Remediation effect of biochar-plant on heavy metal contaminated soil in mining area

Yan Xu 1,2,3,4,*  Juan Li 1,2,3,4, Dongwen Hua 1,2,3,4, Zhen Guo 1,2,3,4

1Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Land and Resources of China, Xi’an 710075, China
2ShaanXi Provincial Land Engineering Construction Group, Xi’an 710075, China.
3Institute of Land Engineering and Technology, ShaanXi Provincial Land Engineering Construction Group, Xi’an 710075, China.
4Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi’an 710075, China.

*Corresponding author e-mail: 1213349323@qq.com

Abstract. Pot experiment was carried out to artificially add different concentrations (0%, 5%, 10%) of swine biochar and fruit biochar in heavy metal contaminated soil in the farmland of the mining area to study the repairing effect on heavy metal contaminated soil. The results showed that the total Cu of the tested soil before planting was 166.51 mg/kg, the average Cd was 1.31 mg/kg, the average Pb was 757.78 mg/kg, and the average Hg was 8.43 mg/kg, which was a mixed contaminated soil of mercury, lead, cadmium and copper. The contents of Hg and Pb of the tested soils decreased after planting 4 plants, and Cd content decreased in addition to the CK group. The Cu content in the Z10 group decreased, but Hg content still exceeded the soil risk control value, the Cu, Cd and Pb contents exceeded the risk screening value, and the potential risk was reduced but still existed. Compared with CK treatment, the two biochars have better remediation effects on the 4 heavy metals in the tested soil, and the swine biochar was better than the fruit biochar. With the increase of the concentration of the two biochars, the repair effect was better. In the combined pollution soil, the overall remediation effect of biochar-plant combined restoration on these four heavy metals was Hg>Pb>Cd>Cu, and Z10-pakchoi had the best repair effect on Hg, Pb and Cu in the tested soil. Z10-spinach had the best effect on the repair of Cd.

1. Introduction

Studies have shown that heavy metal pollution in farmland soils in Xiaoqinling gold mining area in Shaoguan was serious, especially Hg, Pb, Cd, etc[1-4]. A large number of studies at home and abroad have shown that biochar sources were low in cost, with porous structure, a large specific surface area and abundant surface functional groups, and have strong adsorption capacity for heavy metal pollutants [5-9]. The difference in pyrolysis temperature and raw materials affected the physical and chemical properties of biochar, which in turn affected the retention of heavy metals [10-11]. Therefore, the screening of highly efficient and environmentally friendly biochar repair agents was essential for the restoration of heavy metal contaminated soil. At present, there were many studies on soil physical and...
chemical properties and soil remediation of rice husk biochar, straw biochar and bamboo biochar, and there were few studies on biochar (fruit biochar and swine biochar)-plants on heavy metal composite contaminated soil in mining area. In this paper, artificially adding different concentrations (0%, 5%, 10%) of two types of biochar (swine biochar and fruit biochar) in heavy metal contaminated soil in farmland, to study the remediation effect of biochar-plants on heavy metal contaminated soil in mining area, and provide some reference for the follow-up study on the practice of heavy metal contaminated soil in mining area.

2. Materials and Methods

2.1. Test design

In this study, the pot experiment was used to set the biochar application levels of fruit biochar and swine biochar at 0% (CK), 5% (G5 and Z5) and 10% (G10 and Z10, in terms of dry soil). The naturally dried tailings slag and loess were removed from the stones, weeds, and plant roots and sieved through a 5 mm sieve. The test used 250 mm×200 mm (upper diameter×height) plastic flower pots, and the bottom of the pot was covered with mesh. The soil sample was pretreated with a base fertilizer, and the tailings slag, loess, organic fertilizer and biochar were mixed at a set ratio (1:2:0.01:0.05/0.10) and then filled with pots 4-6 cm from the top of the pot. Each pot was kept at a total weight of 2.5 kg, naturally compacted, and each treatment was repeated 3 times for a total of 60 pots.

2.2. Index determination

After harvesting, the disturbed soil samples were drilled with 2 cm diameter soil in each pot, and each of the four drills was taken. After mixing, it was air-dried and ground, and passed through 2 mm and 0.149 mm sieves for testing. The soil pH was measured by DELTA 320 pH meter (water to soil ratio: 2.5:1), heavy metals Cr, Ni, Cu, Zn, Pb and Cd were determined by ICP-MS; Hg and As were determined by atomic fluorescence method.

