Study on speciation and Distribution characteristics of Heavy Metals in soil around typical Coal Gangue in Fengfeng Mining Area

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Abstract. Taking the coal gangue mountain in Hebei Fengfeng mining area as the research object, 30 soil samples were collected in the east, southeast and southwest directions within 300m of the coal gangue mountain boundary, and the coal gangue stacking were used to study the heavy metal pollution of the surrounding soil. The heavy metal form of soil around coal gangue was extracted by Tessier five-step continuous extraction method, and analyzed its morphological characteristics and biological activities. The results showed that: (1) Hg and Cr were mainly retained in the soil as residual, which did little harm to the environment; Pb and Cd are mainly exist in the soil in residual and bound to iron-manganese oxide; Cu is mainly exists in the soil in residual and bound to organic matter. (2) According to the analysis of the available coefficient and migration coefficient of soil heavy metals in soil, Cd belongs to medium risk. Cu and Pb are low risk, and Cr and Hg are considered as risk-free because their available state content is lower than the detection limit.

1. Introduction

Coal resources are the most important energy resources in China, and China is the largest coal producing country and the largest coal consuming country [1]. The coal gangue discharged during coal mining is a rock formed by mixing organic and inorganic compounds deposited together with coal during coal formation [2]. Under the daily natural effects of weathering and leaching, coal gangue can release a large number of heavy metal ions into the soil, which will cause serious soil heavy metal pollution.

Heavy metals of different forms in soil are in different energy states, and they can be transformed into each other under appropriate environmental conditions. The form of heavy metals is the basis for determining their bioavailability [3]. Studying the forms of heavy metals can not only reveal the existing state of heavy metals in the soil, but also reveal their migration and transformation rules, bioavailability, toxicity and possible environmental effects, which provides theoretical basis and experimental basis for a series of soil remediation work.
2. Materials and Methods

2.1. research area Overview
The Fengfeng mining area is located in the southern part of Hebei Province, the eastern foot of Taihang Mountain, with geographical coordinates of 36°20'-36°34' latitude and 114°3'-114°16' east longitude. It is located at the border of Jin, Ji and Yu. The Fengfeng mining area is in the mid-latitude zone, which belongs to the warm temperate semi-humid continental monsoon climate with distinct characteristics in four seasons.

2.2. Collection and processing of soil samples
According to the position and wind direction of the location of the coal gangue mountain, three sampling lines of east (E), southeast (ES) and southwest (WS) are selected. A total of 5 sampling points is selected on each sampling line, and the boundary of the coal gangue mountain is set to zero, which is the 1st point. The distance from the 1-5th point to the boundary of the coal gangue mountain is 0m, 40m, 80m and 150m. And 300m, the sampling point is from dense to sparse. When sampling at each sampling point, take two parallel points at 10m left and right of its horizontal direction, and mix the soil samples from three points evenly for one soil sample treatment.

Sampling is a combination of soil drilling and profile taking soil, and soil sample samples with depths of 0-0.2 m and 0.2-0.4 m depth are collected. Bring the collected soil samples back to the laboratory, remove the stones, garbage and animal and plant residues after drying naturally in the room, grind through the soil grinding and sifter, pass through the 200 mesh nylon screen, seal the numbers and store them.

2.3. Determination of soil samples
Tessier five-step continuous extraction method can be used to classify soil heavy metal morphology into five forms: exchangeable, bound to carbonate, bound to iron-manganese oxide, bound to organic and residual.

2.4. Formatting author affiliations
Data was analysed using Excel input data, charts were plotted with origin 9.1, the distribution results of heavy metal contents were analysed and evaluated.

3. Results and discussion

3.1. Morphological distribution characteristics of heavy metal Cu in coal gangue soil
The morphological distribution of Cu in soil samples is shown in Fig. 1.

