Bioresource Technology 253 (2018) 64–71

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Pyrolysis and reutilization of plant residues after phytoremediation of heavy metals contaminated sediments: For heavy metals stabilization and dye adsorption

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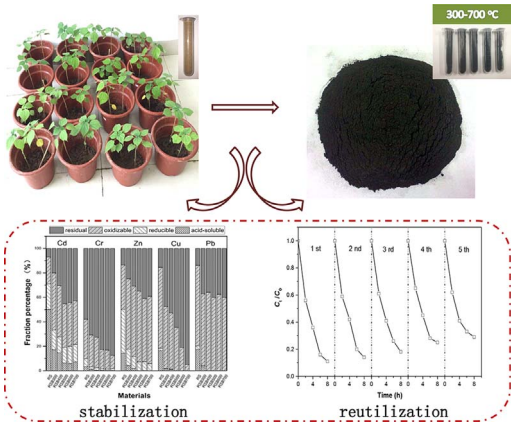
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Plant residues
Heavy metals
Pyrolysis
Adsorption

ABSTRACT

This study aimed to investigate the effect of pyrolysis on the stabilization of heavy metals in plant residues obtained after phytoremediation. Ramie residues, being collected after phytoremediation of metal contaminated sediments, were pyrolyzed at different temperatures (300–700 °C). Results indicated that pyrolysis was effective in the stabilization of Cd, Cr, Zn, Cu, and Pb in ramie residues by converting the acid-soluble fraction of metals into residual form and decreasing the TCLP-leachable metal contents. Meanwhile, the reutilization potential of using the pyrolysis products generated from ramie residues obtained after phytoremediation as sorbents was investigated. Adsorption experiments results revealed that the pyrolysis products presented excellent ability to adsorb methylene blue (MB) with a maximum adsorption capacity of 259.27 mg/g. This study demonstrated that pyrolysis could be used as an efficient alternative method for stabilizing heavy metals in plant residues obtained after phytoremediation, and their pyrolysis products could be reutilized for dye adsorption.

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https://doi.org/10.1016/j.biortech.2018.01.018
Received 7 November 2017; Received in revised form 30 December 2017; Accepted 3 January 2018
Available online 05 January 2018
0960-8524/

1. Introduction

With the speeding up of urbanization and industrialization, heavy metal pollution has become an increasingly serious problem (Huang et al., 2016a; Rezania et al., 2016; Wan et al., 2016; Zeng et al., 2017). Unlike organic pollutants, metals usually are recalcitrant to degradation and their bio-accumulation through the food chain can lead to various human diseases (Huang et al., 2017a; Lasat, 2002). Remediation of metal contaminated environment by phytoremediation has received extensive attention in recent years (Chaney et al., 1997; Huang et al., 2017b). Since it is driven by the solar energy and can remove pollutants from the contaminated sites completely, phytoremediation has been considered as a cost-efficient, high stability and environment-friendly alternative remediation technology (Gong et al., 2017a). Plants are capable to extract, transfer, sequester and stabilize a variety of heavy metals, which make them particularly suitable for removing heavy metals from the contaminated environment. Nevertheless, once heavy metals are uptake by plants, their potential damages to the animals, humans and ecosystems should not be ignored (Ali et al., 2013; Huang et al., 2008). Metals in plants can release back to the environment and cause secondary pollutions to the soils and groundwater (Huang et al., 2015; Zhuykova et al., 2013). Besides, once metal contaminated crops are consumed by animals, the residual metals can be bio-accumulated through the food chain, thus posing a potential threat to human health (Gong et al., 2017b). Accordingly, handling and disposal metal enriched plant residues obtained after phytoremediation are imperative.

A promising and efficient waste processing technique is pyrolysis. Pyrolysis can reduce the mass and volume of waste, which could decrease the transportation cost and improve the disposal efficiency of waste in the landfill. Another important advantage of pyrolysis is that it can decompose and stabilize pollutants in the waste (Bo et al., 2017; Huang et al., 2017c). Previous studies have shown that pyrolysis could immobilize heavy metals in the pyrolysis products and reduce the release of toxic metals into the environment. For example, a study investigated the pyrolysis of Zn-rich antibiotic residue found that Zn was stabilized in the pyrolysis products and its bioavailability and phytotoxicity decreased after pyrolysis (Xiao et al., 2015). Thus, pyrolysis is probably a potential alternative approach for the disposal of plant residues obtained after phytoremediation. During the pyrolysis process, pyrolysis temperature plays a key role in changing the behaviors of heavy metals in the pyrolysis products (Stals et al., 2010). For example, Kistler et al. (1987) found that Cd was volatilized at the pyrolysis temperature higher than 600 °C and Hg was completely evaporated at 350 °C. He et al. (2010) demonstrated that pyrolysis can improve the stabilization of Cu, Cd, Zn and Pb in sewage sludge by decreasing the leachable metal contents when the pyrolysis temperature is high enough. Since plant residues obtained after phytoremediation of metal contaminated sites possess large amounts of heavy metals, it is unclear whether the pyrolysis temperature will influence the stabilization of heavy metals in the pyrolysis products of plant residues.