2.3. Pot planting management

Plant seeds with full and uniform size and no insects were screened. In spinach, cabbage and pepper pots, the seeds were directly seeded in each pot, and the buried depth was 1-2 cm. At the same time, four plants were seeded in the nursery tray, and the clover was transplanted with potted plants. After planting for about 20 days, 4 plants will retain the same number of robust seedlings per pot. The test site was located in the solar greenhouse of the Qinling Wild Monitoring Station of Shaanxi Institute of Land Engineering and Technology. Sowing on April 30, 2018, harvesting on July 10, the temperature change in the greenhouse was 25~35°C, and timely watering was carried out every day. The other management measures were consistent with the average.

During the two-month growing season, the growth of the four plants in the tested soils varied, followed by cabbage, spinach, clover and pepper. On the whole, the plant grew better than the CK group in each growth stage after adding biochar, and the plant growth was better than the fruit biochar after adding the swine biochar, and the Z10 treatment plant had the best growth state.

3. Results and analysis

3.1. Heavy metal content of the tested soil

The background values of soil pH and heavy metals contents of test soil samples, tailings slag, fruit biochar, swine biochar were measured. The results showed that the tailings slag pH was 8.51, and the fruit biochar pH was 9.81. The swine biochar pH was 10.22. The pH of the test soil sample ranged from 8.22 to 8.30, which was alkaline soil. According to the soil environmental quality standard (GB15618-2018) [12], the total Cu and Zn of tailings slag slightly exceeded the standard, while the total Cd and total Pb were 4.35 and 2.36 times of the risk screening value respectively; the total Ni and total Cr of the test fruit biochar slightly exceeded the standard; the total Cu and total Zn in pig manure also slightly
exceeded the standard. Biochar itself also has certain potential ecological risks of heavy metals. Therefore, the positive and negative effects on soil improvement should be considered in the application [13-14]. Heavy metal contaminated soil CK, G5 (adding 5% fruit biochar), G10 (adding 10% fruit biochar), Z5 (adding 5% swine biochar) and Z10 (adding 10% swine biochar) to mercury, lead and cadmium Copper composite pollution. Among them, the average Cu content of the tested soil samples was 166.51 mg/kg, and the average Cd value was 1.31 mg/kg, which was 1.66 and 2.18 times of the screening value, respectively. It was a mild pollution level; the average Pb content was 757.78 mg/kg. It was 4.46 times of the risk screening value, the average Hg content was 8.43 mg/kg, which was 1.41 times of the risk control value, and the soil Hg and Pb were seriously polluted.

3.2. Changes in soil heavy metal content
It can be seen that the test soil was Hg, Pb, Cd and Cu combined contaminated soil. In this experiment, the changes of Hg, Pb, Cd and Cu contents in the soil of biochar-plant restoration system were mainly studied. Compared with pre-planting, the content of heavy metals Hg, Pb, Cd and Cu decreased after planting cabbage, pepper, clover and spinach, but the Hg content still exceeded the soil risk control value, and Cu, Cd and Pb content exceeding the farmland soil risk screening value, the potential risk was reduced but still exists.

Figure 1 showed that after planting, the Hg content in the soil decreased compared with that before planting. The decrease of soil Hg content from large to small was Z10 (20.6%)>Z5 (20.0%)> G10 (18.0%)>G5 (17.2%)>CK (16.4%). Among them, the Hg of the Chinese cabbage group under CK treatment decreased greatly, from 8.36 mg/kg before planting to 6.72 mg/kg. The overall decrease of Hg content in G5 treatment was not significantly different from that in CK group. The decrease of Hg in Chinese cabbage and spinach group was the most obvious. The decrease of Hg in soil under G10 treatment was cabbage to spinach>pepper>clover, and Hg in small cabbage group decreased from 8.24 mg/kg to 6.66 mg/kg. Under the treatment of Z5, the decrease of Hg in the four plant soils was not significant. The decrease of Hg in the spinach group was slightly larger, from 8.61 mg/kg before planting to 6.81 mg/kg. Under the treatment of Z10, the content of Hg in the soil of Chinese cabbage and spinach was the most obvious, followed by clover, and the pepper group was the smallest. For different treatments, the heavy metal Hg of Z10 treatment had the largest decrease and the best repair effect. For the four plants, the cultivation of Chinese cabbage had the best effect on the restoration of Hg, followed by the spinach group. The combined repair of Z10-cabbage had the best effect on the repair of Hg in the tested soil, followed by the spinach group.

