Effect of Modified Biochar on the Remediation of Pb-Contaminated Soil

Miao Liu*
Department of Applied Chemistry, Liaoning Petrochemical Vocational Technology College, Jinzhou, Liaoning, China
*Corresponding author e-mail: amelia_lau820@hotmail.com

Abstract. High levels of heavy metals, particularly of lead, in soil and water occur worldwide in many countries. Due to the harmful consequences on human health, it is mandatory to avoid Pb-contaminated soils and waters to enter in the food chain. In this research, biochar was prepared by corn stalk paralysis and alkali-modification. BCR sequential extraction method was employed to evaluate the morphological changes of lead in soil and a pot experiment was conducted with garland chrysanthemum as an indicator plant to investigate the bioavailability of lead in soil with biochar. The results indicated that alkali-modified biochar KBC showed strong immobilization abilities and could reduce the mobility and bioavailability of lead in soil.

1. Introduction
High levels of heavy metals, and particularly of Pb, in soil and water occur worldwide in many countries. Lead is the most documented heavy metal of all known toxic substances which can damage the nervous system, causing peripheral neuritis and motor and sensory problems [1]. In addition, lead flows into brain tissues with blood, damages cerebellum and cerebral cortex cells, interferes with metabolic activities, causes swelling of small capillary endothelial cells in the brain, and then develops into diffuse brain injury. When the blood lead reaches 60 ~ 80 mg/100 ml, people exposed to low concentrations of lead may appear headache, dizziness, fatigue, memory loss and insomnia, often accompanied by loss of appetite, constipation, abdominal pain and other symptoms of the digestive system. Therefore, many technologies have been developed to intercept lead and prevent it from spreading into the environment.

Biochar is a solid material obtained by thermal chemical transformation of biomass in anoxic environment. It has the characteristics of large specific surface area, high porosity, alkalinity and adsorption of dissolved organic matter. These physical and chemical properties enable it to be used as a chemical passivation agent for contaminated soil, and to transform the pollutants into stable forms through a series of reactions such as adsorption, precipitation, complexation and ion exchange, so as to reduce the transportability and bioavailability of pollutants, so as to achieve the purpose of in-situ remediation of contaminated soil [2,3].

The objective of this study is to evaluate the Pb immobilization effectiveness in Pb-contaminated soil using biochar. Biochar was prepared by corn stalk paralysis and alkali-modification. BCR sequential extraction method was employed to evaluate the morphological changes of lead in soil and a pot experiment was conducted with garland chrysanthemum as an indicator plant to investigate the bioavailability of lead in soil with biochar.
2. Materials and Methods

2.1. Biochar
Corn stalk collection from Qilihe village, Jinzhou city, Liaoning province. The stalks were cut into 8 ~ 10 cm long stalks, 55 °C dried after washing, and pyrolyzed anaerobically in the muffle furnace for 2 h, respectively, at 400 °C, 500 °C, 600 °C and 700 °C [4]. After complete carbonized, the biochar was taken out after cooling to room temperature, respectively labeled BC400, BC500, BC600 and BC700. The sample was mixed and ground, passed through a 100-mesh sieve, treated with 1.0mol ·L HCl solution for 4h, repeated 3 times to remove ash, filtered, washed with deionized water to neutral, dried, passed through a 100-mesh sieve, and stored in a dryer.

2.2. Batch tests
PbNO$_3$ solution with Pb (II) concentration of 50mg/L was prepared. The 50mL solution was put into sealed glass conical bottles, and about 0.1g of BC400, BC500, BC600 and BC700 were added into the solution. The concentration of background electrolyte NaNO$_3$ was 0.01 mol/L. The pH value of the solution was adjusted to 6.8 with dilute HNO$_3$ and NaOH. The solution was oscillated at a speed of 100r/min for 48 hours in a water bath at 25 ℃. The concentration of Pb (II) was determined by supernatant at 1h, 2h, 4h, 6h, 12h, 18h, 24h, 36h and 48h respectively, and the removal rate of Pb (II) from corn stalk biochar was calculated.

\[
W = \frac{C_0 - C_t}{C_0} \times 100\%
\]

*W* is the removal rate (%) ;

*C*$_0$ is the initial Pb (II) concentration (mg/L);

*C*$_t$ is the Pb (II) concentration (mg/L) at sampling time.

