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Physical chemical properties and BCR speciation analysis of cr-contaminated soil in plateau

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Abstract. To explore physical and chemical properties and abundant form of Cr pollution red soil in plateau, study the transition and transform rule of Cr in red soil. In this paper, Cr pollution red soil in plateau as the research object, use the leaching toxicity experiment and BCR(Bureau Community of Reference) three steps extraction method, to study the change of valence state and occurrence form of heavy metal. The result shows that the acid red soil pH value is 6.13, organic matter content is 18.8 g/kg, silt and clay proportion is nearly 50%, 60%, high cation exchange capacity. The carbonate bound state accounted for 30.24% of total species, The Fe-Mn oxidation state accounted for 19.31, the organic matter and sulfide bound state accounted for 29.51%, and the residue state accounted for 20.94%. The result shows that the physical and chemical properties of the red soil in plateau have certain effects on the accumulation migration and transformation of heavy metals.

1. Introduction

The total heavy metal content and its effective state content are inextricably related to the physical and chemical properties of soil [1]. The physicochemical properties of soil will directly influence the adsorption-analytic behavior of soil to heavy metals [2]. The presence of Cr(VI) and Cr(III) in soil is not only related to the valence state, but also the toxicity, mobility, bioavailability and its chemical form are directly related to [3]. So, it is necessary to analyze the physical and chemical properties of Cr-contaminated soil to determine the corresponding analytical methods and treatment plans.

At present, the chemical extraction method is used to study the morphology of heavy metals. The five-step continuous extraction method proposed by Tessier [4-5] is the most widely used. In order to make the results obtained by different extraction methods have comparability, the EC Standard Material Bureau has proposed a three step extraction method (BCR method) [6-7]. The study shows that the BCR method is simple, easy, reproducibility and stability, high accuracy and high comparability. Yunnan is a serious area of heavy metal pollution. The red soil account for 70% of the total land area of the province, which is the main soil resource of Yunnan province [8-9]. The red soil in the plateau mountainous region is mainly distributed in hilly and semi mountainous areas in Yunnan. Plateau red soil has strong acidity, high soil viscosity and little organic matter content [10]. The study of heavy metal morphology, physical and chemical properties are rarely reported.

In this paper, Cr pollution red soil in plateau as the research object, use the leaching toxicity experiment and BCR three steps extraction method, to study the change of valence state and occurrence form of heavy metal. At present, there are few reports on heavy metal pollution analysis and harnessing in plateau red soil. It has important research value for harnessing plateau red soil. The high degree of acidity and high viscosity of red soil in plateau area bring great difficulties to pollution control. Taking the artificial preparation of chromium pollution red soil as the research object. With leaching toxicity, to establish a method system for the determination of Cr(VI) and Cr(III). And Study the migration and transformation of chromium in soil.

2. Experimental part

2.1. Preparation of Cr-pollution soil samples
Yunnan province red soil as the research object, allocation of Cr polluted soil. Collected from the farmland near the university city of Cheng Gong County. Put the mixture open air for three months, add distilled water regularly, hold the soil moisture to 10%. Three months later, dry the soil sample naturally, and crushes, thoroughly sifted, ground with agate mortar, so that all of them can be used for 100 purpose nylon sieve. The sample is well mixed and packed in a bag for analysis.

The main instruments used in the experiment are flame atomic absorption spectra, laser particle analyzer, ultraviolet spectrophotometer and fully automatic flip type oscillator.

2.2. Analysis of physical and chemical properties of red soil samples
The pH value of soil was determined by pH meter. Soil sample at 108 ℃ in the constant temperature box bake for about 2 h, calculation of water content in soil before and after baking; Soil organic matter is an important index to measure the fertility. The organic matter are high, and the heavy metals in soil is also high. The organic matter of soil samples was determined by ammonium ferric sulfate titration. The cation exchange capacity of soil samples was determined by EDTA disodium salt titration. The soil clay content was determined by the laser particle analyzer (Beckman Coulter, LS230).

2.3. leaching toxicity test
By using the TCLP Procedure (TCLP) method issued by epa. The determination method of Cr(VI) concentration was: diphenyl carbonyl dihydrazine spectrophotometry (GB/ t15555.5-1995); The determination method of total Cr concentration is: atomic absorption instrument (yana, novAA400); The experimental process was compared with the blank leaching solution, and the test data was the result after the blank.

2.4. Accuracy and reliability experiment of analysis method
The concentration of Cr standard liquid is 1000 μg/ML, add volume 0.25 ML, 0.3ML, 0.4 ML, 0.5 ML to 1g soil samples. After drying, soil samples were extracted by leaching toxicity, measuring the amount of total Cr and Cr(VI) in the infusion fluid, four times in parallel.

$$\text{standard recovery rate} = \frac{\text{measured value of added sample} - \text{measured value of sample}}{\text{plus scalar}} \times 100\%$$

2.5. BCR analysis of Cr speciation in soil samples

2.5.1. The carbonate binding state.
Weigh accurately (0.40 + 0.01) g the red soil samples in 50 ML plastic centrifuge tube, add 16 ML 0.11 mol/L acetate. Oscillate 16h at room temperature, then centrifuge 20min (4000r/min), collect the centrifuge, add 8 ML two distilled water to the residue, oscillate 15 min, centrifuge, collect the centrifuge again. All centrifuges are packed in 25 ML volume flask, add 1 drop of strong HNO_3 to be tested.

