Adsorption of Heavy Metals on Soil Collected from Lixisol of Typical Karst Areas in the Presence of CaCO$_3$ and Soil Clay and Their Competition Behavior

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Abstract: The content of heavy metals in the soil in Guizhou Province, which is a high-risk area for heavy metal exposure, is significantly higher than that in other areas in China. Therefore, the objective of this study was to evaluate the ability of CaCO$_3$ and clay to accumulate heavy metals in topsoil sample collected from Lixisol using the method of indoor simulation. The results showed that the contents of Cu, Zn, Cd, Cr, Pb, Hg and As in the soil sample were 10.8 mg/kg, 125 mg/kg, 0.489 mg/kg, 23.5 mg/kg, 22.7 mg/kg, 58.3 mg/kg and 45.4 mg/kg, respectively. The soil pH values increased with the CaCO$_3$ concentration in the soil, and the fluctuation of the soil pH values was weak after the CaCO$_3$ concentrations reached 100 g/kg. The adsorption capacity of lime soil increased by approximately 10 mg/kg on average, and the desorption capacity decreased by approximately 300 mg/kg on average. The desorption of all heavy metals in this study did not change with increasing clay content. Pseudo-second-order kinetics were more suitable for describing the adsorption kinetics of heavy metals on the soil material, as evidenced by the higher $R^2$ value. The Freundlich model can better describe the adsorption process of As on lime soil. The process of As, Cr, Cd and Hg adsorption on the soil sample was spontaneous and entropy-driven. Additionally, the process of Cu and Pb adsorption on the soil materials was spontaneous and enthalpy-driven. Generally, the adsorption and desorption of heavy metals in polluted soil increased and decreased, respectively, with increasing CaCO$_3$ content. The effect of calcium carbonate on the accumulation of heavy metals in soil was greater than that of clay. In summary, CaCO$_3$ and pH values in soil can be appropriately added in several areas polluted by heavy metals to enhance the crop yield and reduce the adsorption of heavy metals in soils.

Keywords: heavy metals; Guizhou Province; CaCO$_3$; clay; pseudo-second-order kinetic; Freundlich model

1. Introduction

There are two main soil types, i.e., Lixisols and Acrisol, in Guizhou Province, of which the former are characterized by high content of calcium and magnesium carbonate (CaCO$_3$, MgCO$_3$), and carbonate...
plays an important role in the biogeochemical process of heavy metals [1,2]. The parent material, carbonate rock, consists mainly of calcite, dolomite and other carbonate minerals [3]. The major chemical components of Lixisols are CaCO$_3$ and MgCO$_3$ (more than 90%), and the other components are mainly SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, etc. [4]. However, excessive heavy metals in the soil sample will damage the ecosystem and harm human health because of their refractory accumulation through the food chain [5]. Ning et al. [6] measured the concentrations of heavy metals (Cu, Zn, Mn, Cd, Ni, Pb and Co) in limestone forests in Huaxi district, Guizang, and the heavy metal pollution was assessed by comparing our results with the background values of heavy metals in limestone soils in Guizhou Province, China. The results showed that the measured contents of Cu, Mn, Cd, Pb, Ni and Co were higher than or similar to these background values. Sun et al. [7] found that the concentrations of heavy metals in calcareous soil profiles remarkably exceeded the national standards in the study area, especially the concentrations of Cd and As. Therefore, it is necessary to understand the adsorption of heavy metals in topsoil samples collected from Lixisol.

The content of CaCO$_3$ in soil can significantly affect the total content and activities of heavy metals, thereby enhancing or restraining their absorption by plants. Especially, under the higher acidity and lower CaCO$_3$ content in soil, heavy metals in soil are of higher activity, rendering them easy to absorb by plants [8]. In contrast, in alkaline and CaCO$_3$-rich soils, heavy metals easily form hydrated hydroxides and insoluble carbonates or are adsorbed and fixed by soil colloids, which has a certain buffer effect [9]. The reason for this finding may be that calcium carbonate has a certain influence on the buffering performance of acids. Liu et al. [10] studied the buffer effect of different types of soils in the Changchun region and the influence of the physical and chemical characteristics of soil on the soil buffer action in a simulated experiment. According to the experiment, the average acid buffer capacity of calcareous soil containing calcium carbonate was 1.8 times that of non-calcareous meadow soil, black soil, albic soil and dark brown soil. Similarly, Huang et al. [11] investigated the effect of phosphate and carbonate on the immobilization of multiple heavy metals (Pb, Cu and Cd) in contaminated soils. The results showed that the application of calcium carbonate can significantly reduce exchangeable and carbonate-bound metals. In addition, calcium carbonate is an important cement for microaggregates and can form humic substances with soil organic matter, which can increase the surface area and negative charge of the soil, thus enhancing the Cr$^{3+}$, Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, etc. [12,13]. Unfortunately, the stability of the aggregates formed with calcium carbonate as a binder was poor due to the hydrolysis effect in a water environment [14]. Generally, the concentration of calcium carbonate in soil significantly affects the content of heavy metals.