Bechmeria nivea (L.) Gaud. (Ramie) is a widely distributed textile crop, which is extensively grown in China, Vietnam and Laos. Previous studies have demonstrated that ramie is a promising species for the phytoremediation of heavy metal contaminated environment due to its high metal accumulation capacity and large biomass (Gong et al., 2016; Liu et al., 2007). To date, very few studies have investigated the availability and feasibility of using pyrolysis to stabilize heavy metals in ramie residues obtained after phytoremediation. Additionally, a previously published study have confirmed that pyrolysis could convert ramie residues into biochar and the generated biochar possessed high Cr adsorption capacity (Zhou et al., 2016). Therefore, the pyrolysis products of ramie residues obtained after phytoremediation are likely to be efficient sorbents for removing pollutants from wastewater.

In this study, oxygen-limited pyrolysis was used to dispose ramie residues obtained after phytoremediation at the pyrolysis temperature from 300 to 700 °C, and their pyrolysis products were applied to remove methylene blue (MB) from wastewater. The objectives of this study were to: i) investigate the stabilization of heavy metals in ramie residues obtained after phytoremediation by pyrolysis; ii) determine the relationship between pyrolysis temperature and metals stabilization in the pyrolysis products; and iii) explore the reutilization potential for using the pyrolysis products from ramie residues obtained after phytoremediation as sorbents. This study will provide new insights into the disposal of metal-enriched plant waste and offer an alternative approach to reutilize plant residues obtained after phytoremediation.

2. Materials and methods

2.1. Pyrolysis products preparation

Ramie seedlings cultivated in metal contaminated sediments for 6 months were harvested. Ramie stems (RS) were collected separately, and washed with ultrapure water. After drying in oven at 60 °C till constant weight, RS were powdered and sieved to a size ≤ 0.15 mm. The powders were pyrolyzed at 300, 400, 500, 600 and 700 °C using a vacuum tube sintering furnace to produce biochar. The furnace was continued to heat up at the heating rate of 8 °C/min until the design temperature and then the temperature was maintained for 2 h. All the pyrolysis processes were carried out with N_2 protection. After pyrolysis, the products were cooled to normal atmospheric temperature and stored in a desiccator before use. Based on the pyrolysis temperature, the ramie stems biochar (RSB) were abbreviated as RSB300, RSB400, RSB500, RSB600, and RSB700. The yield (Y) of RSB was calculated as follows:

$$Y = \frac{w_2}{w_1} \times 100\% \quad (1)$$

where w_1 and w_2 are the weights of RS (g) before and after pyrolysis, respectively.

2.2. Metal analysis

To assess the total metals concentrations, 0.5 g samples were digested with a mixture of HF, $HClO_4$ and HNO_3 at a volume ratio of 1:1:3 using a graphite digestion apparatus (DS-360). The contents of Cd, Cr, Zn, Cu, and Pb were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA8000, PerkinElmer, U.S.A.). The relative enrichment factor (*Ref*) of metal was calculated as follows:

$$Ref = \frac{C_2}{C_1} \quad (2)$$

where C_1 and C_2 are the concentrations of metal (mg/kg) in the RS and RSB, respectively.

The speciation of Cd, Cr, Zn, Cu, and Pb in the RS and RSB were measured using the BCR (European Community Bureau of Reference) sequential extraction procedure described previously (Xue et al., 2017).

Leaching behavior of Cd, Cr, Zn, Cu, and Pb in the RS and RSB were determined using the toxicity characteristic leaching procedure (TCLP) according to the method provided by the United States Environmental Protection Agency (EPA, 2015).

2.3. MB adsorption and desorption experiments

MB adsorption experiments were carried out using RSB500 as the sorbent. 100 mL conical flasks which contain 50 mg RSB500 and 50 mL MB were placed on a thermostat water bath shaker at 120 rpm and 25 °C for 24 h. The influence of pH on MB adsorption by RSB500 was investigated by adjusting the initial solution pH of MB from 2 to 10. The pH was adjusted by HNO_3 and NaOH solutions at the concentration of 0.1 mol/L. The adsorption capacity of MB by RSB500 was estimated by performing the batch adsorption experiments with varied initial MB concentrations (25, 50, 100, 150, 300, 500, 700 and 1000 mg/L). MB

content in the solution was determined by the ultraviolet spectrophotometer (UV-2550, Shimadzu, Japan) at the absorbance of 664 nm according to the method described previously (Cheng et al., 2015). The removal percentage (R) and adsorption capacity (q_e) of MB by RSB500 were calculated as follows:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (3)$$

$$q_e = \frac{V \times (C_0 - C_e)}{W} \quad (4)$$

where C_0 and C_e are the initial and equilibrium concentrations of MB (mg/L), respectively; V represents the solution volume (L), and W is the mass (g) of RSB500.