2.3. Modification of corn stalk biochar
Corn stalks were put into KOH solution with a mass concentration of 10% (solid-liquid ratio 1:10), impregnated at 60℃ for 24h before pyrolyzed anaerobically in the muffle furnace for 2 h at 700 ℃. Then the modified biochar denoted as KBC was washed repeatedly with distilled water to pH value of about 7, filtered and put into a vacuum drying oven at 105℃ to constant weight.

2.4. Soil test
PbNO$_3$ was used as the lead source mixing into the soil and incubated for 6 weeks [5]. The final content of lead in incubated soil was 417.65 mg/kg. Then biochar BC700 and KBC was added into leaded soil about 10g/kg soil in different groups, mixed and stirred thoroughly, and incubated for another 30 days. soil digestion was used to determine the total lead content in the soil. Take 0.2g of soil, add 10 mL of concentrated hydrochloric acid, heat and boil to 3 mL, after cooling, add 10 mL of concentrated nitric acid, 5 mL of hydrofluoric acid, 10 mL of perchloric acid, and heat the soil at 170℃ for digestion. After digestion, 1 mL of dilute nitric acid was added to the soil digestion solution, and then the concentration of lead was determined. To analyse the stabilization effect of lead by modified activated carbons, BCR sequential extraction method was employed to evaluate the morphological changes of lead in soil. The residue content was calculated by difference subtraction method.

2.5. Pot experiment
PbNO$_3$ was used as the lead source for the preparation 400 mg/kg lead- contaminated soil. After regular culture for 6 weeks, BC700 and KBC was added into leaded soil about 10g/kg soil in different groups and mixed. Then take 3kg of mixed soil and add them to the porcelain flowerpot with diameter of 20 cm and height of 20 cm. The Soil was divided into different treatment groups. Garland chrysanthemum was used as the experimental plant. It was watered 3 times a week, and maintained 70% field water capacity. Harvest the plants after planting for 60 days, wash the roots and dry to constant weight at 105℃. The content of lead in the digestion solution was determined.
3. Results and discussion

As shown in Fig.1, Pb (II) adsorption rate of corn stalk biochar in each group reached adsorption equilibrium at 24h. After adsorption for 48h, BC400, BC500, BC600 and BC700 of Pb (II) removal rate is 51.77%, 73.69%, 79.45% and 83.96%, respectively. Therefore, the pyrolysis temperature in the range of 400 ~ 700 ℃, the corn stalk biochar removal effect of Pb (II) in aqueous solution was improved as the increase of pyrolysis temperature. Therefore, 700 ℃ is the best pyrolysis temperature for corn stalk biochar.

![Figure 1. Lead percentage removal versus contact time.](image)

Lead exists in different forms in contaminated soil, and each form has different effects on the ecological environment. Therefore, the harm degree of lead to ecological environment cannot be evaluated simply by the total amount of lead in soil, and the proportion of various forms of lead in soil should be considered comprehensively. It is conducive to more objective evaluation of the impact of lead contaminated soil by investigating the lead in the presence of various forms in the soil contents. Lead in its residual form is very stable and hard to migrate which leads little harm to the ecological environment. Lead in exchangeable form is easy to migrate and with large biological toxicity. Lead in reducible and oxidizable form is relatively stable under the certain condition without acid or redox.