2.5.2. The Fe-Mn oxide binding state. Adding the currently formulated $HONH_3Cl$ 16 ML 0.l mol/L to the residue of the first step, adjust the soil pH to 2 with HNO_3, and the oscillating test tube to disperse the residue completely, oscillation, centrifugal, fluid transfer and washing are performed according to the first step method. Weigh accurately (0.40 + 0.01) g the red soil samples in 50 ML plastic centrifuge tube, add 16 ML 0.11 mol/L acetate. Oscillate 16h at room temperature, then centrifuge 20min (4000r/min), collect the centrifuge, add 8 ML two distilled water to the residue, oscillate 15 min, centrifuge, collect the centrifuge again. All centrifuges are packed in 25 ML volume flask, add 1 drop of strong HNO_3 to be tested.

2.5.3. Organic matter and sulfide binding state. Add 4 ML 8.8 mol/L hydrogen peroxide to the residue of second step, pH to 2 by HNO_3, then cover the centrifuge tube at room temperature for 1 hours, oscillate once at 15 min intervals, then take the lid. At a constant temperature water bath at 85℃ for 1 hours, the solution is steamed to the dry and cool. Repeat the above operation once again, and then add 20 ML 1 mol/L ammonium acetate. PH to 2 by HNO_3, oscillate, centrifuge, remove liquid, wash and transfer in the 50 ML bottle. Use the flame atomic absorption method to measure the concentration of three forms of Cr in soil samples.

3. Results and discussion

3.1. Standard curve of instrument
The measuring instrument is atomic absorption spectrophotometer and ultraviolet spectrophotometer, and the Table 1 is the linear regression equation and correlation coefficient of the two analytical methods.

Table 1. Linear regression equation and correlation coefficient.

Sample	Linear regression equation	Correlation coefficient
Cr	A=0.0049C+0.0184	R^2=0.9999
Cr(VI)	A=2.0975C-0.0023	R^2=0.9998

3.2. Soil physical and chemical properties analysis
Soil collected from nearby cropland, by air drying, grinding, through 100 mesh sieve, bag sealing save standby. The physical and chemical properties of the red soil were shown as follows Table 2.

Table 2. Physical and chemical properties of red soil.

Sample	pH	Organic matter (g/kg)	Cation exchange capacity (mol/kg)	Moisture content (%)	Sand (%)	Powder (%)	Clay (%)
Red soil	6.13	18.8	16.7	5.78	10.25	38.28	21.38

From the above table, the pH of red soil is 6.13, and the organic content is 18.8 g/kg, which relatively low. The proportion of powder and clay in red soi was nearly 50-60%, that red soil has big acidity, high viscosity, etc. Due to the high content of Cr(VI) and Cr(III). in the contaminated soil samples, the cationic exchange capacity also higher.

3.3. Leach toxicity of Cr in soil

Table 3. The Cr content of soil leaching solution. (n=4).

Species	Concentration(μg/g)				Average	Relative standard
	1	2	3	4	(μg/g)	deviation(%)
Cr(VI)	280.13	273.35	270.99	278.56	275.76	1.30%
Cr	299.26	292.12	289.95	297.46	294.70	1.25%

With a pH=2.88 acetic acid solution to extract the soil samples with the solid-liquid ratio was 1:20, and the oscillation was 18 ~ 20 h under 30 r/min. The analytical method of Cr(VI) and total Cr concentration are spectrophotometry and atomic absorb, each sample takes four parallel. From the Table 3, we know the relative standard deviation is 1.30% and 1.25%, which is within the range, means that the method is reproducing, with high accuracy and precision. The determination results shows that the Cr(VI) leaching concentration was 13.79 mg/L, and the total Cr leaching concentration was 14.74 mg/L. The soil environmental quality standard (GB15618-1995) stipulates that the maximum allowable concentration of Cr(VI) and total Cr in dry land is 0.5 mg/L and 0.05 mg/L. Means that the soil has been seriously contaminated, which must be treat to reach the natural environment.

3.4. Recovery rate
To calculate the recovery rate and do four parallel experiments, calculate the average.

Table 4. Soil Sample Determination (n=4).

| Species	Content (μg/g)	Adding the standard(μg/g)				After adding the standard(μg/g)				Average recovery rate(%)
		1	2	3	4	1	2	3	4	
Cr(VI)	288	250	300	400	500	518.33	557.25	664.21	770.23	98.24%
Cr	297.81	250	300	400	500	522.50	583.23	676.58	789.47	97.68%

It can be seen from the above Table 4, the average recovery rate of Cr(VI) is 98.24% and the average recovery rate of total Cr is 98.24%. The recovery rate all above 90% shows that the reliability of the method and reproducibility of measuring instrument are all good, the accuracy and precision density are high.