The regeneration of RSB500 was investigated by conducting five successive cycle adsorption-desorption tests. The adsorption experiments were carried out at 25 °C by adding 50 mg RSB500 to 50 mL MB solution (100 mg/L) in the conical flasks. Then, the conical flasks were shaken in a thermostat water bath shaker at 120 rpm for 8 h. MB content was determined at the designed time periods (2, 4, 6 and 8 h). After the adsorption experiments, the sorbents were collected and the adsorbed MB was desorbed with HNO_3 solution (pH = 2). And then, the regenerated sorbents were washed thoroughly with ultrapure water and dried for the next cycle.

2.4. Statistical analysis

The results are presented as means of 3 replicates. The adsorption isotherm was fitted by Origin Pro 9.1. The correlation analysis was performed by Pearson correlation analysis using Statistic Package for Social Science.

3. Results and discussion

3.1. Pyrolysis products yield

The yield of biochar generated from RS obtained after phytoremediation was calculated (see Supplementary material). A 58.59% weight reduction could be achieved after pyrolysis the RS at 300 °C. With the increase of pyrolysis temperature, the yield of RSB decreased from 41.41 wt% to 28.27 wt%. These results indicated that pyrolysis could be used as a high-efficiency practical technique to dispose plant residues obtained after phytoremediation since it could massively decrease the weight of plant residues. The weight reduction could be resulted from the dehydration and volatilization reaction during the pyrolysis process (Zhou et al., 2016). Another possible way of weight reduction was the degradation of organic matters into low molecular weight materials during the temperature-rising process (Thangalazhy-Gopakumar et al., 2010). Similar weight decrease of biochar was observed in the biochar generated from bamboo, maize straw and coconut shell with the increase of pyrolysis temperature (Yu et al., 2013).

3.2. Effects of pyrolysis on metal stabilization

In order to investigate the effect of pyrolysis on the behavior of heavy metals in plant residues obtained after phytoremediation, the total metals contents, different metals speciation, and metals leachability in RS and RSB were determined.

3.2.1. Total metals contents

The contents and *Ref* of heavy metals in RS and RSB were shown in Fig. 1. The concentrations of Cd, Cr, Zn, Cu, and Pb in RS were 1.04, 6.14, 25.01, 6.69 and 0.84 mg/kg, respectively. All the concentrations of the measured metals in RS increased after pyrolysis. With the increase of pyrolysis temperature up to 500 °C, a further increase in the concentrations of heavy metals was observed. However, Cd was an exception since its content decreased in the RSB with the increase of pyrolysis temperature. The contents of Zn and Cu in RSB decreased with increasing the pyrolysis temperature from 500 to 700 °C, while the concentration of Cr in RSB reduced after heating to 600 °C. In addition, the *Ref* of heavy metals in RS was greater than 1 after pyrolysis at 300 °C. With the pyrolysis temperature rising, the *Ref* of Cr, Zn, Cu, and Pb exhibited varying degrees of growth, and the changes of *Ref* and total metals contents along with the temperature increase followed similar pattern.

The concentrations of all the measured heavy metals in RS, except for Cd, were lower than the limit of environmental quality standard for soils in China. However, those metals in RS, especially for Cd, still have potential risks to the ground water and organisms. The increased concentrations and *Ref* of heavy metals in RS after pyrolysis indicated that heavy metals were concentrated in plant residues, which is probably due to the mass loss of plant residues during the pyrolysis process. These concentrate of heavy metals might provide favorable conditions for the post-processing of plant residues obtained after phytoremediation. In addition, the decreased Cd content in RSB with the pyrolysis temperature rising could be due to the transform and/or volatility of Cd at higher temperatures. A study conducted by Kistler et al. (1987) demonstrated that Cd compounds were reduced to Cd^0 and then volatilized to the off-gas at high temperature. Meanwhile, the concentrations of Cr, Zn and Cu in RSB increased at first and then reduced with the pyrolysis temperature rising. Similar to what was observed in this study, Stefaniuk et al. (2016) found that the contents of Zn and Ni decreased in the biochar produced from biogas residues at 800 °C, and they ascribed this phenomenon to the fractionation and volatility of metals at elevated temperature.

