochar from hydrothermal conversion of giant reed [32]. The acidity of the obtained biochar also decreased, resulting in an alkali condition and a beneficial reducing environment for heavy metal immobilization [33]. The conclusions are consistent with the results that heavy metals in biochar mainly exist in oxidizable fractions (Fig. 8).

Cd in biochar with Al_2O_3 mainly existed as $Cd(AlCl_4)_2$, for biochar with NaOH, Cd mainly existed as $CdPbO_3$; and for biochar with $FeCl_3$, Cd mainly existed as $CdSO_3$, according to the XRD analysis (Fig. 9). In biochar with $CaCO_3$ or Al_2O_3, Pb mainly existed as $Pb_3O_2SO_4$. The fraction of Pb in biochar was affected by

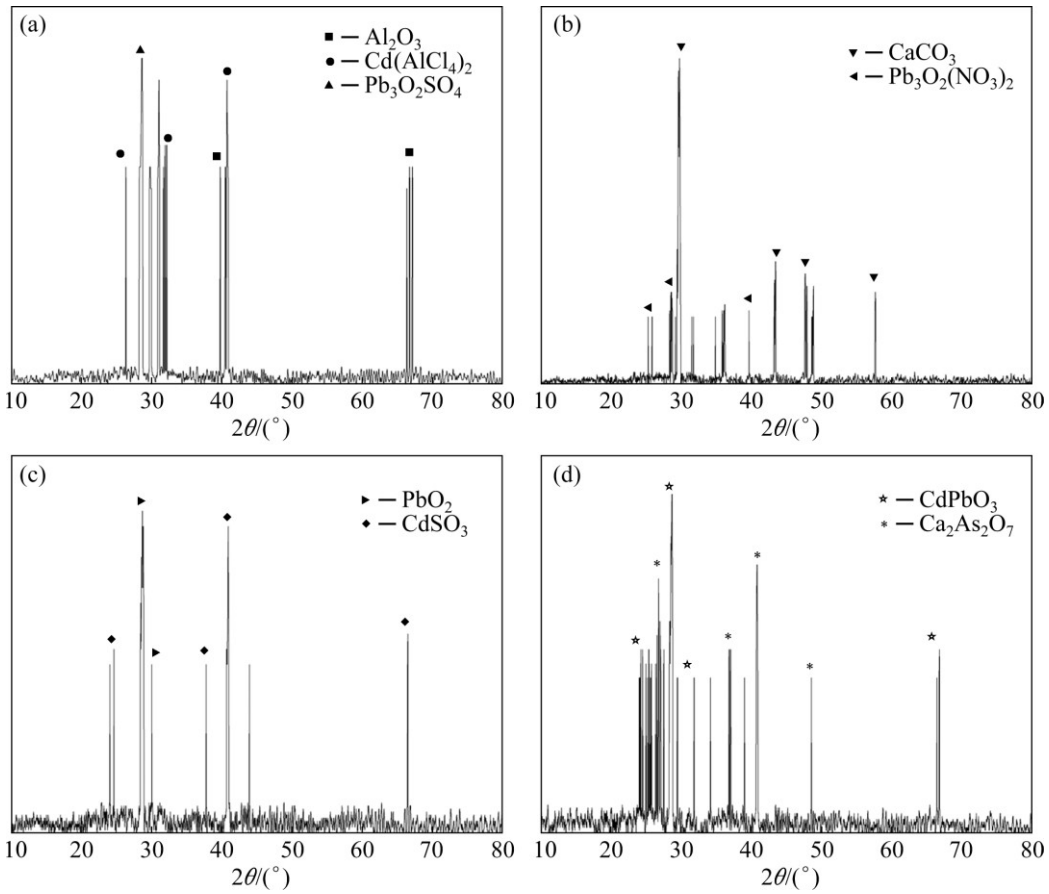

Fig. 9 XRD patterns of biochar produced under optimal orthogonal pyrolysis condition: (a) 2% Al_2O_3, 400 °C, 0.5 h; (b) 5% $CaCO_3$, 400 °C, 1 h; (c) 0.5% $FeCl_3$, 400 °C, 1.5 h; (d) 1% NaOH, 400 °C, 2 h