![Fig.1 Changes of Hg content in the tested soil after planting](image-url)
Figure 2 showed that after planting, the Pb content in the soil decreased compared with that before planting. The decrease of soil Pb content from large to small was Z10 (25.0%) > Z5 (16.1%) > G10 (10.2%) > G5 (10.0%) > CK (4.9%). After planting 4 plants, the overall Pb of the CK group decreased the least, and the reduction of the Chinese cabbage group was slightly better than that of the spinach group. The Pb content in the soil under the G5 treatment was the largest, and the decrease was 12.6% before planting. The Pb content in the cabbage group under G10 treatment was the most obvious, and the other three plants had little difference. Under the treatment of Z5, the Pb content of the four plants decreased little, and the decrease of the pakchoi group was slightly higher than that of the other three plants. The Z10 treatment showed the most significant decrease in Pb compared with other treatments, among which the spinach group had the most significant decline and the soil Pb content decreased 27.9% before planting, followed by the clover group. For different treatments, the repair effect of heavy metal Pb after adding swine biochar was better than that of fruit biochar, and Z10 treatment had the best repair effect; for these 4 plants, planting Chinese cabbage had the best effect on soil Pb repair. The spinach group was second. The combined repair of Z10-cabbage had the best effect on the repair of Pb in the tested soil, followed by the spinach group.

Figure 3 showed that the Cd content in the soil decreased after planting 4 plants compared with the CK group. The decrease of Cd content from large to small was Z10 (19.4%) > Z5 (17.6%) > G10 (9.5%) > G5 (10.0%). In the CK group, except for the pepper, the Cd content of the other groups was relatively enriched, and the increase was 6.7% before planting. Under G5 treatment, the Cd of the spinach group had the largest decline, which was 22.3% before planting. Under G10 treatment, the Cd of the spinach group had the largest decrease, and the decrease was slightly smaller than that of the C5 treatment, which was 13.9% before planting. Under Z5 treatment, the cabbage group had the largest decline, which was 23.8% before planting, followed by the spinach group. Under the treatment of Z10, the Cd of the Chinese cabbage group was the most significant, which was 33.7% before planting, followed by the spinach group, which was 21.8% before planting. For different treatments, the effect of adding swine biochar on the repair of heavy metal Cd was better than that of fruit biochar, and Z10 treatment had the best repair effect; for 4 plants, the effect of planting spinach on soil Cd was better. Z10-spinach combined repair had the best effect on the repair of Cd in the tested soil, followed by the small cabbage group.
Changes of Cd content in the tested soil after planting

Figure 4 showed that after planting 4 plants, Cu content in the soil changed significantly compared with that before planting. The Cu content in the soil of CK treatment increased, and the Cu content in Z10 treatment decreased. Under the treatment of G5, the soil Cu decreased significantly in the cabbage group, which was 9.1% before planting, followed by the pepper group. Under the G10 treatment, the Chinese cabbage and pepper groups had larger declines, 11.4% and 9.3% before planting, respectively. Under the treatment of Z5, only Cu in the pepper group had the largest decrease, which was 8.8% before planting, and the other groups had little difference with the Cu content before planting. Under the treatment of Z10, the Cu content of various plant soils decreased, and the cabbage group had the largest decline, which was 16.9% before planting. For different treatments, the effect of adding swine biochar on the repair of heavy metal Cu was better than that of fruit biochar, and the repair effect of Z10 treatment was the best, but the repair effect was not proportional to the concentration of swine biochar; for 4 plants, planting Chinese cabbage has a better effect on the repair of soil Cu, followed by the pepper group. The combined repair of Z10-cabbage had the best effect on the repair of Cu in the tested soil, followed by the pepper group.

Fig.4 Changes of Cu content in the tested soil after planting

4. Conclusions and suggestions

4.1. Conclusions
The average Cu value of the soil sample before planting was 166.51 mg/kg, and the average Cd value was 1.31 mg/kg, which was 1.66 and 2.18 times of the risk screening value, respectively. It was mildly polluted; the average Pb value was 757.78 mg/kg, which was 4.46 times of risk screening value. The average value of Hg was 8.43 mg/kg, which was 1.41 times of the risk control value. The Hg and Pb of
the tested soil were seriously polluted, belonging to the combined pollution of mercury, lead, cadmium and copper. The contents of Hg and Pb in the soil treated with biochar-four plants decreased, and the Cd content decreased in addition to the CK group. The Cu content decreased under the Z10 treatment, but the Hg content still exceeded the soil risk control value. The Cu, Cd, and Pb contents exceeded the soil risk screening value, and the potential risk was reduced but still existed.