3.2.2. Metals speciation

The speciation of Cd, Cr, Zn, Cu, and Pb in RS and RSB were shown in Fig. 2. As shown in this figure, the acid-soluble and reducible fractions of all the measured metals decreased, while the oxidizable and residual proportions of metals increased in RS after pyrolysis. Specifically, the residual percentage of Cd, Cr, Zn, Cu, and Pb in RS after pyrolysis increased by 1.86–5.46, 0.21–0.51, 0.84–2.01, 2.06–5.12 and 1.68–1.89 times, respectively. In addition, metals speciation in RSB varied with metal types and pyrolysis temperature. The acid-soluble fraction of Cd in RSB decreased from 17.17% to 6.33% with increasing the pyrolysis temperature from 300 to 500 °C, and then it tended towards stability. At 500 °C, the acid-soluble fraction of Cr, Zn, Cu, and Pb were transformed to other stable fractions. On the other hand, the residual fraction of Cu increased with the pyrolysis temperature rising while the temperature seems had no significant effect on the residual form of Pb in RSB.

In general, the mobility and bio-toxicity of metals decrease in the order of acid-soluble fraction > reducible fraction > oxidizable fraction > residual fraction (Huang et al., 2016c). Acid-soluble fraction is also known as the exchangeable fraction, which mainly contains metals that are in ionic form or bond to carbonate. The reducible fraction mainly includes metals bound to iron and manganese oxides or hydroxides. These two fractions, especially acid-soluble fraction, are considered to be the most loosely bound phases (Kazi et al., 2005). Metals in these fractions are more likely to be released, and therefore pose potential threat to the organisms and natural ecosystem. On the other hand, the oxidizable fraction represents metals bound to stable organic matter or sulfides, and metals in this fraction are hard to be released in general environmental conditions. The residual fraction refers mainly to the metals present in the crystal phases, which is the mostly stable fraction of metals and has been considered as inert and inaccessible to organisms (He et al., 2010). In this study, pyrolysis reduced the acid-soluble and reducible fractions and increased the oxidizable and residual proportions of Cd, Cr, Zn, Cu, and Pb in RS, which indicated that pyrolysis can be used as an efficient alternative method for the stabilization of metals in plant residues obtained after