The adsorption and desorption mechanism of heavy metals is closely related to soil components [15,16]. The behavior of heavy metals in soil mainly depends on the interaction between them and different soil components. Clay (less than 2 µm) includes crystalline aluminate, amorphous aluminosilicate and hydrated metal oxide. It is of large surface area, surface charge characteristics and cation exchange characteristics, which means it is a relatively active adsorption component of soil [17,18]. Wu et al. [19] reported that the amount of total organic carbon (TOC) and heavy metals in different size fractions of the fine particles increases as the particle size decreases. Qin et al. [20] exhibited that the clay positively correlated with Cd, As, Hg, and the sand negatively correlated with Hg and As. Hence, it is necessary to study the adsorption of heavy metal ions by clay particles with soil.

The residence time of the adsorbate on the surface of the adsorbent was an important factor in the evaluation of whether the adsorption process was completed and the calculation of the total amount of solute adsorption [21]. The adsorption kinetics can be evaluated by the adsorption rate, equilibrium time and adsorption capacity or by discussing the limit of the total amount of heavy metals adsorbed by soil. Furthermore, the adsorption isotherm model was also a major method for investigating the adsorption characteristics. The main objectives in this study were to (1) explore the adsorption and desorption behavior of heavy metals onto topsoil sample collected from Lixisol, considering calcium carbonate and soil clay; (2) understand the adsorption nature of heavy metals adsorbed by topsoil
sample collected from Lixisol using kinetics, adsorption isotherms and thermodynamic study; and (3) investigate the effect of pH and electrolytes on adsorption capacity.

2. Methods and Materials

2.1. Materials

Lixisols, a typical soil in Guizhou Province, Southwest China, was selected in this study. All soil samples used in the experiment were collected from the topsoil with a stainless-steel shovel and packed back with cloth bags. After natural air drying at room temperature and removal of plants, gravel and other impurities in the soil, the soil was ground with a porcelain mortar, a container for crushing experimental materials in an experiment, and sifted to 100 mesh. After sifting, all the soil was collected in plastic bags for future use.

2.2. Analysis Method

The collected soil was divided into many parts, which was used to analyze the several indexes. For one of the soil samples, the pH of the soil was determined by potentiometry (soil-to-water ratio = 1:2.5) [22,23]. Soil organic matter was measured by the high-temperature external heat potassium dichromate oxidation volumetric method [24,25]. The calcium carbonate content in the soil was calculated using the volumetric titration method [26]. The soil particle size distribution was gauged by the hydrometer method [27]. The soil samples were digested by a microwave digester using HNO₃-H₂O₂-HF (5:2:5), and acid was removed by a graphite furnace [28]. Hg and As were determined by an atomic fluorescence photometer (AFS-2100, Beijing Haiguang Instrument Co., Ltd., Beijing, China). Pb, Cu, Zn, Cd and Cr of soils were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Prodigy XP, Leeman Labs Inc., Hudson, NY, USA).

2.3. Effect of Different Calcium Carbonate Contents on Adsorption and Desorption

Eleven soil samples of 0.5 g (accurate to 0.0001 g) were accurately weighed and added to 100 mL centrifuge tubes. Super pure CaCO₃ was added to each sample at 0, 0.25, 0.5, 1, 3, 5, 7, 10, 15, 20 and 25 g/kg. The standard heavy metal (Cd, Pb, Cr, Zn, As and Hg) mixed solutions (nitric acid medium), which were purchased from the National Center of Analysis and Testing for Non-ferrous Metals and Electronic Materials, of 50 mL with a concentration of 20 mg/L, were added to the above mixture. These compounds were oscillated on a constant-temperature oscillator (25 ± 1 °C). After 2 h, the cells were removed and cultured in a constant-temperature incubator (25 ± 1 °C) for 22 h and then centrifuged for 30 min (4000 r/min). The supernatant was taken and measured with the aid of a computer, and the formula used to calculate the adsorption capacity is as follows:

$$q_e = \frac{(C_i - C_e) \times V}{m}$$ (1)

where $q_e$ (mg/kg) is the capacity of soil adsorption/desorption in the solution at equilibrium; $C_i$ (mg/L) is the initial concentration of heavy metals in the supernatant; $C_e$ (mg/L) is the equilibrium concentration of heavy metals in the supernatant; $V$ (mL) is the volume of the total mixed solution used; and $m$ (g) is the weight of the added soil material.