![Morphological distribution of Cu](image)

Figure 1. Morphological distribution of Cu

It can be seen from Fig. 1 that the existing forms of Cu mainly consist of residual and bound organic matter, and the total content of each form is: exchangeable < bound to carbonate < bound to iron-manganese oxide < bound to organic matter < residual. Cu residuals are abundant, indicating that Cu is not easy to migrate in the environment; In addition, bound to organic matter content is higher than the other three forms, which is related to the physical and chemical properties of Cu itself. In
nature, Cu generally exists in compounds in the form of Cu\(^+\) and Cu\(^{2+}\). Cu\(^{2+}\) is not only easy to form copper salts, but also Cu\(^+\) and Cu\(^{2+}\) easily form complexes and chelates with inorganic substances and organic active groups [4] and combine with sulfur ions to form sulfide precipitation.

3.2. Morphological distribution characteristics of heavy metal Hg in coal gangue soil

The morphological distribution of Hg in soil samples is shown in Fig. 2.

![Figure 2. Morphological distribution of Hg](image)

It can be seen from Fig. 2 that the exchangeable and bound of carbonate of Hg in the three sampling lines are lower than the detection limit. It shows that the Hg content of exchangeable and bound to carbonate in the soil around gangue of a mine in the Fengfeng mining area is extremely low. In addition to the maximum percentage of residual, the bound to iron-manganese oxide is roughly equivalent to the organic bound state. The total content of each form is: exchangeable ≈ bound to carbonate < bound to iron-manganese oxide < bound to organic < residual.

3.3. Morphological distribution characteristics of heavy metal Cd in coal gangue soil

The morphological distribution of Cd in soil samples is shown in Fig. 3.

![Figure 3. Morphological distribution of Cd](image)

It can be seen from Fig. 3 that the residual and the bound to iron-manganese oxide are higher, the bound to carbonate and the bound to organic matter are the next, and the exchangeable is less. The effective state of Cd is higher, indicating a certain biological toxicity of Cd, and has certain potential harm to the environment, especially in the direction of line E. The total content of each form is: exchangeable < bound to carbonate < bound to organic < bound to iron-manganese oxide < residual.

3.4. Morphological distribution characteristics of heavy metal Cr in coal gangue soil

The morphological distribution of Cr in soil samples is shown in Fig. 4.
Figure 4. Morphological distribution of Cr

It can be seen from Fig. 4 that the residual of heavy metal Cr is the largest, and the content is basically between 75% and 85%. The exchangeable state and carbonate binding state of Cr were not detected. The total content of each form is: exchangeable ≈ bound to carbonate < bound to iron-manganese oxide ≈ bound to organic < residual.

3.5. Morphological distribution characteristics of heavy metal Pb in coal gangue soil

The morphological distribution of Pb in soil samples is shown in Fig. 5.

Figure 5. Morphological distribution of Pb

It can be seen from Fig. 5 that the residual state of Pb is also the largest, about 35%-55%. The next is the bound to iron-manganese oxide, between 28% and 48%, which is similar to the conclusions drawn by Cong Xin [5]. The total content of each form is: bound to carbonate < exchangeable < bound to organic matter < bound to iron-manganese oxide < residual.

3.6. Bioactivity analysis of soil heavy metals

The ion exchangeable and bound to carbonate of the element are referred to as the effective state of the element. In general, whether heavy metals in soil can be absorbed and transformed by plants depends on the effective state of the elements. The higher the effective state of heavy metals, the higher the biological activity and the greater the risk to the environment [5]. The bioactivity analysis of heavy metals in soil is commonly used at present by Adriano and Maiz et al. for the migration coefficient and bioavailability coefficient.

Bioavailability is described by the factor of k:

\[
k = \frac{\text{exchangeable+bound to carbonate}}{\text{full metal}} \times 100\% \tag{1}
\]

\[
k = \frac{F_1+F_2}{F_1+F_2+F_3+F_4+F_5} \tag{2}
\]

The migration coefficient is used to describe the migration capacity of heavy metals in soil:

\[
M_i = \sum_{i=1}^{n} \frac{F_i}{T_i} / n \tag{3}
\]
Where, $M_j$--the mobility coefficient of heavy metal $j$
$I$--for the soil sample
$F_i$--The exchangeable state of $j$ element in soil $i$
$T_i$--the total amount of element $j$ in soil sample $i$, here the sum of the five morphological contents.

