Study of the effect of weathered coal activated by ultrasonic on speciation of Cr in soil

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Abstract. The humic acid in weathered coal contains a large number of reactive functional groups which can stably combine with heavy metal ions in the environment. This changes its biochemical stability and water solubility, reducing the migration of heavy metal ions in the soil environment to achieve the purpose of remediation of heavy metal pollution. The goal of this paper is to investigate the effects of ultrasonic activated weathered coal on the speciation of chromium (Cr) in soil and bioavailability of Cr under pakchoi cultivation. The results showed that in comparison to the control group, both the content of exchangeable, reducible and oxidizable Cr and the absorption of Cr in the soil decreased after adding weathered coal. Under the conditions of 60g/kg of ultrasonic activated weathered coal, the content of Cr absorbed by pakchoi plants was the lowest, which was 62.0% lower than that of the control group. Additionally, the content of Cr in soil reached the maximum value, which was 12.7% higher than that of the control group. Cr mainly exists as a residual state in the environment and this was 755.8% higher than that of the control group. Under the same conditions of weathered coal addition, U-WC can significantly reduce the Cr content of the weak acid extracted, reducible and oxidizable fraction in the soil, and the effective Cr content is reduced, thereby reducing Cr migration and biotoxicity in soil. This provides a theoretical basis for the application of weathered coal humic acid fertiliser in the application of weathered coal fertiliser in Cr-polluted areas.

1. Introduction

In recent years, soils around the world have been polluted to a greater extent. For example, the average annual emissions of Hg, Cu, Pb, Mn and Ni are approximately $1.5 \times 10^4$, $3.4 \times 10^6$, $5 \times 10^6$, $1.5 \times 10^7$ and $10^6$ t respectively [1]. In Europe, there are millions of hectares of farmland polluted by heavy metals [2] and in Japan, the area of farmland polluted by heavy metals is 7592 hm² [3]. Currently, the area of cultivated land contaminated by heavy metals in China is approximately $2 \times 10^7$ hm². The direct economic losses caused by heavy metal pollution in soil amounts to 20 billion RMB per year [4].
Cr is considered one of the 17 most dangerous chemical pollutants, as assessed by the U.S. Environmental Protection Agency (EPA) [5]. According to the “National Soil Pollution Status Survey Bulletin” published in 2014, the over-standard rate of heavy metal Cr in China accounts for 6.83% of the total soil over-standard rate [6]. The 2010 national survey of soil pollution sources states that 145 industries are involved in the production of Cr-containing waste, amounting to a total of 940,000 t [7]. The majority of Cr that enters the environment is through industrial activities such as tanning, electroplating and chromium salt production [8].

China has an abundance of weathered coal in reserve which is widely distributed and rich in the natural macromolecule organic humic acid [9]. This weathered coal contains a variety of oxygen-containing active functional groups, such as carboxyl, phenolic hydroxyl, quinone and alcohol hydroxyl [10]. The metal ions in the environment undergo chemical reactions such as exchange, adsorption, complexation and chelation, which affect the biochemical stability, water solubility and migration of heavy metal ions. The use of weathered coal to control heavy metal pollution in the soil is not only convenient, effective, economical and reliable, but can also improve soil ecology. Therefore, it has broad application prospects and practical significance in terms of using weathered coal to control soil heavy metal pollution.

This study aims to provide a theoretical basis for increasing the application of weathered coal humic acid fertiliser in Cr speciation by studying the effect of ultrasonic activation of weathered coal on Cr in soil and the content of Cr in soil and pakchoi plants.

2. Methodology

2.1. Materials
The tested soil was the leaching soil of the South Campus Experimental Station of Shandong Agricultural University (N36°10′14.10″, E117°09′1.19″). After collecting approximately 0.1t of 0-20 cm surface soil, it was naturally air-dried, grounded, and after being sieved through a 2mm sieve, stored in plastic bag.

The tested plant is the "Beijing Green Stem" pakchoi. The seeds were purchased from Tai'an Building for Selling Seeds. The weathered coal was supplied by Shandong Agricultural University Fertiliser Technology Co., Ltd, with a free state humic acid content of 1.03%. The ratio of water to weathered coal was 8:1 and this mixture was put into high-necked flask and placed in an ultrasonic apparatus. The activation treatment was carried out at 200W for 25 minutes and stored for use after drying. The content of free humic acid in weathered coal increased to 7.79% after ultrasonic activation.

2.2. Physical and chemical properties of the soil
The soil pH value was determined by the soil water leaching method [11] and the total nitrogen was determined by Kjeldahl method. The available phosphorus was calculated using the method of NaHCO₃ leaching Molybdenum-Antimony anti-colorimetric and the available potassium was calculated using NH₄OAC Extraction Flame photometry. The soil organic matter was determined by a K₂Cr₂O₇ volumetric method; the content of heavy metal Cr in soil was determined by aqua regia HClO₄ digestion and the content of Cr in soil was determined by NovAA300 atomic absorption spectrophotometer in Jena, Germany. Furthermore, the content of Cr in pakchoi was determined by nitric acid-perchloric acid digestion and NovAA300 atomic absorption spectrophotometer in Jena, Germany[12]. The speciation of heavy metals in the soil was extracted by sequential extraction (BCR) and determined by NovAA300 atomic absorption spectrophotometer in Jena, Germany [13].