Although the Ni and Cr of the fruit biochar slightly exceeded the risk screening values; the Cu and Zn of swine biochar slightly exceeded the risk screening values, the test showed that compared with CK treatment, the two biochar additions have better repair effect on the 4 heavy metals in the test soil. The repair effect of swine biochar was better than that of fruit biochar, and with the increase of the concentration of two biochars, the repair effect was more remarkable. In the combined pollution of mercury, lead, cadmium and copper, there were competitive adsorption phenomena when 4 heavy metal elements coexist. The overall restoration effect of biochar-plant combined repair on these 4 heavy metals was Hg>Pb>Cd>Cu, and Z10-cabbage had the best repair effect of Hg, Pb and Cu, and Z10-spinach had the best repair effect on Cd.

4.2. Suggestions

The use of biochar has certain repairing effect on the combined pollution of mercury, lead, cadmium and copper in the mining area, and the application prospect was good [15]. However, most of the relevant researches are currently in the laboratory simulation and small-scale field trials, and there are few studies on the negative impact of biochar itself on the environment. In the future, it can be transferred to large-scale field trials. In addition, the release of pollutants after biochar application and the impact of the aging process on the adsorption of pollutants remain to be studied.

References

[1] Xu Y N, Xu D Y, Zhang J H, et al. Study on the difference of mine geo-environmental problem response to mineral resource exploitation: a case study about the mining areas in Tongguan and Dalita of Shaanxi and Fuxin of Liaoning[J].Journal of Earth Sciences and Environment,2011,33(1):89-94,100.

[2] Qiao G, Xu Y N, Chen H Q. Evaluation of heavy metal and cyanide pollution of the shallow groundwater in a gold mining area[J].Geological Bulletin of China, 2015, 34(11):2032-2035.

[3] Zhang Rui. The study of heavy metal pollution of soil and vegetation around gold mine tailings[D].Shannxi:Xi'an University of Science and Technology,2011.

[4] Tian Tian. The characteristics study on vertical distribution and adsorption-desorption of water-soluble salts and heavy metals in soil-different landscape soil Tongguan gold mining area as an example[D].Shannxi:Xi’an, Chang’an University, 2016.

[5] Liu Y X, Wang Y F, Lv H H. Effects of different application rates of rice straw biochar and bamboo biochar on yield and quality of greengrocery (Brassica chinensis) and soil properties[J].Journal of Plant Nutrition and Fertilizer,2013,19(6):1438-1444.

[6] Zhang Q F, Wang G H. Research progress of physiochemical properties of biochar and its effects as soil amendments [J]. Soil and crop, 2012,1(4):219-226.

[7] Cao X D, Ma L N, Gao B, et al. Dairy-Manure derived biochar effectively sorbs lead and atrazine[J]. Environmental Science & Technology, 2009, 43(9): 3285-3291.

[8] Xu X Y. The sorption and transformation of inorganic contaminants by biochars and the underlying mechanisms [D].Shanghai: Shanghai Jiao Tong University, 2015.

[9] Jin H P, Girish K, Choppala N, et al. Biochar reduces the bioavailability and phytotoxicity of heavy metals[J]. Plant Soil, 2011, 348: 439-451.

[10] Zhang W M. Physical and chemical properties of biochar and its application in crop production[D].Shenyang Agricultural University,2012.

[11] Li H B, Xiao L, Evandro B, et al.Mechanisms of metal sorption by biochars: Biochar characteristics and modifications[J]. Chemosphere. 2017,178:466-478.

[12] Environmental quality standard for soils[S].GB15618-2018.
[13] Sun X, Liu Q Q, Guo H, et al. Effects of swine manure biochar on soil fertility and cabbage (Brassica chinensis) growth[J]. Journal of Agro-Environment Science, 2016, 35(9):1756-1763.

[14] Mohan D, Pittman C U, Jr B M, et al. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production[J]. Journal of Colloid and Interface Science, 2007, 310(1):57-73.

[15] Kong H, He J, Gao Y, et al. Cosorption of phenanthrene and mercury(II) from aqueous solution by soybean stalk-based biochar[J]. Journal of Agricultural and Food Chemistry, 2011, 59(22):1216-1213.