The supernatants of the above soil samples were removed, and 20 mL of 0.1 mol/L NaNO₃ was added. The mixtures were oscillated on a constant temperature oscillator (25 ± 1 °C) for 2 h. The solutions were cultured in a constant-temperature incubator (25 ± 1 °C) for 22 h after transfer to a volumetric flask and then centrifuged at 4000 r/min for 30 min. Finally, the concentration of heavy metals in the supernatant was determined using ICP-OES. The desorption capacity was the concentration
difference of heavy metals in the supernatant before and after adding NaNO₃. The formula for calculation is as follows:

\[ S = \frac{(C_1 - C_2) \times v}{m} \]  

where \( S \) (mg/kg) is the desorption capacity of soil in the solution at equilibrium; \( C_1 \) and \( C_2 \) are the concentrations of heavy metals in the supernatant before and after adding NaNO₃ (mg/L), respectively; \( v \) (mL) is the volume of the total mixed solution used; and \( m \) (g) is the capacity of the added soils. Figure 1 shows the adsorption/desorption flow chart.

2.4. Particle Size Distribution of Soil

The particle size distribution of soil was measured by the hydrometer method. A soil sample of 50 g passing a 2 mm sieve was weighed into a triangular flask. The appropriate dispersant, 0.5 mol/L NaOH solution to acidic soil of 40 mL or sodium hexametaphosphate solution to alkaline soil of 60 mL, 250 mL pure water were successively added to the above triangular flask. After the mixture soaked overnight, the mixtures in flasks were boiled on the heating plate for 1 h (using the defoamer to prevent overflow). After cooling, the sieve was washed through 0.2 mm, and the suspension was washed into a 1 L measuring cylinder. After all the suspension had passed, the mixtures were sieved through 0.2 mm and the suspension was washed into a measuring cylinder of 1 L. After all the suspension had passed through, the sieve was washed with pure water. The particles left on the screen were washed into the aluminum box, dried and weighed. The part washed into the measuring cylinder was added with water to a constant volume of 1 L.

The solution in the measuring cylinder was stirred up and down repeatedly for one minute with an agitator. The time was counted at the end of mixing, which were respectively 30 s, 1 min, 2 min, 4 min, 8 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 24 h, 48 h, and put it into the hydrometer to read, and measure and record the water temperature before reading. The particle size content was calculated according to the following equation,

\[ \% = \frac{(\rho_1 + \rho_2 + \rho_3 + \rho_0) \times v}{m} \times 100 \]  

where \( \rho_1 \) is the hydrometer reading, g/L; \( \rho_2 \) is the correction value of hydrometer calibration curve, g/L; \( \rho_3 \) is the calibration temperature value of hydrometer, g/L; \( \rho_0 \) is the corrected value of dispersant.
for hydrometer reading, g/L; \( v \) is the volume of suspension, mL; \( m \) is the weight of soil sample, g. The diameter (d) of soil is calculated by the following Equation (4):

\[
d = \sqrt{\frac{1800\eta L}{g(\rho_s - \rho_f)t}}
\]  

(4)

where \( d \) is the diameter of soil sample, mm; \( \eta \) is the viscosity coefficient of water; \( L \) is the settlement depth of soil particles, g is the acceleration of gravity, cm/s; \( \rho_s \) is the soil particle density, g/cm\(^3\); \( \rho_f \) is the density of water, g/cm\(^3\); \( t \) is settlement time, s.

2.5. Adsorption Kinetic

Prepared solutions of 1 L contained 20 mg/L heavy metals and 0.01 mol/L NaNO\(_3\) (as supporting electrolyte) in a beaker. A 25.00 g aliquot of soil material was added to each prepared solution of 1 L. At room temperature, the mixtures were stirred at a constant speed for 1 min, 2 min, 4 min, 6 min, 8 min, 10 min, 15 min, 20 min, 30 min, 45 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 6 h, 8 h, 10 h, 12 h and 24 h, and an aliquot (20 mL) was selected and centrifuged at 4000 r/min for 3 min. Pseudo-first-order kinetics, pseudo-second-order kinetics and particle internal diffusion were used to fit the data of the adsorption process of heavy metals on the soil sample [29,30],

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

(5)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t
\]  

(6)

\[
q_t = k_{int}t^{0.5} + C
\]  

(7)

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the adsorption capacity at equilibrium and after time t (min), respectively; \( k \) is the kinetic adsorption rate constant. \( k_{int} \) (mg/g·min\(^{-0.5}\)) is the diffusion rate constant in particles.

2.6. Adsorption Isotherm

Six soil samples (0.5 g, accurate to 0.0001 g) were weighed into a 100 mL centrifuge tube, and then 20 mL of heavy metals (Cd, Pb, Cr, Zn, As, Hg) with concentrations of 0.00, 10.00, 20.00, 30.00, 40.00, and 50.00 mg/L were added to the centrifuge tube. NaNO\(_3\) (0.01 mol/L) as the supporting electrolyte was dropped into these mixtures, which were oscillated at 25 °C for 24 h to reach adsorption equilibrium. After centrifugation and filtration, the supernatant was used to determine the concentration of heavy metals. The Langmuir and Freundlich models were frequently utilized to describe the isotherm adsorption effect at the soil/water interface [31,32]. Their equations are as follows:

\[
q_e = \frac{kQ_mC_e}{1+kC_e}
\]  