2.3. Experiment
The test was a pot experiment which was carried out in a greenhouse. A total of 11 treatments were set up, including control groups with no humic acid, and control groups with no pollution (blank group). Four groups of a single addition of 20, 40, 60, 80g/kg of the inactivated weathered coal (WC) and the
ultrasonically activated weathered coal (U-WC) were set up and each treatment was repeated three times, as shown in Table 1.

The analytical pure sodium dichromate (Na₂Cr₂O₇) solution was uniformly applied to the soil, and the concentration of Cr in the soil reached the soil risk screening value of 200 mg/kg[14]. Urea, potassium dihydrogen phosphate and potassium sulfate were added and fully blended according to the nutrient needs of potted crops. A series of concentrations of weathered coal were added to the cultivated chrome-contaminated soil and filled into plastic flowerpots with 2kg of soil per pot. After a week, 15 pakchoi seeds were planted in each pot, and 4 fixed seedlings were planted in each pot after emergence. The soil was replenished with water every day by weighing method, and the soil moisture was maintained at 60% of the field water holding capacity, with relevant indicators sampled and measured simultaneously.

Table 1. Lists of experimental treatments.

| Add substance | Add amount (Cr, mg/kg; Weathered coal, g/kg) |
|---------------|--------------------------------------------|
| Cr + WC       | 0+0 200+0 200+20 200+40 200+60 200+80     |
| Cr + U-WC     | 200+0 200+20 200+40 200+60 200+80         |

2.4. Data processing and analysis
The data was statistically analysed using Excel and SPSS software, and a significant analysis was performed using the SPSS software.

3. Results

3.1. Effect of ultrasound activation of weathered coal on the speciation of Cr in soil
The migration, transformation and biological toxicity of heavy metals in soils are not only related to the content of heavy metals in soils, but also to the existing forms of heavy metals in soils. The speciation of heavy metals in soils, as well as their activity, biological toxicity and migration characteristics, differ between soils[15]. The heavy metal that is easily absorbed by plants in the soil is used as an indicator to evaluate the pollution intensity, which can effectively reflect the fraction of soil pollution and its degree of harm to plants[16]. The exchangeable form of this heavy metal can migrate easily. Furthermore, it can easily be transformed and absorbed by plants, which has biological validity and direct toxicity. The reducible and oxidizable form can be transformed into a weak acid extractive state under certain conditions, which indirectly plays a toxic role. In general, the residual state remains stable in the soil lattice for a long time and is not easily absorbed by plants. Therefore, reducing the weak acid extraction state content of heavy metals and increasing the residual state content of heavy metals can effectively reduce the mobility of heavy metal ions, thus reducing the toxicity and biological effectiveness of heavy metals.

From Table 2, it can be seen that the content of exchangeable, reducible and oxidizable Cr initially decreased following the addition of weathered coal. The content of Cr then increased (Table 2, P < 0.05).

In comparison to the control group, the content of exchangeable, reducible and oxidizable Cr in the treatment of inactivated weathered coal decreased by 4.1% - 44.4%, 8.1% - 32.1%, 8.4% - 26.8%, and the content of residual Cr increased by 146.4% - 755.8%. The content of exchangeable, reducible and oxidizable Cr in the treatment of ultrasonic activated weathered coal decreased by 9.2% - 40.9%, 14.2% - 40.4%, 16.5% - 33.8%, and the content of residual Cr increased by 239.1% - 784.1%. Under the condition of 60 g/kg of weathered coal, the content of exchangeable, reducible and oxidizable Cr is the lowest, the content of residual Cr is the highest and the treatment effect is the most remarkable. Under the same amount of weathered coal, activated weathered coal can reduce the content of exchangeable, reducible and oxidizable Cr in Cr-contaminated soil to a greater extent than inactivated weathered coal, and increase the content of residual Cr in soil to a greater extent.
The reasons for this may be as follows: (1) It could be argued that due to the alkaline nature of the weathered coal, the pH value of the soil increases, promoting the activity of Cr in the soil. (2) The humic acid in weathered coal may act as a negatively charged macromolecular colloid, participating in the exchange reaction and complexation of Cr ions in the soil [17] and passivating heavy metal ions. (3) The ultrasonic energy is high, destroying the macromolecular structure of humic acid, breaking the combined state of humic acid, forming free humic acid, thereby enhancing the passivation effect of Cr ions in the soil. (4) Research such as that by Luo Hongyi has focused on the activation effect of weathered coal under different conditions. The results showed that the total acid content, phenolic hydroxyl content and carboxyl content of most weathered coal humic acid treated by ultrasonic treatment are significantly increased [18] with an increase in the number of reactive functional groups. This increase can enhance the interaction between redox, adsorption, hydrogen bonding, van der Waals force and other heavy metal elements in the soil [18].