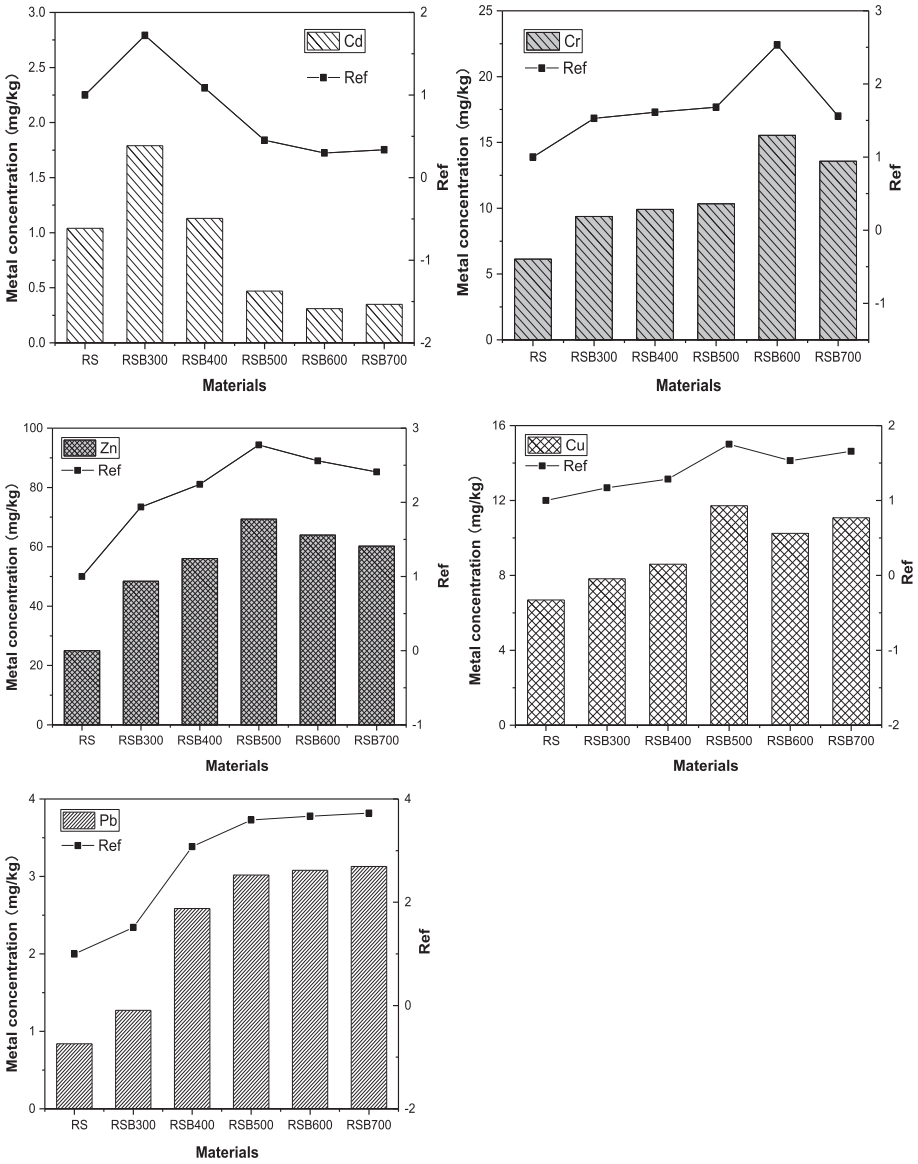

Fig. 1. Total metal contents and the relative enrichment factor (*Ref*) of Cd, Cr, Zn, Cu and Pb in the pyrolysis products of plant residues obtained after phytoremediation of heavy metals. RS correspond to ramie stems. RSB300, RSB400, RSB500, RSB600 and RSB700 denote ramie stems pyrolysis at 300, 400, 500, 600 and 700 °C, respectively.

phytoremediation. Metals speciation in RSB was different from each other with the pyrolysis temperature rising, suggesting that the stabilization of heavy metals in RSB depends on the metal types and the pyrolysis temperature. What is noticeable is that the acid-soluble fraction of Cr, Zn, Cu, Pb and Cd was transformed to other stable fractions or reduced to a relatively lower level in RS after pyrolysis at 500 °C. Therefore, plant residues obtained after phytoremediation were less toxic after pyrolysis at this temperature.

3.2.3. Metals TCLP leachability

Table 1 illustrated the effect of pyrolysis on metals leaching in RS obtained after phytoremediation. As shown in this table, the original TCLP-leachable Cd, Cr, Zn and Cu contents in RS were 0.018, 0.027, 1.109, and 0.015 mg/L, respectively. There was no detectable Pb leached from RS, which is probably due to its high stability and relatively lower content in RS. Pyrolysis sufficiently reduced the leaching of metals in RS. The TCLP-leachable Cu content in RS was below the detection limits after pyrolysis. A temperature dependent decrease of Zn leaching was observed. The leaching potential of Cd and Cr in RSB decreased with increasing the pyrolysis temperature from 300 to 500 °C. At 500 °C, the TCLP-leachable Cd and Cr contents in RSB decreased by 89% and 91% compared with those in RS. And there was no further change for the leaching of Cd and Cr with temperature rising.

The concentrations of metals in the leachate were very low, and all the concentrations were below the permissible norms by USEPA. However, if the RS was long-term consumed by organisms or the metals in RS migrated to the ground water, it will pose potential threats to human health and/or the ecosystem. Besides, the leachability of metals is a major restrictive factor for the reutilization of plant residues obtained after phytoremediation. In this study, the TCLP-leachable metal contents in RS were decreased by pyrolysis, indicating that pyrolysis could reduce the leaching toxicity of plant residues obtained after phytoremediation. The reduction of metals leaching may result from the conversion of acid-soluble, reducible and oxidizable fractions of metals into their residual form in RSB. In addition, the decrease of metals leaching in RSB was more pronounced with the pyrolysis temperature rising in most instances and was consistent with previously published studies. For example, He et al. (2010) demonstrated that in the biochar derived from sewage sludge, the TCLP-leachable Cu, Cd, Zn and Pb declined sharply with the pyrolysis temperature rising.

3.2.4. Correlation between pyrolysis temperature and metal stabilization

Pearson correlation analysis was conducted to explore the relationship between pyrolysis temperature and metal stabilization in RS.