(8)

\[
q_e = k_F \times C_e^{1/n}
\]  

(9)

where \( q_e \) (mg/g) is the adsorption capacity of adsorbate on the adsorbent surface at equilibrium; \( k \) (L/mg) is the Langmuir constant; \( Q_m \) (mg/g) is the maximum adsorption capacity of adsorbate on the adsorbent surface; \( C_e \) (mg/L) is the concentration of adsorbate in solution at equilibrium; \( k_F \) (mg/g) is the Freundlich constant; and \( n \) is the index of anisotropy, which is usually greater than 1. A larger value indicates the significance of the nonlinear characteristic of the adsorption isotherm.
2.7. Estimation of Thermodynamic Parameters

The change in Gibbs free energy associated with a chemical reaction can be used to evaluate the spontaneity of the adsorption reaction [33]. Thermodynamic parameters can be obtained as follows [34]:

\[ K_T = \frac{C_s}{C_e} \] (10)

\[ \Delta G^\circ = RT \ln K_T \] (11)

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \] (12)

where \( C_s \) is the initial concentration of heavy metals on the soil material; \( C_e \) is the concentration of heavy metals in solution at equilibrium; and \( R \) is the gas constant (8.31 J·mol\(^{-1}\)·K\(^{-1}\)).

2.8. Effect of Initial pH on Adsorption

Eight soil samples (0.5 g, accurate to 0.0001 g) were weighed into a centrifuge tube of 100 mL. A 20 mL aliquot of 20 mg/L heavy metal (0.01 mol/L NaNO\(_3\) as supporting electrolyte) was added into the above centrifuge tube, and the pH values of the mixture were adjusted between 3.00 and 10.00 using 0.1 mol/L NaOH and HNO\(_3\). The pH values in this experiment were set as 8 gradients (3, 4, 5, 6, 7, 8, 9 and 10). After shaking, centrifuging and filtering, the supernatant was used to determine the concentration of heavy metals. Their adsorption capacity was calculated as in Section 2.3.

2.9. Effect of Temperature on Adsorption

The processing steps were the same as those described in Section 2.3, and the adsorption isothermal experiments were carried out at 50 °C, 45 °C, 40 °C, 35 °C and 30 °C. Their adsorption capacity was calculated as in Section 2.3.

2.10. Influence of Electrolyte on Adsorption

Five soil samples (0.5 g, accurate to 0.0001 g) were weighed into 100 mL centrifuge tubes. Different concentrations of NaNO\(_3\) (10\(^{-1}\), 10\(^{-2}\), 10\(^{-3}\), 10\(^{-4}\) and 10\(^{-5}\) mol/L) were added to the above centrifuge tubes. The treatment process and adsorption capacity were calculated as in Section 2.3.

3. Results and Discussion

3.1. Physical and Chemical Indexes of Topsoil Sample Collected from Lixisol

The pH of topsoil in Guizhou Province was 7.64 in this study, which corresponds to weak alkaline soil (Figure 2a). The contents of organic matter and calcium carbonate were 70.3 g/kg and 50.9 g/kg, respectively, which exhibited that the organic matter in soil of study area was rich according to Nutrient grading standard of the second national soil survey (China). The soil organic matter can inhibit or promote the adsorption of heavy metals in soil through a series of reactions, such as ion exchange adsorption, complexation and chelation between heavy metals and other functional groups, which affect the precipitation, migration, transformation and bioavailability of heavy metals [35]. The particle size distribution of the soil sample in our study was 37.78% sand, 26.79% powder and 35.44% clay, which pertained to loamy clay. The moisture content of calcareous soil was 3.58%.
was 806 mg and the minimum desorption capacity was 409 mg/kg, respectively. For Hg, the maximum and minimum adsorption capacities were 790 mg/kg and 661 mg/kg, respectively. The minimum adsorption and desorption capacities of Cd were 3.20 mg/kg and 23.5 mg/kg, respectively. The maximum and minimum adsorption capacities of Zn were 802 mg/kg and 30 mg/kg, respectively. According to the “soil environmental quality: risk control standard for soil contamination of agricultural land” (GB 15618-2018) released by Ministry of Ecology and Environment of the People’s Republic of China, Cd and As exceed their control values which are 0.3 mg/kg and 30 mg/kg, respectively. As shown in Figure 2a, the soil pH values increased with CaCO3 concentration in the soil, and the fluctuation of the soil pH values was weak after the CaCO3 concentrations reached 100 g/kg. In soil, the effect of CaCO3 on pH was due to the hydrolysis of carbonate (MCO3 + H2O ⇌ M2+ + HCO3− + OH−) [36]. Liu et al. [37] reported that CaCO3 concentrations slightly affected the soil pH when the content of calcium carbonate was 50–100 g/kg, which is consistent with our study. The different clay contents caused a difference in soil pH values, and the maximum and minimum pH values of the soil were 6.44 and 6.39, respectively.