$n$--the number of soil sampling points

Use the bioavailability coefficient of heavy metals to assess their environmental risk, when the value of $K$ is less than 1% of the whole, it can be regarded as safe environment. When the $K$ value is greater than 50% of the whole, it is considered highly dangerous and easy to enter the food chain. That is, the proportion of the effective state (exchangeable + bound to carbonate) is less than 1%, which is considered as no risk. 1% to 10% is low risk; 11% to 30% is medium risk; 31% to 50% is high-risk; more than 50% is deemed extremely high risk. The migration coefficients and bioavailability coefficients of heavy metal factors Cu, Hg, Pb, Cr and Cd around the coal mine of a coal mine in Fengfeng mining area are shown in Table 1 below.

Table 1. Bioactivity coefficient of soil heavy metal factor (%)

| coefficient | Cu | Hg | Cd | Cr | Pb |
|-------------|----|----|----|----|----|
| $k$         | 7.54 | -  | 21 | -  | 7.83 |
| $M$         | 2.7 | -  | 5.8| -  | 7.83 |

From Table 1, it is concluded that the availability factor of Cu is 7.54%, during to between 1% and 10%, which belongs to low risk. The mobility coefficient of Cu was 2.7%. The availability factor of Cd is 21%, during to between 11% and 30%, which is regarded to medium risk. The mobility coefficient of Cd is 5.8%, and the available coefficient of Pb is 7.83%, which is between 1% and 10%, which is low risk. The migration coefficient of Pb is 7.83%. The exchangeable and bound to carbonate of Hg and Cr are lower than the detection limit, so the available coefficient and the migration coefficient are both less than 1%, which is regarded as no risk.

4. Conclusion

Through the study of coal gangue in Fengfeng mining area of Hebei Province, the heavy metal form of soil around coal gangue was extracted, and its morphological characteristics and biological activity were analysed. The following conclusions were drawn:

1) Hg and Cr in the soil mainly exist in residual, which is less harmful to the environment; Pb and Cd mainly exist in a residual and bound to iron-manganese oxide; Cu mainly exists in residual and bound to organic matter.

2) According to the analysis of soil heavy metal availability coefficient and migration coefficient, Cd is medium risk, while Cu and Pb are of low risk. Cr and Hg are considered risk-free because their effective state content is below than the detection limit.

Acknowledgments

The study was funded by the Science and Technology Planning Project of Hebei Academy of Sciences (19108), Hebei Engineering Research Center, to acknowledge assistance or encouragement from technical staff or financial support from organizations.

References

[1] Chou R.1., Chou H., Lei M. (2009) Advances in research on remediation of multi-metal contaminated soil in mine and surrounding area [J]. Agro-Environment Science, 28(6): 1085-1091.

[2] Du Z.Y., Wang X.P., Guo Q.M. (2016) Review of meteorite pollution prevention [C]. Proceedings of the Annual Meeting of the Chinese Society of Environmental Sciences (2016), Taiyuan: China Environmental Science Society, 3429.

[3] Li G.Q., Ma C.Y. (2018) Analysis of the Forms of Heavy Metal Elements in Soil [J]. Soil and fertilizer, 24:79.
[4] Dang Z., Liu C.Q., Shang A. (2001) Review of the mobility and bioavailability of heavy metals in the soil contaminated by mining [J]. Advance in Earth Science, 16(1): 86.

[5] Cong X., Zhang R.X. (2017) Study on distribution characteristics and influencing factors of heavy metals in soil around coal Gangue Mountain in mining city [N]. Journal of Ecology and Environment., 26(3): 479-485.