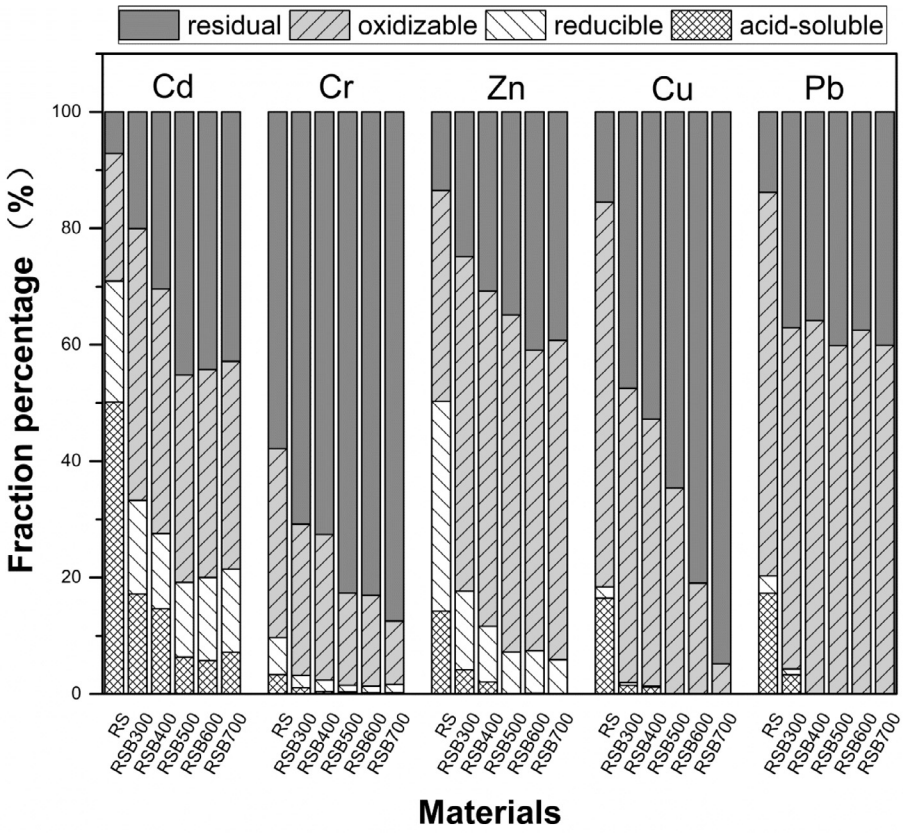

Fig. 2. Speciation of heavy metals in plant residues obtained after phytoremediation of heavy metals. RS correspond to ramie stems. RSB300, RSB400, RSB500, RSB600 and RSB700 denote ramie stems pyrolysis at 300, 400, 500, 600 and 700 °C, respectively.

Table 1
TCLP-leachable metal contents of ramie stems (RS) and ramie stems biochar generated at 300 (RSB300), 400 (RSB400), 500 (RSB500), 600 (RSB600) and 700 °C (RSB700).

Metals (mg/L)	RS	RSB300	RSB400	RSB500	RSB600	RSB700
Cd	0.018	0.006	0.006	0.002	0.002	0.002
Cr	0.033	0.014	0.012	0.003	0.003	0.003
Zn	1.109	0.359	0.036	0.024	0.005	nd[a]
Cu	0.015	nd	nd	nd	nd	nd
Pb	nd	nd	nd	nd	nd	nd

[a] Not detected.

Table 2
Correlation coefficients between pyrolysis temperatures and metal fractions, and that of pyrolysis temperatures and TCLP-leachable metal contents.

Metals	Acid-soluble	Reducible	Oxidizable	Residual	TCLP
Cd	−0.927**[a]	−0.813*[b]	0.419	0.944**	−0.936**
Cr	−0.921**	−0.895**	−0.962**	0.985**	−0.959**
Zn	−0.934**	−0.922**	0.680	0.982**	−0.918**
Cu	−0.870*	−0.908**	−0.957**	0.992**	−0.822*
Pb	−0.884*	−0.909*	−0.556	0.872*	/[c]

[a] **Correlation is significant at the 0.01 level.
[b] *Correlation is significant at the 0.05 level.
[c] /no correlation.

The correlation coefficients between pyrolysis temperature and metal speciation, and that of pyrolysis temperature and the leaching of Cd, Cr, Zn, Cu, and Pb are presented in Table 2. A significant negative correlation ($p < .05$) was found between pyrolysis temperature and the acid-soluble fraction of all the five measured heavy metals, while a positive correlation ($p < .05$) was observed between pyrolysis temperature and the residual proportion of metals in RS. In addition, there was a significant negative correlation between the pyrolysis temperature and the TCLP-leachable Cd, Cr, Zn, and Cu contents in RS.

The Pearson correlation analysis results revealed that the behavior of heavy metals in RS depends strongly on the pyrolysis temperature. Most biochar produced at higher temperature is alkaline, which could lead to the formation of metal hydroxide and stable complex salts by precipitation (Devi and Saroha, 2014). The increased stabilization of heavy metals at higher pyrolysis temperature may attribute to the precipitation of heavy metals in the biochar generated from plant residues obtained after phytoremediation. Another possible reason was the adsorption of heavy metals by biochar. Previous studies have demonstrated that the surface area of biochar increased as the pyrolysis temperature rising (Chen et al., 2015; Trigo et al., 2016), which might improve the adsorption ability of biochar for heavy metals. The enhanced adsorption efficiency of biochar generated at higher temperature probably will stabilize heavy metals and reduce metals leachability in the pyrolysis products of plant residues obtained after phytoremediation.