Table 2. Effect of weathered coal addition on Cr concentration in soil samples received during sequential.

| The content of Cr in each step of sequential extraction (mg/kg) | 0(control group) | Weathered coal additive amount |
|---------------------------------------------------------------|------------------|-------------------------------|
|                                                               | 20(g/kg)         | 40(g/kg)                     | 60(g/kg) | 80(g/kg) |
| Exchangeable                                                  |                 |                               |         |          |
| WC                                                            | 68.66±0.543     | 54.21±0.50                   | 39.78±0.856 | 51.68±0.5  |
| U-WC                                                          | 59.27±1.191     | 51.61±1.68                   | 43.76±1.835 | 50.98±0.7  |
| Reducible                                                     |                 |                               |         |          |
| WC                                                            | 55.30±2.138     | 45.25±1.97                   | 38.44±1.598 | 43.35±0.4  |
| U-WC                                                          | 35.57±2.498     | 32.87±2.62                   | 28.19±1.270 | 34.97±2.2  |
| Oxidizable fraction                                           |                 |                               |         |          |
| WC                                                            | 28.01±1.592     | 50.21±2.10                   | 97.30±1.696 | 51.29±2.1  |
| U-WC                                                          | 38.56±1.795     | 69.06±3.77                   | 100.52±1.13 | 71.23±3.0  |

Significant difference level P <0.05.

3.2. Effect of weathered coal activated by ultrasound on Cr content in soil and pakchoi plants

It can be seen from Table 3 and Figure 1 that after adding weathered coal in Cr-contaminated soil, the Cr content in the Pakchoi plants was significantly reduced (Table 3, P<0.05). The higher the amount of weathered coal added, the lower the Cr content in the plants. Compared with the control groups, Cr content was reduced by 8.5%-62.0%. When the amount of WC added was 80g/kg and the amount of U-WC was 60g/kg, the Cr content in the Pakchoi plants decreased by 49.9% and 62.0% respectively. U-WC treated soils had lower Cr content than WC under the same amount of addition. It can be seen that the addition of U-WC can effectively inhibit the enrichment of Cr in the soil and reduce the Cr content in the Pakchoi.

From Table 3 and Figure 2, it can be seen that weathered coal treatment can significantly increase the content of heavy metal chromium in soil (Table 3, P < 0.05). Compared with the control group, the
content of chromium in soil increases with the increase in amount added to the soil. This value is 2.2%-12.7% higher than that found in the control group. When the U-WC dosage was 60 g/kg, the effective Cr content in the soil was 209.44 mg/kg, which was 12.7% higher than the control treatment (185.77 mg/kg). Under the condition of WC addition amount of 80 g/kg and U-WC addition amount of 60 g/kg, the effective Cr content increased by 7.9% and 12.7%, respectively, which is the optimal.

![Figure 1. Impact of weathered coal addition on Cr content in Pakchoi plant samples.](image1)

![Figure 2. Impact of weathered coal addition on Cr content in soil.](image2)

**Table 3.** Effect of weathered coal addition on concentrations of Cr in soil and pakchoi plant samples.

| Cr Content (mg/kg) | Addition of weathered coal |
|-------------------|---------------------------|
|                   | 0 (control group) | 20 (g/kg) | 40 (g/kg) | 60 (g/kg) | 80 (g/kg) |
| **Pakchoi Plants** | WC                  | 17.33±0.279 | 15.85±0.544 | 12.55±0.260 | 9.20±0.300 | 8.68±0.333 |
|                   | U-WC                | 14.34±0.292 | 10.04±0.210 | 6.58±0.213 | 7.34±0.254 |
| **Soil**          | WC                  | 185.77±4.29 | 189.88±1.681| 195.56±2.287| 197.71±2.854| 200.53±2.21 |
|                   | U-WC                | 194.46±2.311| 200.22±1.771| 209.44±2.187| 205.43±1.05 |

Significant difference level P < 0.05

4. Conclusions

The content of exchangeable, reducible and oxidizable Cr in soil can be reduced to varying degrees by adding different amounts and types of weathered coal. The content of residual Cr in soil increases
when WC is added and the activity and migration of Cr in soil are reduced. Furthermore, the bioavailability and toxicity of Cr in soil are reduced when weathered coal is added to soil. The WC effectively reduced the absorption of Cr by pakchoi and the treatment effect of weathered coal activated by ultrasonic waves performs better than that of inactivated weathered coal. Under the conditions of adding 60-80g/kg of weathered coal by ultrasonic activation, the toxicity of single pollution of heavy metal Cr in soil to pakchoi was significantly reduced, which provides a theoretical basis for increasing the application of humic acid fertiliser in the area of Cr toxicity.

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