the pyrolysis temperature. Pb existed only as PbO_2 at low pyrolysis temperatures while it existed as $Pb_3O_2SO_4$ and $Pb_3O_2(NO_3)_2$ at high pyrolysis temperatures. Similarly, As in biochar with $FeCl_3$ or NaOH mainly existed as $Ca_2As_2O_7$, which was able to stabilize As. The results indicated that metal salts would contribute to the stabilization of heavy metals in biochar with external materials. When 5% $FeCl_3$ and 5% NaOH were used, biochar has the potential to stabilize heavy metals and assist in the clean-up contaminated environmental media particularly.

4 Conclusions

1) The biochar yields and stabilization percentages of heavy metals in biochar with external materials, including Al_2O_3, $CaCO_3$, $FeCl_3$ and NaOH, are significantly increased. The biochar yield reached 86% with 0.5% NaOH at 250 °C for 0.5 h. The stabilization percentages of As and Cd in biochar were 37% and 97% with 5% Al_2O_3 at 250 °C for 2 h and that of Pb was 59% with 5% $CaCO_3$ at 400 °C for 1 h, respectively.

2) Based on the orthogonal experiments, Cd in biochar mainly existed in residual fraction at 400 °C while those of Pb and As mainly existed in oxidizable fraction. The optimal pyrolysis conditions of metal-containing giant reed biomass were 1% NaOH, 400 °C and 2 h.

3) The stable compounds with external materials in biochar are significantly contributed to the stabilization of heavy metals in biochar. Oxygen content and the acidity of produced biochar decreased with appearance of functional groups in biochar. The stabilization of heavy metals is also contributed to the adsorption of pore structure in biochar.

References

[1] LIU Zhen-gang, ZHANG Fu-shen. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks [J]. Energy Conversion & Management, 2008, 49: 3498−3504.

[2] GUO Zhao-hui, WANG Feng-yong, SONG Jie, XIAO Xi-yuan, MIAO Xiu-feng. Leaching and transferring characteristics of arsenic, cadmium, lead and zinc in contaminated soil-giant reed-water system [J]. Journal of Central South University, 2011, 42: 2184−2192. (in Chinese)

[3] LEWANDOWSKI I, SCURLOCK J M O, LINDVALL E, CHRISTOU M. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe [J].

Biomass & Bioenergy, 2003, 25: 335−361.

[4] KINET R, DESTAIN J, HILIGSMANN S, THONART P, DELHALLE L, TAMINIAU B, DAUBE G, DELVIGNE F. Thermophilic and cellulolytic consortium isolated from composting plants improves anaerobic digestion of cellulosic biomass: Toward a microbial resource management approach [J]. Bioresource Technology, 2015, 189: 138−144.

[5] ENT A, BAKER A J M, BALGOOY M M J, TJOA A. Ultramafic nickel laterites in Indonesia (Sulawesi, Halmahera): Mining, nickel hyperaccumulators and opportunities for phytomining [J]. Journal of Geochemical Exploration, 2013, 128: 72−79.

[6] PÖYKIÖ R, NURMESNIEMI H, DAHL O, MÄKELÄ M. Chemical fractionation method for characterization of biomass-based bottom and fly ash fractions from large-sized power plant of an integrated pulp and paper mill complex [J]. Transactions of Nonferrous Metals Society of China, 2014, 24: 588−596.

[7] STALS M, CARLEER R, REGGERS G, SCHREURS S, YPERMAN J. Flash pyrolysis of heavy metal contaminated hardwoods from phytoremediation: Characterisation of biomass, pyrolysis oil and char/ash fraction [J]. Journal of Analytical & Applied Pyrolysis, 2010, 89: 22−29.

[8] CARRIER M, HARDIE A G, ÜMIT U, GÖRGENS J, KNOETZE J. Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar [J]. Journal of Analytical & Applied Pyrolysis, 2012, 96: 24−32.