The Pearson correlation analysis indicated that metal stabilization in RS was positive correlated with the pyrolysis temperature. However, higher temperature (T > 500 °C) are not advisable because maintaining such a high temperature for a long time was both energy consumption and costly. RSB produced at 500 °C possessed the highest contents of Zn and Cu, and the TCLP-leachable metal contents, except for Zn, reached their minimum levels at this temperature. Thus, pyrolysis at 500 °C seems well suited for the stabilization of heavy metals in RS without enormous energy loss, and RS pyrolyzed at this temperature were conductive to dispose or reutilization with mass loss and volume reduction.

3.3. Reuse of pyrolysis products from plant residues obtained after phytoremediation

Published works have demonstrated that biochar possesses high efficiency for removing pollutants from the contaminated environment (Abdel-Fattah et al., 2015; Chen et al., 2016; Huang et al., 2016b). The

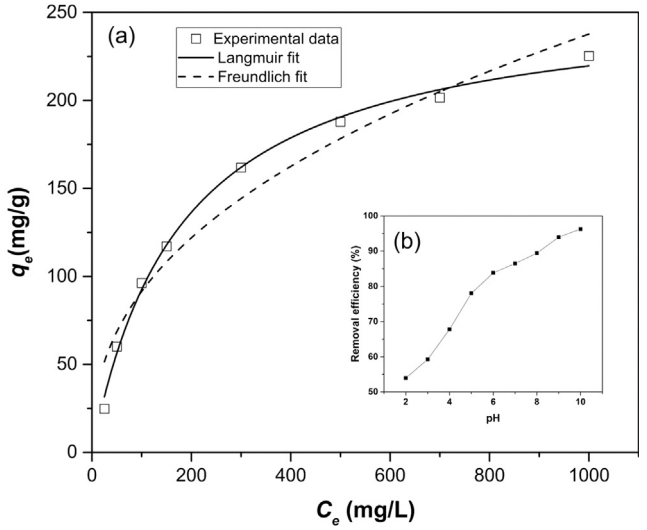

Fig. 3. (a) Langmuir and Freundlich isotherms of methylene blue adsorption on the pyrolysis products (500 °C) generated from plant residues obtained after phytoremediation of heavy metals; (b) Effect of the initial pH on methylene blue adsorption.

usage of pyrolysis products to adsorb dye is likely to be a feasible approach for the reutilization of plant residues obtained after phytoremediation. As mentioned above, the temperature most suitable for the stabilization of heavy metals in RS is 500 °C. Therefore, RSB500 was chosen as the sorbent to investigate the adsorption of MB by the pyrolysis products generated from plant residues obtained after phytoremediation.

3.3.1. MB adsorption

To investigate the effects of pH on the adsorption of MB by RSB500, the initial pH of MB solution was set as 2–10. As shown in Fig. 3b, the removal efficiency of MB increased with pH rising. The removal efficiency of MB increased from 53.93% to 96.27% as increasing the pH from 2 to 10. Thus, the initial solution pH of 10 was selected as the optimum pH for further experiments. Furthermore, the study of adsorption isotherms was performed by varying the concentration of MB from 25 to 1000 mg/L at the initial pH of 10. Langmuir and Freundlich isotherm models were used to fit the experimental data (Fig. 3a). By fitting the experimental data with the two models, it can be observed that the adsorption of MB on RSB500 fitted better with Langmuir isotherm model (R^2 = 0.996) than Freundlich isotherm model (R^2 = 0.953). According to the Langmuir isotherm model, the predicted maximum adsorption capacity of MB by RSB500 was 259.27 mg/g (see Supplementary Material).

The initial pH of solution affects the surface charge of sorbents, which probably will influence the adsorption performance of biochar (Dong et al., 2017). In this study, the adsorption of MB by RSB500 was more efficient at higher pH values. With the increase of pH, the surface of RSB500 might be negatively charged, and this could provide preferable conditions for the adsorption of cationic dye, such as MB. The result indicated that ion exchange and electronic interactions performed important roles in the adsorption of MB by RSB500, which was consistent with previously published studies of MB adsorption (Zhu et al., 2015). In addition, the experimental adsorption data were better fitted by the Langmuir isotherm model, suggesting that the adsorption was predominantly monolayer adsorption. The result is consistent with previous studies on MB adsorption by biochar generated from eucalyptus and palm bark (Sun et al., 2013). Moreover, the maximum adsorption capacity of MB by RSB500 (259.27 mg/g) was much higher than those observed in activated carbon produced from bamboo dust and groundnut shell (Kannan and Sundaram, 2001), indicating that MB could be easily adsorbed by RSB500. Therefore, biochar prepared from plant residues obtained after phytoremediation is a type of low-cost and efficient sorbent for cationic dye, and the usage of RSB500 to remove pollutants from wastewater could provide a new insight into the reutilization of plant residues obtained after phytoremediation.

