Research Progress of Biochar Materials for Remediation of Heavy Metal Contaminated Soil

Han Wang¹ª, Yuheng Tang²ª

¹Wuhan University of Technology, School of Resources and Environmental Engineering, Wuhan, China
²Wuhan University of Technology, School of Energy and Power Engineering, Wuhan, China
ªCorresponding Author e-mail: 2995314490@qq.com
ªe-mail: yuheng.tang@whut.edu.cn

Abstract—In recent years, with the acceleration of urbanization and the high-speed development of industry, heavy metal pollution of soil has become increasingly serious, posing a huge threat to economic development and human health. The use of biochar to control soil pollution has become a research hotspot. Biochar has unique physical and chemical properties. It can lessen the transfer and transformation of heavy metals when being used to adsorb and fix heavy metals, and has great application potential in repairing heavy metal pollution. This article reviews the factors affecting biochar remediation of soil heavy metal pollution, the preparation and application of functional biochar, and the adsorption mechanism and remediation effect of biochar on heavy metals. Finally, the article summarizes the current problems of biochar repair technology and makes prospects for future development, hoping to provide reference for future research by science and technology workers.

1. INTRODUCTION

Heavy metal pollution in the soil has accumulated to toxic levels due to its persistence and non-biodegradability in the environment, which has become a serious global problem [1]. It is extremely urgent to find a cost-efficient method for remediation of soil pollution. Biochar is a solid substance which is obtained by thermal decomposition of biomass under conditions of hypoxia or anaerobic. It has abundant functional groups, large specific surface area and developed pore structure. These special physical and chemical properties make it possible not only to absorb and fix soil heavy metals, but also to improve the soil. Therefore, it is usually used to remediate soil pollution by heavy metals [2–4]. Former studies have shown, the addition of biochar can lessen the content of available heavy metals in the soil and heavy metals in crops, change the form of heavy metals in the soil, and reduce its risk to the ecological environment and human health [5,6]. The addition of biochar can lessen the mobility and bioavailability of heavy metals to a certain extent, but the single biochar has limited adsorption capacity for certain heavy metal pollutants, and its repair effect on heavy metal composite pollution cannot meet expectations. Single biochar has limitations in environmental applications. Lots of modification methods have been developed to enhance the remediation efficiency of biochar, such as ultraviolet
modification, acid/base treatment, and combining biochar with other functional materials (such as graphene [7-9]) to form a biochar composite.

2. **INFLUENCING FACTORS OF BIOCHAR ON SOIL REMEDIATION CONTAMINATED BY HEAVY METAL**

2.1 **Raw materials**

According to the source of biomass raw materials, biochar is basically divided into: sludge biochar, animal manure biochar and plant residue biochar [10]. Specifically, it consists of animal excrement biochar, bamboo biochar, wood biochar, rice husk biochar, straw biochar, etc. Biochar is a very complex carbon material. The chemical and physical properties of biochar made from different raw materials under the same conditions have certain differences, which often affects its adsorption effect on soil remediation capacity and different heavy metals [11]. For example, manure-derived biochar has many advantages compared with plant biochar, such as lower total C, higher ash, and content of cations (N, P, K, S and Mg, etc.). These characteristics are very important factors for the remediation of heavy metal polluted soil, and in the experimental research, fecal biochar also showed better fixation capacity for heavy metals [12]. Research of Manhattan Lebrun shows, compared to sapwood and heartwood biochar, the improvements in soil pore water physico-chemical properties were higher with the bark biochar. Therefore, bark seems to be the best part of the trunk to use for producing a biochar that will allow Pb immobilization, soil physico-chemical improvements and better plant growth [13]. Liu et al. found in the research of using biochar to remove heavy metals Pb in water, with different raw materials, the removal rate of Pb in water by biochar will be different. The adsorption amount of biochar made from mori wood is about twice that of biochar made from rice husk [14].