The results in Fig.2 showed that after PbNO3 incubation, lead in soil existed mainly in the exchangeable form, followed by the residue form, and the least in the reduced form and the oxidizable form, which accounted for 65.27%, 15.74%, 9.80% and 8.19% of the total lead, respectively. When corn stalk biochar was added to the soil, the morphology of lead in the soil changed obviously, and the exchangeable form and residue form of lead in the soil changed most obviously. The exchangeable lead in the soil was lower after the addition of corn straw biochar KBC than before which was reduced from 65.27% to 25.33%, while the residual lead content increased from 15.74% to 55.43%. After adding BC700, the exchangeable content of lead in soil decreased from 65.27% to 40.67%, and the residue content of lead increased from 15.74% to 30.77%. The addition of corn stalk biochar in lead-bearing soil can effectively reduce the exchangeable content of lead, which plays an important role in promoting the stabilization of lead.
Some heavy metals are necessary for the growth of plants, such as Zn and Cu, but when the heavy metal content exceeds a certain concentration, the plants will have super saturated absorption, causing heavy metal poisoning in plants and some damage symptoms. According to the experimental records, in the Pb-contaminated soil without corn straw biochar, garland chrysanthemum germinated late and grew normally in the early stage, but the later stage did not grow as well as the BC700 and KBC groups. It indicates that adding corn straw biochar to Pb-contaminated soil can inhibit the adverse effects of lead on the growth of garland chrysanthemum.

Content of lead in dry mass of garland chrysanthemum with different treatments is shown in Fig.3. The lead content is very small in the normal soil group, which is much increased in the Pb-contaminated soil due to the enrichment of garland chrysanthemum. Lead in garland chrysanthemum harvested from biochar treatment groups is significantly reduced, especially in KBC group. It indicates that adding corn straw biochar can inhibit the enrichment of lead in garland chrysanthemum.

Content of lead in different treatment groups was analyzed after the pot experiment as well. The incubated soil without pot experiment was taken as control. As shown in fig.4, without biochar addition, the lead content was 293.11mg/kg in Pb-contaminated soil which was significantly lower than 417.65
mg/kg in control group, while content of lead in BC700 and KBC groups was higher than Pb soil group. It is because that lead in soil was migrated by enrichment and transpiration in garden chrysanthemum during the pot experiment. BC700 and KBC could improve the stability of Pb in soil and reduce its migration to air and food chain. Therefore, modified corn stalk biochar can be applied to the polluted agricultural land to improve the safety of vegetables.

![Figure 4. Effect of biochar on changing the form of lead in soil.](image)

### 4. Conclusions

In this study, biochar was pyrolyzed anaerobically in the muffle furnace at 700 °C for 2 h and alkali-modified before applied to the remediate Pb-contaminated soil. BCR sequential extraction method and the pot experiment with garland chrysanthemum were employed to evaluate the morphological changes of lead in soil and to investigate the bioavailability of lead in soil with biochar. The results indicated that both BC700 and KBC remediate Pb-contaminated soil by reducing the exchangeable lead and KBC showed a stronger immobilization ability that could reduce the bioavailability of lead in soil and prevent the migration of lead from soil into the air or food chain. Further studies should be conducted for a deeper characterization of KBC properties.

### Acknowledgments

This work was financially supported by Liaoning Provincial Natural Foundation of China (No. 20180550390), Jinzhou science and technology plan project (No. 17B1E35), and LNPC Applied Technical Project (LSHYJ1912).

### References

[1] A. H. Fahmi, A. W. Samsuri, H. Jol and D. Singh, Bioavailability and leaching of Cd and Pb from contaminated soil amended with different sizes of biochar, J. R. Soc. open sci. 5 (2018) 181328.

[2] Z. He, Study on Biochar’s Remediation of Heavy Metal Pollution in Soil, J. J. Anhui Agric. Sci. 47(2019) 12-13,27.

[3] M. Lee, J. Park, J. Chung, Adsorption of Pb(II) and Cu(II) by Ginkgo-Leaf-Derived Biochar Produced under Various Carbonization Temperatures and Times, J. Int. J. Environ. Res. Public Health, 14 (2017) 1528.

[4] E. Weidemann, W. Buss, M. Edo, O. Mašek and S. Jansson, Influence of pyrolysis temperature and production unit on formation of selected PAHs, oxy-PAHs, N-PACs, PCDDs, and PCDFs in biochar—a screening study, J. Environ Sci Pollut Res. 25 (2018) 3933–3940.

[5] A. D. Igalavithana, E. E. Kwon, M. Vithanage, Jörg Rinklebe, D. H. Moon, E. Meers, D. C.W. Tsang, and Y. S. Ok. Soil lead immobilization by biochars in short-term laboratory incubation studies, J. Environ Int, 127 (2019) 190-198.