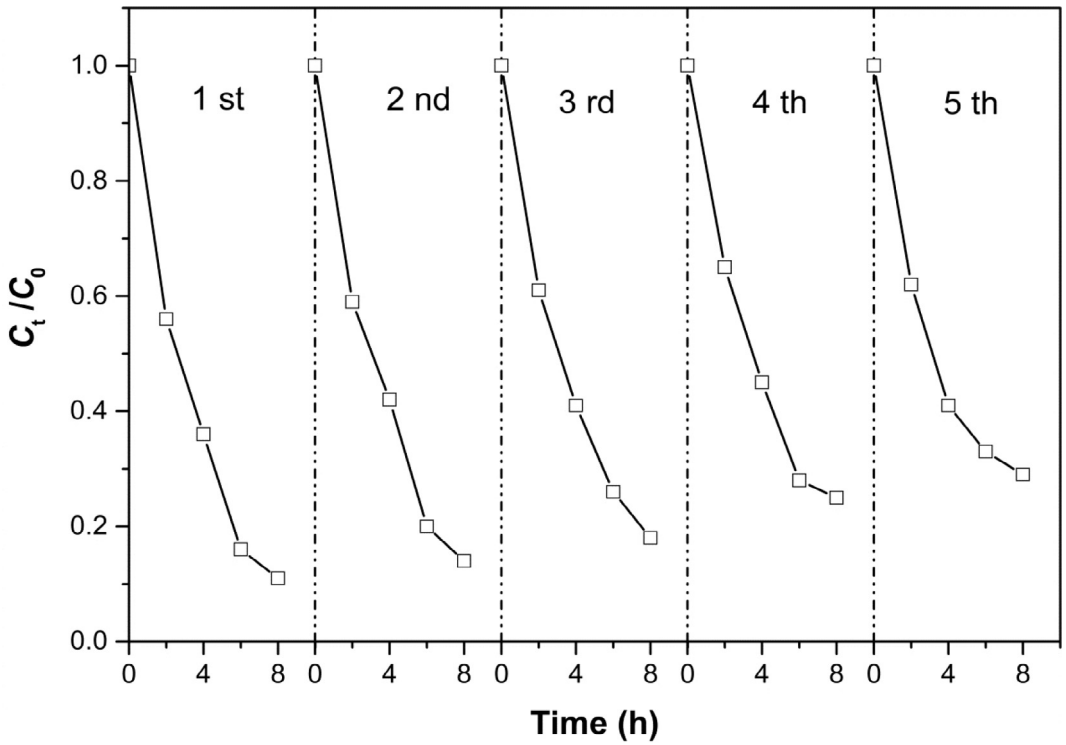

Fig. 4. Five successive cycles for the adsorption of methylene blue on the pyrolysis products (500 °C) generated from plant residues obtained after phytoremediation of heavy metals (C_t/C_0 are the ration of methylene blue concentration at time t and in the initial stage).

3.3.2. Desorption and regeneration analysis

In order to explore the potential regeneration of RSB500, desorption experiments were performed using HNO_3 as the eluent. As shown in Fig. 4, the adsorption efficiency of MB by RSB500 decreased from 89% to 82% at the third cycle, and it further reduced to 71% in the fifth experiment run. The regeneration and reusability of sorbent are very important for the practical applications. Although the removal efficiency decreased gradually with the increase of cycles, the adsorption efficiency of MB by RSB500 was no less than 70% at the fifth cycle. These results indicated that the adsorption of MB onto RSB500 was reversible, and the RSB500 sorbent could be regenerated. The decreased removal efficiency could be ascribed to the sorbent loss and the changes of biochar's physic-chemical properties during the regeneration processes. In general, the pyrolysis products generated from plant residues obtained after phytoremediation exhibited excellent adsorption and regeneration ability, and they could be used as efficient and recycled sorbents for the decontamination of environmental pollutants from wastewater.

4. Conclusions

Plant residues obtained after phytoremediation contain large amounts of heavy metals. Plant residues pyrolysis at 500 °C was effective in stabilizing heavy metals and reducing the mass of plant waste, which provided preferable conditions for the further treatment and the reutilization of plant residues obtained after phytoremediation. In addition, the pyrolysis products generated from plant residues obtained after phytoremediation exhibited excellent performance in dye adsorption. Hence, pyrolysis is a feasible approach for the disposal of plant residues obtained after phytoremediation and their pyrolysis products can serve as potential alternative sorbents for the decontamination of environmental pollutants from wastewater.

Acknowledgements

This work was supported by the Program for the National Natural Science Foundation of China (51579098, 51779090, 51709101, 51278176, 51408206, and 51521006), the National Program for Support of Top–Notch Young Professionals of China (2014), Hunan Provincial Science and Technology Plan Project (No.2016RS3026), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2018.01.018.

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