3.2. Effect of Calcium Carbonate and Soil Clay on Adsorption and Desorption of Heavy Metals in Topsoil Sample Collected from Lixisol

Generally, the adsorption capacity of heavy metals in soil was higher than the desorption capacity, which implied that these heavy metals could be fixed by the soil sample, and few heavy metals were desorbed; thus, the migration capacity of fixed heavy metals will also be reduced. The soil material is extensively distributed in Guizhou Province, which is a reason for the higher heavy metal concentrations in the soil in Guizhou Province. As shown in Figure 3 and Table 1, the order of the maximum adsorption capacities for heavy metals is Cu > Pb > Zn > Cd > Hg > Cr > As. For Cu, the maximum adsorption capacity was 807 mg/kg, and the minimum adsorption capacity was 806 mg/kg. The maximum desorption capacity was 172 mg/kg, and the minimum desorption capacity was 18.1 mg/kg. The maximum and minimum adsorption capacities of Pb were 802 mg/kg and 799 mg/kg, respectively. The maximum and minimum desorption capacities of Pb were 3.45 mg/kg and ~2.60 mg/kg, respectively. The maximum and minimum adsorption capacities of Zn were 802 mg/kg and 800 mg/kg, respectively. The maximum desorption capacity of Zn is 674 mg/kg and the minimum desorption capacity is 282 mg/kg. The maximum adsorption and desorption capacities of Cd were 795 mg/kg and 661 mg/kg, respectively. The minimum adsorption and desorption capacities of Cd were 790 mg/kg and 409 mg/kg, respectively. For Hg, the maximum and minimum adsorption capacities were 771 mg/kg and 758 mg/kg, respectively. The maximum desorption capacity was ~0.436 mg/kg, and the minimum desorption capacity was ~7.70 mg/kg. The maximum adsorption capacity of Cr was 767 mg/kg, and the minimum adsorption capacity was 760 mg/kg. The maximum desorption capacity of Cr was 510 mg/kg, and the minimum desorption capacity was 268 mg/kg. The maximum adsorption...
capacity of As was 763 mg/kg, and its minimum value was 666 mg/kg. The maximum and minimum desorption capacities of As were 8.90 mg/kg and −2.36 mg/kg. The desorption efficiency for Pb, Cd, Zn, Cu, Cr, Hg and As is 0.43%, 83.09%, 83.98%, 20.83%, 35.14%, not detected and 0.13%, respectively.

Figure 3. The adsorption and desorption capacities of Pb, Cd, Zn, Cu, Cr, Hg and As at different CaCO$_3$ contents on soil sample.

Table 1. Relationship between different CaCO$_3$ contents and adsorption or desorption of heavy metals in soil sample.

| CaCO$_3$ Contents(g/kg) | Pb (mg/kg) | Cd (mg/kg) | Zn (mg/kg) | Cu (mg/kg) | Cr (mg/kg) | Hg (mg/kg) | As (mg/kg) |
|-------------------------|------------|------------|------------|------------|------------|------------|------------|
| 58.8                    | AQ 802     | DQ 3.45    | AQ 795     | DQ 661     | AQ 802     | DQ 673     | AQ 807     | DQ 168     | AQ 762     | DQ 268     | AQ 767     | DQ −7.07   | AQ 752     | DQ 0.970   |
| 59.8                    | 800 −0.492 | 790 653    | 800 674    | 807 172    | 767 270    | 758 −7.07  | 763 −2.36  |           |           |           |           |           |           |            |
| 60.8                    | 801 −0.830 | 795 614    | 802 596    | 807 109    | 760 300    | 763 −4.36  | 746 −1.14  |           |           |           |           |           |           |            |
| 62.8                    | 802 −0.332 | 795 623    | 801 590    | 807 120    | 763 290    | 762 −4.84  | 750 2.16   |           |           |           |           |           |           |            |
| 70.8                    | 799 −2.24  | 792 596    | 801 565    | 807 103    | 759 319    | 760 −7.24  | 746 1.31   |           |           |           |           |           |           |            |
| 78.8                    | 802 −1.75  | 793 575    | 801 542    | 807 116    | 760 3577   | 763 −4.06  | 738 0.146  |           |           |           |           |           |           |            |
| 86.8                    | 800 −2.17  | 792 596    | 801 591    | 807 118    | 760 341    | 763 −3.71  | 743 5.61   |           |           |           |           |           |           |            |
| 98.8                    | 800 −2.12  | 794 549    | 802 488    | 807 70.1   | 764 372    | 768 −3.18  | 724 0.864  |           |           |           |           |           |           |            |
| 119                     | 802 −2.03  | 793 507    | 802 442    | 806 46.6   | 762 448    | 770 −2.64  | 697 0.842  |           |           |           |           |           |           |            |
| 139                     | 801 −1.92  | 791 462    | 801 349    | 806 33.5   | 762 478    | 771 −0.436 | 686 8.90   |           |           |           |           |           |           |            |
| 159                     | 801 −2.60  | 791 409    | 801 282    | 806 18.1   | 761 510    | 767 −4.04  | 666 2.22   |           |           |           |           |           |           |            |

Note: AQ and DQ represent adsorption and desorption capacity, respectively.