3.5. BCR analysis of Cr morphology in soil samples
According to Table 5, the total amount of chromium in the soil sample is 1373.28 μg/g. The total BCR morphology was 1373.28 μg/g The content of carbonate state are 410.38 μg/g, Fe - Mn oxidation state are 262.08 μg/g, organic matter and sulfide combination state are 400.59 μg/g,and residue state are 284.23 μg/g.

Table 5. Morphological Analysis of Cr

Carbonate binding state	Fe - Mn oxidation state	Organic matter and sulfide combination state	Residue state	Total BCR morphology	Total metal
410.38	262.08	400.59	284.23	1357.28	1373.16
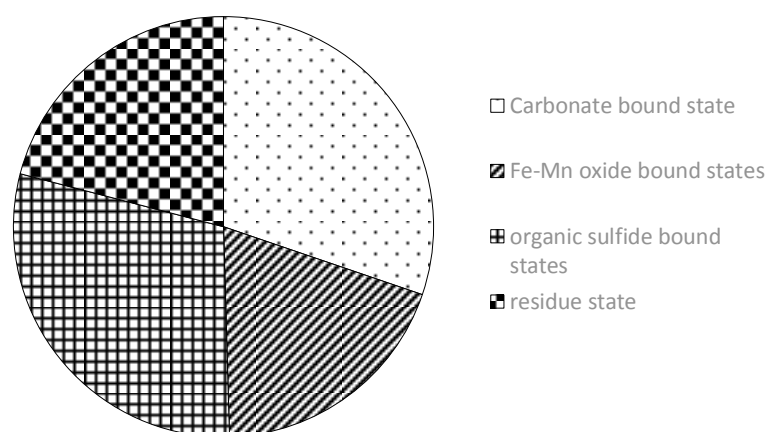
Figure 1. Distribution of BCR form of Cr in soil samples.

Exchangeable and carbonate-bonded heavy metals are sensitive to environmental changes, easy to migrate and transform, can be absorbed by plants, are most sensitive to pH and easily released under acidic conditions. In all the extraction forms of BCR, the exchangeable state and the carbonate bound state are the most harmful and toxic to the environment and organism. From the Figure 1. The content of carbonate in soil sample was 410.38 μg/g, the highest proportion in BCR, 30.24%. In addition, the pH value of red soil is 5.6 and is partial to acid, which is beneficial to the release of carbonate bound metal. The Fe-Mn oxidation state is the main body of the metal bioavailable state. However, when the pH is low, it is not conducive to the formation of iron-manganese oxides. The pH of red soil is 5.6, so the content of Cr in Fe-Mn oxide bound state is relatively low, which is 262.08 g/g, and the proportion is also the smallest, which is 19.31%. The Cr content of organic matter and sulphide bound state is 400.59 g/g, accounting for 29.51% of the total form. Cr(VI) and Cr(III) have a strong binding capacity to organic matter in the soil, so the organic content of Cr is also higher.

Heavy metal residue state mainly occurs in the native biological mineral lattice and secondary silicate mineral lattice. They are very stable in nature, do not participate in the re-equilibrium of the water-soil system, there is little contribution to the migration and bioavailability of heavy metals in soil, so it is generally considered safe for the environment. The residue state content of Cr in soil sample was 284.23 μg/g, accounting for 20.94% of the total amount. The higher the proportion of residual state, the greater of inertness and the lower risk. Carbonate bound states, Fe-Mn oxide bound states, and organic sulfide bound states are the main bioavailable forms. So the bioavailable Cr in soil sample accounts for 70.06% of total form.

4. Results and discussion

The leaching toxicity of Cr(VI) and total Cr has exceeded the soil three-level standards specified in the National Soil Environmental Quality Standard (GB15618-1995). The recovery rate all above 90% shows that the reliability of the method and reproducibility of measuring instrument are all good, the

accuracy and precision density are high. The analysis method of Cr(VI) and total Cr content in red soil was established.

By analyze the physical and chemical properties of red soil. Including the pH, moisture, cation exchange capacity, organic matter, mechanical composition. Obtain the basic parameters of soil. We know the pH of red soil is 6.13, with high content of Cr(VI) and Cr(III), in the contaminated soil samples, the cationic exchange capacity also higher. which lead to a high proportion of carbonate bound form of Cr, accounted for 30.24%. Because the more Cr(VI) and Cr(III) is in free state, the larger the proportion of Cr in carbonate bound state. And the organic content of soil is 18.8 g/kg, which relatively low, so the Fe-Mn oxide bound state of Cr in soil is relatively low, which is 19.31%. The proportion of powder and clay in red soi was nearly 50-60%, that red soil has big acidity, high viscosity. It is also the reason why the Cr content in the residue state is high. we can conclude that the physical and chemical properties are consistent with the existence form of Cr. The presence of Cr(VI) and Cr(III) in soil is not only related to the valence state, but also the toxicity, mobility, bioavailability and its chemical form are directly related to.

Acknowledgements

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