2.2 **Pyrolysis temperature**

Pyrolysis temperature will significantly affect the chemical and physical properties of biochar such as yield, ash content, element content, pH, type and number of surface functional group and pore structure [15]. In most cases, the effect of biochar on remediation of heavy metal contaminated soil also improves significantly with the increase of pyrolysis temperature. In the study of Priya Pariyar, eighteen different types of biochar were prepared by pyrolyzing raw materials at four different temperatures (350°C, 450°C, 550°C and 650°C). The raw material used to make biochar is organic waste materials such as rice husk, pine saw dust, food waste, paper sludge and poultry litter (Table 1-3). For example, the specific surface area of sawdust and rice husk increased from 3.39 to 443.79 m² g⁻¹ and 11.61 to 280.97 m² g⁻¹, the pH of poultry waste and paper sludge biochar increased from 6.2 to 10.3, while cation exchange capacity value decreased with the increase in temperature. With the increase of pyrolysis temperature, degree of aromaticity increased and polarity reduced significantly. This study showed that biochar prepared at higher temperature (550°C or 650°C) is more suitable for carbon sequestration and agricultural use [16].
### TABLE 1. Surface Properties of Different Feedstock Biochar Prepared at 350, 450, 550 and 650°C

| Sample             | pH   | Cation exchange capacity (cmol kg⁻¹) | Specific surface area (m² g⁻¹) |
|--------------------|------|-------------------------------------|--------------------------------|
| Saw dust biochar   |      |                                     |                                |
| 350°C              | 5.75 ± 0.02 | 56.13                               | 3.39 ± 0.79                   |
| 450°C              | 6.31 ± 0.04 | 52.43                               | 179.77 ± 2.35                 |
| 550°C              | 6.66 ± 0.08 | 47.43                               | 431.91 ± 5.46                 |
| 650°C              | 6.84 ± 0.03 | 39.22                               | 443.79 ± 0.98                 |
| Rice husk biochar  |      |                                     |                                |
| 350°C              | 6.41 ± 0.07 | 41.36                               | 11.61 ± 0.31                  |
| 450°C              | 6.92 ± 0.04 | 36.22                               | 18.58 ± 0.16                  |
| 550°C              | 7.89 ± 0.03 | 29.59                               | 248.99 ± 5.74                 |
| 650°C              | 7.97 ± 0.03 | 6.69                                | 280.97 ± 5.91                 |

### TABLE 2. Total Elemental Composition of Different Biochar at Varying Temperature

| Sample             | C (%) | H (%) | N (%) | O (%) | H/C  | O/C  |
|--------------------|-------|-------|-------|-------|------|------|
| Saw dust biochar   |       |       |       |       |      |      |
| 350°C              | 52.28 | 5.17  | 0.15  | 30.50 | 1.19 | 0.44 |
| 450°C              | 58.20 | 4.23  | 0.16  | 25.11 | 0.87 | 0.32 |
| 550°C              | 59.19 | 3.97  | 0.51  | 20.73 | 0.80 | 0.26 |
| 650°C              | 62.87 | 3.44  | 0.18  | 11.81 | 0.66 | 0.14 |
| Rice husk biochar  |       |       |       |       |      |      |
| 350°C              | 44.32 | 4.08  | 0.78  | 30.65 | 1.10 | 0.52 |
| 450°C              | 46.56 | 3.54  | 0.85  | 18.58 | 0.91 | 0.30 |
| 550°C              | 48.20 | 2.61  | 0.73  | 10.98 | 0.65 | 0.17 |
| 650°C              | 50.62 | 2.45  | 0.79  | 7.15  | 0.58 | 0.11 |
The study of Zhang has proved that pyrolysis is an effective method for cattle manure treatment. More heavy metals were concentrated on the cow dung biochar as the pyrolysis temperature increased from 300°C to 700°C. The reducible fractions and acid soluble/exchangeable of heavy metals were gradually converted into oxidizable fractions and residual fractions, and the leaching concentration was reduced, thereby greatly reducing the bioavailability and leaching risk. The ecotoxicity evaluation and environmental safety in his research indicated that higher-temperature biochar had lower potential ecological toxicity and environmental risks [17]. Yuan conducted research on biochar at different pyrolysis temperatures (300°C, 400°C, 500°C, 600°C, 700°C), and the results showed that biochar production would decrease with increasing temperature. But 700°C seems to be a suitable temperature for the production of biochar in terms of more developed pore structure, stronger alkalinity, less dissolved salts and higher nutrient content (except nitrogen). And the pyrolysis can aggravate the enrichment of heavy metals in biochar [18].