The adsorption capacity of Cu, Zn, Cd and Pb did not obviously change with the increase in CaCO$_3$ content in soil. However, the adsorption capacities of Hg and Cr slightly increased with increasing CaCO$_3$ content in the soil sample. A negative correlation between the adsorption capacities of As and the CaCO$_3$ content was observed because the adsorption capacity of As decreased significantly as the CaCO$_3$ content of the soil material increased. Zhong et al. [38] reported effects of CaCO$_3$ addition on uptake of heavy metals and arsenic in paddy fields, and the exchangeable arsenic content in the soils decreased significantly by adding CaCO$_3$. The reason may be that Ca in soil can form insoluble precipitation with As, which was conducive to the fixation of As. The desorption capacities of Cu, Cd
and Zn were decreased with increasing CaCO$_3$ content in the soil sample. However, with the increase in CaCO$_3$ content in the soil material, the desorption capacities of As and Pb did not significantly change. The desorption capacities of Cr were increased with increasing CaCO$_3$ content in soil sample. Therefore, with the increase in the CaCO$_3$ content in the soil sample, the adsorption and fixation of Cu, Cd and Zn were enhanced, and the adsorption and fixation of Cr and As were weakened, but Pb had no obvious effect. With the increase in CaCO$_3$ content, the adsorption capacity of soil material was increased by approximately 10 mg/kg on average, and the desorption capacity decreased by approximately 300 mg/kg on average. The pH value of soil increased after adding calcium carbonate, which promoted the precipitation reaction of exchangeable Cd$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ with carbonate and hydroxide in soil. Meanwhile, the coprecipitation of Ca$^{2+}$ and metal ions is also conducive to the transformation of the exchange state to other forms. Additionally, the increase of soil pH can enhance the chelating capacity of clay and organic matter, promote the adsorption capacity of soil, and reduce the desorption of heavy metals, thus decreasing the solubility of heavy metals in soil [39]. In contrast, the adsorption capacity of the soil materials was continuously increased with the decrease in CaCO$_3$ content. This may be because with the decrease of pH value, the negative charges on the surface of clay minerals, hydrated oxides and organic matter in the soil decreased, and the adsorption capacity of heavy metals weakened. Meanwhile, the specific adsorption of heavy metals on the surface of oxides and the stability of soil organic matter metal complexes decreased with the decrease of pH value. With the decrease of pH, the concentrations of H$^+$ and Fe$^{2+}$ in soil increase, and the competitive adsorption with heavy metals increases, which is not conducive to the adsorption of heavy metals. The decrease of pH is not conducive to the formation of metal hydrate ions, and the affinity of hydrated ions on soil adsorption sites is significantly lower than that of heavy metal ions, which is not conducive to the adsorption of heavy metals on soil [40]. However, the effects on different elements are different, such as inhibiting the transport of nitrate nitrogen from the underground of wheat to the aboveground, promoting the uptake of chromium in the aerial parts of Chinese cabbage, and enhancing the enrichment of lead in lettuce stems and leaves.

As shown in Table 2, the order of the maximum adsorption capacities for heavy metals is Pb > Cu > Hg > Zn > As > Cd > Cr. Firstly, the maximum and minimum adsorption capacities of Pb were 434 mg/kg and 399 mg/kg, respectively. The maximum desorption capacity of Pb was 293 mg/kg, and the minimum desorption capacity was 236 mg/kg. The maximum adsorption capacity of Cu was 431 mg/kg, and the minimum adsorption capacity was 378 mg/kg. The maximum desorption capacity was 412 mg/kg, and the minimum desorption capacity was 375 mg/kg. The maximum adsorption capacity of Hg was 415 mg/kg, and its minimum value was 389 mg/kg. The maximum and minimum desorption capacities were 98.7 mg/kg and 62.9 mg/kg, respectively. For the adsorption capacity of Zn, the maximum value was 372 mg/kg, and the minimum value was 288 mg/kg. The maximum desorption capacity of Zn was 391 mg/kg, and the minimum desorption capacity was 344 mg/kg. The maximum and minimum adsorption capacities of As were 368 mg/kg and 353 mg/kg, respectively. The maximum desorption capacity was 288 mg/kg, and the minimum desorption capacity was 272 mg/kg. The maximum adsorption capacity of Cd was 292 mg/kg, and the minimum adsorption capacity was 236 mg/kg. The maximum desorption capacity of Cd was 413 mg/kg, and the minimum desorption capacity was 378.1 mg/kg. For the adsorption capacity of Cr, its maximum and minimum values were 231 mg/kg and 145 mg/kg, respectively. The maximum desorption capacity was 448 mg/kg, and the minimum desorption capacity was 434 mg/kg. However, the adsorption concentration of heavy metals in soil increased with the contain of clay (from 382 g/kg to 454 g/kg). The phenomenon may be that the clay in the soil had a large surface energy, which made its adsorption capacity relatively strong. Therefore, the migration of pollutants was limited.
Table 2. Relationship between clay content and adsorption or desorption of heavy metals in soil sample.