[9] MAYER Z A, APFELBACHER A, HORNUNG A. A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char [J]. Journal of Analytical & Applied Pyrolysis, 2012, 96: 196−202.

[10] XINDE C, LENA M, BIN G, WILLIE H. Dairy-manure derived biochar effectively sorbs lead and atrazine [J]. Environmental Science & Technology, 2009, 43: 3285−3291.

[11] LIEVENS C, YPERMAN J, VANGRONSVELD J, CARLEER R. Study of the potential valorisation of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part I. Influence of temperature, biomass species and solid heat carrier on the behavior of heavy metals [J]. Fuel, 2008, 87: 1894−1905.

[12] CHAMI Z A, AMER N, SMETS K, YPERMAN J, CARLEER R, OUMONTET S, VANGRONSVELD J. Evaluation of flash and slow pyrolysis applied on heavy metal contaminated *Sorghum bicolor*, shoots resulting from phytoremediation [J]. Biomass & Bioenergy, 2014, 63: 268−279.

[13] SHATALOV A A, PEREIRA H. High-grade sulfur-free cellulose fibers by pre-hydrolysis and ethanol-alkali delignification of giant reed (*Arundo donax L.*) stems [J]. Industrial Crops & Products, 2013, 43: 623−630.

[14] CHEN X C, CHEN G C, CHEN L G, CHEN Y X, LEHMANN J, MCBRIDE M B, HAY A G. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution [J]. Bioresource Technology, 2011, 102: 8877−8884.

[15] HUANG Lei, CHEN Yu-cheng, LIU Geng, LI Sheng-nan, LIU Yun, GAO Xu. Non-isothermal pyrolysis characteristics of giant reed (*Arundo donax*, L.) using thermogravimetric analysis [J]. Energy, 2015, 87: 31−40.

[16] GALADIMA A, MURAZA O. In situ fast pyrolysis of biomass with zeolite catalysts for bioaromatics/gasoline production: A review [J]. Energy Conversion & Management, 2015, 105: 338−354.

[17] LEE S W, NAM S S, KIM S B, LEE K W, CHOI C S. The effect of Na_2CO_3 on the catalytic gasification of rice straw over nickel catalysts supported on kieselguhr [J]. Korean Journal of Chemical Engineering, 2000, 17: 174−178.

[18] ZHANG Shu-ping, DONG Qing, ZHANG Li, XIONG Yuan-quan. High quality syngas production from microwave pyrolysis of rice husk with char-supported metallic catalysts [J]. Bioresource Technology, 2015, 191: 17−23.

[19] JEON M J, KIM S S, JEON J K, PARK S H, KIM J M, SOHN J M, LEE S H, PARK Y K. Catalytic pyrolysis of waste rice husk over mesoporous materials [J]. Nanoscale Research Letters, 2012, 7: 18−23.

[20] WHYTE H E, LOUBAR K, AWAD S, TAZEROUT M. Pyrolytic oil production by catalytic pyrolysis of refuse-derived fuels: Investigation of low cost catalysts [J]. Fuel Processing Technology, 2015, 140: 32−38.

[21] GUO Z H, MEGHARAJ M, BEER M, MING H, RAHMAN M M, WU W H, NAIDU R. Heavy metal impact on bacterial biomass based on DNA analyses and uptake by wild plants in the abandoned copper mine soils [J]. Bioresource Technology, 2009, 100: 3831−3836.

[22] DONG K S, SANG S P, HWANG J, YU T. Study of the pyrolysis of biomass using thermo-gravimetric analysis (TGA) and concentration measurements of the evolved species [J]. Journal of Analytical & Applied Pyrolysis, 2010, 89: 66−73.

[23] ZHANG Jing, NOTLE M W, SHANKS B H. Investigation of primary reactions and secondary effects from the pyrolysis of different celluloses [J]. Acs Sustainable Chemistry & Engineering, 2014, 2: 2820−2830.