2.3 Physical and chemical properties of soil

The physical and chemical properties of soil such as water content, pH and organic matter also play a certain role in the biochar repair process. Due to the different physical and chemical properties of the soil, the mobility of biochar and its heavy metals on the surface will also be different. Uchimiya et al. found that biochar prepared from household waste has different effects when applied to soils with different properties. When the soil is acidic, the adsorption of copper by biochar is better than that in alkaline soil [19].

3. PREPARATION AND APPLICATION OF FUNCTIONAL BIOCHAR

3.1 Biochar-based composite materials

The adsorption performance of biochar on heavy metal pollutants can be significantly enhanced through biochar composites. In terms of the adsorption mechanism, biochar and its composites are mainly based on electrostatic effects, ion exchange effects, and surface functional groups to repair heavy metal pollution. In addition, biochar and its composites can indirectly enhance soil resistance to pollutants by improving soil quality. Although nanomaterials can enhance the performance of biochar, its mechanism of toxicity to soil microorganisms is not fully understood.

Due to their outstanding physical and chemical properties, biochar / iron (BC / Fe) composites, such as iron sulfide / BC, nano-zero valent iron (nZVI) / BC and iron oxide / BC, have been exploited and used to treat various pollutants. A lot of methods have been used to synthesize BC / Fe composites, including hydrothermal carbonization, pyrolysis, ball milling and fractional precipitation. Besides, the
introduction of stabilizers (carboxymethyl cellulose, etc.) in the fractional precipitation process further prevents the agglomeration of Fe particles. And the introduction enhances the stability and fluidity of the resultant composites which facilitate the application of the composites in water and soil remediation. In general, owing to the combination of the specific properties of Fe, the composites showed the synergistic effect of BC and Fe (such as catalysis, reduction and magnetism), which can enhance the properties of BC with abundant functional groups, larger surface area and increased electron transfer efficiency [20]. It is reported that a new type of calcium-based magnetic biochar (Ca-MBC) developed through the pyrolysis of straw mixed with calcium carbonate and iron oxide can stabilize the pollution of various metals. The double pollution of cadmium and arsenic can be eliminated by the composite material: (1) increasing the cation exchange capacity and pH (the effect on Cd), (2) formation of ternary surface complex and bidentate chelate on the surface of iron oxide, (3) enhancing adsorption capacity of porous biochar. In addition, it increases the diversity and abundance of bacterial communities, and changes the relative abundance of bacterial groups which leads to changes in composition (Figure 1) [21].

Figure 1. Preparation and application process of calcium-based magnetic biochar material.

3.2 Modification of biochar
According to studies, phosphoric acid modification can control the adsorption of metal ions by modified biochar through the mechanism of surface complexation between metals and oxygen-containing functional groups. The biochar modified with phosphoric acid has higher content of functional groups, larger specific surface area and stronger adsorption of Cu (II) and Cd (II) compared with the original biochar. X-ray photoelectron spectroscopy analysis showed, at the same pyrolysis temperature, the number of hydroxyl (-OH) and carboxyl (-COOH) functional groups of the modified biochar was greater than that of the original biochar. The strong ability of -OH and -COOH to form complexes with Cu (II) / Cd (II) ions leads to higher adsorption of two metal ions compared to the original biochar [22]. Jiajun Fan et al. used β-mercaptoethanol esterification to prepare thiol-modified straw biochar (RS) and used it to remediate soil contaminated by Cd and Pb. In his experiments, RS reduced effective Pb by 8.6% –11.1% and reduced the effective Cd by 34.8% –39.2% [23].