| Clay Particle (g/kg) | Pb (mg/kg) | Cd (mg/kg) | Zn (mg/kg) | Cu (mg/kg) | Cr (mg/kg) | Hg (mg/kg) | As (mg/kg) |
|---------------------|------------|------------|------------|------------|------------|------------|------------|
| AQ                  | DQ         | AQ         | DQ         | AQ         | DQ         | AQ         | AQ         |
| 354                 | 400        | 304        | 292        | 413        | 352        | 391        | 404        |
| 355                 | 400        | 309        | 281        | 407        | 346        | 388        | 403        |
| 356                 | 402        | 310        | 280        | 403        | 337        | 379        | 401        |
| 358                 | 400        | 315        | 280        | 401        | 341        | 376        | 403        |
| 366                 | 400        | 328        | 257        | 391        | 315        | 367        | 395        |
| 374                 | 399        | 337        | 240        | 385        | 288        | 355        | 378        |
| 382                 | 400        | 315        | 277        | 404        | 335        | 381        | 397        |
| 394                 | 401        | 319        | 280        | 405        | 341        | 382        | 402        |
| 414                 | 417        | 293        | 236        | 378        | 353        | 344        | 425        |
| 434                 | 434        | 301        | 252        | 388        | 361        | 360        | 420        |
| 454                 | 431        | 306        | 289        | 412        | 372        | 389        | 431        |

Note: AQ and DQ represent adsorption and desorption capacity, respectively.

Figure 4 shows that the effect of clay on heavy metals in lime soil was not as significant as that of CaCO₃. Their adsorption capacities gradually increased with increasing clay content. However, the desorption capacity of As was slightly decreased with increasing clay content. Generally, the desorption of all heavy metals in this study did not change with increasing clay content. The desorption efficiencies for Pb, Cd, Zn, Cu, Cr, Hg and As are 93.79%, 79.63%, 20.12%, 99.65%, 94.88%, 54.55% and 69.44%, respectively.

Figure 4. The adsorption and desorption capacities of Pb (a), Cd (b), Zn (c), Cu (d), Cr (e), Hg (f) and As (g) at different clay on soil material.

3.3. Adsorption Kinetics of Heavy Metals Adsorbed on Topsoil Sample Collected from Lixisol

The rate of metal ions moving in solution and fixing on the surface of the soil determined the efficiency of the adsorption process. The residence time of a solute on the surface of the soil adsorbent
was an important factor to judge whether the adsorption process was completed and to calculate the total amount of solute adsorption. The study of adsorption dynamic characteristics can be used to explore the possible adsorption mechanism from the perspective of the adsorption path.

The adsorption capacities of heavy metals on the soil sample dramatically increased with increasing contact time (Figure 5). When the adsorption capacity reached a certain value, it weakly increased or decreased with increasing contact time. The adsorption rate of the soil material can reach 50% in 5 min, 80% in 15 min, 95% in 90 min and 99% after 720 min. The adsorption process of heavy metals by the soil sample was mainly concentrated in the first 90 min, and the subsequent adsorption was relatively slow. The reason for this difference may be physical adsorption (fast adsorption stage) and chemical adsorption (slow adsorption stage). Generally, physical adsorption can achieve local equilibrium in a few milliseconds to a few seconds; however, chemical adsorption requires a certain activation energy to adsorb, resulting in a slow adsorption process.

![Figure 5. The fitting of heavy metals adsorbed on the soil material by pseudo-first-order kinetics (a), pseudo-second-order kinetics (b), intraparticle diffusion (c) and experimental value (d).](image)