[24] LIU Wu-jun, KE Tian, HONG Jiang, ZHANG Xue-song, DING Hong-sheng, YU Han-qing. Selectively improving the bio-oil quality by catalytic fast pyrolysis of heavy-metal-polluted biomass: Take copper (Cu) as an example [J]. Environmental Science & Technology, 2012, 46: 7849−7856.

[25] KIM K H, BROWN R C, BAI X. Partial oxidative pyrolysis of acid infused red oak using a fluidized bed reactor to produce sugar rich bio-oil [J]. Fuel, 2014, 130: 135−141.

[26] MURADOV N, FIDALGO B, GUJAR A C, GARCEAU N, TRAISSI A. Production and characterization of lemna minor bio-char and its catalytic application for biogas reforming [J]. Biomass & Bioenergy, 2012, 42: 123−131.

[27] BAIG S A, ZHU J, MUHAMMAD N, SHENG T T, XU X H. Effect of synthesis methods on magnetic Kans grass biochar for enhanced As (III, V) adsorption from aqueous solutions [J]. Biomass & Bioenergy, 2014, 71: 299−310.

[28] HU Zhi-feng, MA Xiao-qian, LI Long-jun. Optimal conditions for the catalytic and non-catalytic pyrolysis of water hyacinth [J]. Energy Conversion & Management, 2015, 94: 337−344.

[29] KONG Z Y, LIAW S B, GAO X P, YU Y, WU H W. Leaching characteristics of inherent inorganic nutrients in biochars from the slow and fast pyrolysis of mallee biomass [J]. Fuel, 2014, 128: 433−441.

[30] ÖZKAN A, GÜNKAYA Z, BANAR M. Pyrolysis of plants after phytoremediation of contaminated soil with lead, cadmium and zinc [J]. Bulletin of Environmental Contamination & Toxicology, 2016, 96: 415−419.

[31] LIU Zhen-gang, ZHANG Fu-Shen, WU Jian-zhi. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment [J]. Fuel, 2010, 89: 510−514.

[32] LICURSI D, ANTONETTI C, BERNARDINI J, CINELLI P, COLTELLI M B, LAZZERI A, MARTINELLI M, GALLETTI A M R. Characterization of the *Arundo Donax* L. solid residue from hydrothermal conversion: Comparison with technical lignins and application perspectives [J]. Industrial Crops & Products, 2015, 76: 1008−1024.

[33] LU Qiang, ZHANG Zhi-bo, WANG Xiao-qiang, DONG Chang-qing, LIU Yong-qian. Catalytic upgrading of biomass fast pyrolysis vapors using ordered mesoporous ZrO_2, TiO_2 and SiO_2 [J]. Energy Procedia, 2014, 61: 1937−1941.

芦竹修复收获物热解过程中重金属的稳定性

刘亚男，郭朝晖，孙 阳，侍 维，韩自玉，肖细元，曾 鹏

中南大学 冶金与环境学院，长沙 410083

摘 要：芦竹修复收获物的热解过程会造成重金属的二次污染，本文作者研究外加物料 Al_2O_3、$CaCO_3$、$FeCl_3$ 和 NaOH 的添加对热解过程中重金属稳定性的影响。结果表明，当芦竹粉在外加 5% Al_2O_3、250 °C 下热解 2 h，37% As 和 97% Cd 固定在芦竹生物炭中；在外加 5% $CaCO_3$、400 °C 下热解 1 h，59% Pb 固定在芦竹生物炭中。在芦竹热解最优条件下通过 BCR 法分析可知，Cd 主要以残渣态存在，Pb 和 As 主要以可氧化态存在。由 XRD 分析可知，As 主要存在于 $Ca_2As_2O_7$ 中，Cd 主要存在于 Cd $(AlCl_4)_2$、$CdPbO_3$ 或 $CdSO_3$ 中，Pb 主要存在于 $Pb_3O_2SO_4$ 中。

关键词：植物修复后芦竹；热解；生物炭；重金属；稳定

(Edited by Wei-ping CHEN)