4. MECHANISM AND REMEDIATION EFFECT OF BIOCHAR ON SOIL HEAVY METAL POLLUTION

4.1 Mechanism of action
Biochar has different mechanisms of action on different heavy metals. Generally speaking, it mainly includes five aspects: physical adsorption, ion exchange, complexation, electrostatic interaction and precipitation. Biochar and its composite materials will produce a pore structure during the preparation process, which will have a large specific surface area. Meanwhile, the organic substances on the surface will be carbonized to form functional groups such as acid anhydride, carboxyl and phenolic hydroxyl. These functional groups contain a part of basic groups, making the biochar basic. Therefore, the mechanism is determined by a variety of factors [24].

4.2 Remediation effect

4.2.1 Effects of biochar on soil physical and chemical properties: It is generally believed that the application of biochar can neutralize acid soil, improve soil water retention and soil structure and
increase the ability of soil to retain nutrients. The effect of biochar on improving the physical and chemical properties of soil is affected by many factors such as application amount, soil environmental conditions, biochar properties, time scale of reaction between biochar and soil [25], etc. In a four-year field trial conducted in a paddy field, the effects of an on-site biomass (rice straw) equivalent biochar-returning strategy (RSC) on soil nutrients, rice yield and bacterial community composition were examined. Results showed that a low RSC could remarkably increase rice yield in four successive years. The increase in rice yield is mainly due to the existence of unique surface functional groups of biochar, which leads to an increase in soil potassium and magnesium content. The soil bacterial cooperation in RSC was improved through the improvement of biochar [26].

4.2.2 Effect of biochar on available heavy metal content: The migration and accumulation of soil heavy metal elements show that the biological toxicity of heavy metals is not only related to the total amount, but also determined by their morphological distribution. Passivation repair technology that reduces the bioavailability by reducing the effective state content of heavy metals is one of the ways to remediation of soil heavy metal pollution. The forms of heavy metals in soil can be divided into reducible state, weak acid extraction state, residue state and oxidizable state. The weak acid extraction state is easily absorbed by plants, which is more harmful to crops; the reducible state is less stable under redox conditions and has potential harm to crops; the oxidizable state is generally not easily absorbed and used by plants. Studies have shown that the addition of biochar can reduce the content of weakly acid-extractable, reduce soil Pb activity and promote the conversion of weakly acid-extracted Cd to oxidizable Cd.

5. POTENTIAL RISKS OF BIOCHAR IN HEAVY METAL CONTAMINATED SOIL REMEDIATION APPLICATIONS

The addition of biochar may introduce toxic substances (such as polychlorinated dibenzodioxins and polycyclic aromatic hydrocarbons, etc.) into the soil, thereby affecting soil microbial communities and plant growth. The characteristics of biochar, its interactions with pollutants, and the endogenous pollutants it contains may affect the function of soil and the composition and structure of biological communities. Therefore, in the process of exploring the impact mechanism and environmental risk of biochar on the soil environment system, researchers need to consider a variety of factors, such as microbial species, heavy metal species and content and soil pH value. In addition, the aging of biochar and the changes caused by subsequent changes in chemical structure and physical properties are also one of the potential problems in long-term risk control of biochar applications.

6. CONCLUSION AND OUTLOOK

In recent years, biochar, as a rapidly developing green repair agent, can significantly improve soil physical and chemical properties after being applied to the soil. Through a series of reaction mechanisms, it can solidify or remove heavy metals in the soil. In recent years, domestic and foreign researches on remediation of heavy metal contaminated soil with biochar have achieved many results, showing the great potential and development prospects of biochar as a green repair agent. Currently, the research work on biochar adsorption of heavy metals is mainly concentrated on improving the adsorption performance of heavy metal ions by modifying or preparing biochar-based composite materials. However, the research on biochar remediation of heavy metal soil pollution is still incomplete: (1) The adsorption mechanism of biochar remediation of heavy metal contaminated soil has not yet been fully revealed at the molecular level; (2) the current experimental scale and time span are small, the data are not obviously representative, and long-term experiments need to be conducted in outdoor fields; (3) the economic benefits of modified or composite biochar materials applied to farmland soils need to be considered; (4) the long-term existence of biochar needs to be considered for impact of security.
REFERENCES

[1] J. Tang, J. Zhang, L. Ren, Y. Zhou, J. Gao, and L. Luo et al., “Diagnosis of soil contamination using microbiological indices: A review on heavy metal pollution,” J. Environ. Manage., vol. 242, pp. 121–130, 2019.

[2] R. Bian, S. Joseph, L. Cui, G. Pan, L. Li, and X. Liu et al., “A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment,” J. Hazard. Mater., vol. 272, pp. 121–128, 2014.

[3] S. Mukherjee, L. Weihermüller, W. Tappe, D. Hofmann, S. Köppchen, and V. Laabs et al., “Sorption–desorption behaviour of bentazone, boscalid and pyrimethanil in biochar and digestate based soil mixtures for biopurification systems,” Sci. Total Environ., vol. 559, pp. 63–73, 2016.

[4] X. Chao, X. Qian, Z. Han-hua, W. Shuai, Z. Qi-hong, and H. Dao-you et al., “Effect of biochar on peanut shell on speciation and availability of lead and zinc in an acidic paddy soil,” Ecotoxicol. Environ. Saf., vol. 164, pp. 554–561, 2018.

[5] B. Zhao, R. Xu, F. Ma, Y. Li, and L. Wang, “Effects of biochars derived from chicken manure and rape straw on speciation and phytoavailability of Cd to maize in artificially contaminated loess soil,” J. Environ. Manage., vol. 184, pp. 569–574, 2016.

[6] L. Niu, P. Jia, S. Li, J. Kuang, X. He, and W. Zhou et al., “Slash-and-char: an ancient agricultural technique holds new promise for management of soils contaminated by Cd, Pb and Zn,” Environ. Pollut., vol. 205, pp. 333–339, 2015.

[7] K. Sun, J. Tang, Y. Gong, and H. Zhang, “Characterization of potassium hydroxide (KOH) modified biochars from different feedstocks for enhanced removal of heavy metals from water,” Environ. Sci. Pollut. Res., vol. 22, no. 21, pp. 16640–16651, 2015.

[8] Z. Peng, H. Zhao, H. Lyu, L. Wang, H. Huang, and Q. Nan et al., “UV modification of biochar for enhanced hexavalent chromium removal from aqueous solution,” Environ. Sci. Pollut. Res., vol. 25, no. 11, pp. 10808–10819, 2018.

[9] J. Tang, H. Lv, Y. Gong, and Y. Huang, “Preparation and characterization of a novel graphene/biochar composite for aqueous phenantrene and mercury removal,” Bioresour. Technol., vol. 196, pp. 355–363, 2015.

[10] S. Wang, Y. Xu, N. Norbu, and Z. Wang, “Remediation of biochar on heavy metal polluted soils,” in IOP Conference Series: Earth and Environmental Science, 2018, vol. 108, no. 4, p. 42113.

[11] J. H. Park, G. K. Choppala, N. S. Bolan, J. W. Chung, and T. Chuasavathi, “Biochar reduces the bioavailability and phytotoxicity of heavy metals,” Plant Soil, vol. 348, no. 1–2, p. 439, 2011.

[12] P. Qin, G.K. Choppala, N.S. Bolan, J.W. Chung, and T. Chuasavathi, “Bamboo-and pig-derived biochars reduce leaching losses of dibutyl phthalate, cadmium, and lead from co-contaminated soils,” Chemosphere, vol. 198, pp. 450–459, 2018.

[13] M. Lebrun, F. Miard, N. Hattab-Hambil, G. S. Scippra, S. Bourgerie, and D. Morabito, “Effect of different tissue biochar amendments on As and Pb stabilization and phytoavailability in a contaminated mine technosol,” Sci. Total Environ., vol. 707, p. 135657, 2020.

[14] Z. Liu and F.-S. Zhang, “Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass,” J. Hazard. Mater., vol. 167, no. 1–3, pp. 933–939, 2009.

[15] H. Yuan, T. Lu, D. Zhao, H. Huang, K. Noriyuki, and Y. Chen, “Influence of temperature on product distribution and biochar properties by municipal sludge pyrolysis,” J. Mater. Cycles Waste Manag., vol. 15, no. 3, pp. 357–361, 2013.

[16] P. Pariyar, K. Kumari, M. K. Jain, and P. S. Jadhao, “Evaluation of change in biochar properties derived from different feedstock and pyrolysis temperature for environmental and agricultural application,” Sci. Total Environ., p. 136433, 2020.

[17] P. Zhang, X. Zhang, Y. Li, and L. Han, “Influence of pyrolysis temperature on chemical speciation, leaching ability, and environmental risk of heavy metals in biochar derived from cow manure,” Bioresour. Technol., p. 122850, 2020.
[18] H. Yuan, T. Lu, H. Huang, D. Zhao, N. Kobayashi, and Y. Chen, “Influence of pyrolysis temperature on physical and chemical properties of biochar made from sewage sludge,” J. Anal. Appl. Pyrolysis, vol. 112, pp. 284–289, 2015.

[19] M. Uchimiya, K. T. Klasson, L. H. Wartelle, and I. M. Lima, “Influence of soil properties on heavy metal sequestration by biochar amendment: I. Copper sorption isotherms and the release of cations,” Chemosphere, vol. 82, no. 10, pp. 1431–1437, 2011.

[20] H. Lyu, J. Tang, M. Cui, B. Gao, and B. Shen, “Biochar/iron (BC/Fe) composites for soil and groundwater remediation: Synthesis, applications, and mechanisms,” Chemosphere, vol. 246, p. 125609, 2020.

[21] J. Wu, Z. Li, D. Huang, X. Liu, C. Tang, and S.J. Parikh et al., “A novel calcium-based magnetic biochar is effective in stabilization of arsenic and cadmium co-contamination in aerobic soils,” J. Hazard. Mater., p. 122010, 2020.

[22] H. Peng, P. Gao, G. Chu, B. Pan, J. Peng, and B. Xing, “Enhanced adsorption of Cu (II) and Cd (II) by phosphoric acid-modified biochars,” Environ. Pollut., vol. 229, pp. 846–853, 2017.

[23] J. Fan, C. Cai, H. Chi, B.J. Reid, F. Coulon, and Y. Zhang et al., “Remediation of cadmium and lead polluted soil using thiol-modified biochar,” J. Hazard. Mater., p. 122037, 2020.

[24] A. El-Naggar, S. M. Shaheen, Y. S. Ok, and J. Rinklebe, “Biochar affects the dissolved and colloidal concentrations of Cd, Cu, Ni, and Zn and their phytoavailability and potential mobility in a mining soil under dynamic redox-conditions,” Sci. Total Environ., vol. 624, pp. 1059–1071, 2018.

[25] Y. Luo, M. Durenkamp, M. De Nobili, Q. Lin, and P. C. Brookes, “Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH,” Soil Biol. Biochem., vol. 43, no. 11, pp. 2304–2314, 2011.

[26] Q. Nan, C. Cai, H. Chi, B.J. Reid, F. Coulon, and Y. Zhang et al., “Biochar drives microbially-mediated rice production by increasing soil carbon,” J. Hazard. Mater., vol. 387, p. 121680, 2020.