The pseudo-second-order kinetic equation was more suitable to describe the adsorption kinetics of heavy metals on the soil sample, as evidenced by the higher $R^2$ value (Table 3). The maximum adsorption capacities of As, Cu, Zn, Pb, Cr, Cd and Hg were 0.777 mg/g, 0.793 mg/g, 0.391 mg/g, 0.808 mg/g, 0.378 mg/g, 0.325 mg/g and 0.804 mg/g, respectively, implying Pb $>$ Hg $>$ Cu $>$ As $>$ Zn $>$ Cr $>$ Cd. The adsorption rates of As, Cu, Zn, Pb, Cr, Cd and Hg were 0.159 g·mg$^{-1}$·min$^{-1}$, 0.0476 g·mg$^{-1}$·min$^{-1}$, 0.0382 g·mg$^{-1}$·min$^{-1}$, 0.303 g·mg$^{-1}$·min$^{-1}$, 0.256 g·mg$^{-1}$·min$^{-1}$, 0.079 g·mg$^{-1}$·min$^{-1}$ and 0.650 g·mg$^{-1}$·min$^{-1}$, respectively, signifying Hg $>$ Pb $>$ Cr $>$ As $>$ Cd $>$ Cu $>$ Zn. In addition, the fitting degree of the intraparticle diffusion model was also relatively good. For this kind of porous adsorbate, intraparticle diffusion was also an important process of heavy metal adsorption.
which was more favorable for the combination with adsorbate and adsorbent. However, the capacity of each heavy metal combined with the soil material was different since these heavy metals had different properties. Hence, the maximum adsorption capacity of each heavy metal has a higher difference, of which As was the most obvious with the increase in initial As concentration. In this study, As was selected for specific discussion due to its sensitivity to the initial concentration of heavy metals in soil sample (Figure 7).

Table 3. Kinetics parameters of heavy metals adsorbed on the soil sample.

|               | As   | Cu   | Zn   | Pb   | Cr   | Cd   | Hg   |
|---------------|------|------|------|------|------|------|------|
| Pseudo-first-order kinetic | Qe (mg/g) | k1 (10^{-3} min^{-1}) | R   |      |      |      |      |
|               | 0.703 | 0.925 | 0.281 |      |      |      |      |
| Pseudo-second-order kinetic | Qe (mg/g) | k2 (10^{-3} g mg^{-1}min^{-1}) | R   |      |      |      |      |
|               | 0.787 | 0.343 | 0.999 |      |      |      |      |
| Particle diffusion model | k3 (mg g^{-1}min^{-0.5}) | C   |      |      |      |      |      |
|               | 0.007 | 0.603 | 0.950 |      |      |      |      |

3.4. Adsorption Isotherms of Heavy Metals Adsorbed on Topsoil Sample Collected from Lixisol

The shape and change rule of the adsorption isotherm can be used to understand the action intensity of the adsorbate and adsorbent, the state of the adsorbate on the interface and the structure of the adsorption layer. All heavy metals exhibit a larger slope at a lower equilibrium concentration (the heavy metal concentration which was no longer improved after the different initial concentrations of heavy metals adsorbed by the soil sample) (Figure 6). The adsorption capacities of heavy metals were added with increasing initial heavy metal concentrations; however, the slope of the isotherm adsorption curve was gentle at higher equilibrium concentrations. The slope of As was the largest, followed by those of Hg, Cr and Pb, which were dramatically adsorbed and then slowly adsorbed. The slopes of Cu, Zn and Cd slowly increased with increasing initial concentration. The reason may be that the concentration of adsorbate in the solution was enhanced with increasing initial concentration, which was more favorable for the combination with adsorbate and adsorbent. However, the capacity of each heavy metal combined with the soil material was different since these heavy metals had different properties. Hence, the maximum adsorption capacity of each heavy metal has a higher difference, of which As was the most obvious with the increase in initial As concentration. In this study, As was selected for specific discussion due to its sensitivity to the initial concentration of heavy metals in soil sample (Figure 7).

Figure 6. Adsorption capacities of heavy metals adsorbed on soil material at equilibrium concentration.
capacity no longer increased with increasing adsorbate concentration. The L-type curve may be caused by monolayer adsorption or micropore filling of a small amount of silica gel in the clay.

Figure 8 shows the Langmuir and Freundlich isotherm model fitting of As adsorption on lime soil. The isotherm adsorption parameters obtained by the fitting are shown in Table 4. The correlation coefficients ($R^2$) of the Langmuir and Freundlich models were 0.817 and 0.920, respectively, which implied that the Freundlich model can better describe the adsorption process of As on lime soil. In addition, the $k$ and $n$ values of the Freundlich model were 166 L/mg and 2.37.

Table 4. Adsorption isotherm fitting parameters for As adsorption onto lime soil.

|          | Langmuir | Freundlich |
|----------|----------|------------|
| $q_m$    | 757      |            |
| $K_L$    | 0.161    |            |
| $R^2$    | 0.817    |            |
| $K_F$    | 166      |            |
| $1/n$    | 2.370    |            |
| $R^2$    | 0.920    |            |
with increasing temperature; however, there was no significant increase or decrease. This may be due to the increase in temperature, which may be caused by stable chemical adsorption or monolayer adsorption or micropore filling of a small amount of silica gel in the clay. Additionally, the process of Cu and Pb adsorbed by the soil sample was spontaneous and entropy-driven. The process of As, Cr, Cd and Hg adsorption onto the soil material was spontaneous and entropy-driven (Table 5). Therefore, the adsorption has reached a balance (the binding sites of the surface and inner pores of the soil particles have been filled). Both adsorption and desorption were promoted with increasing temperature, which showed that the adsorption amount of heavy metals in lime soil did not obvious increase.

### Thermodynamic Study

The thermodynamics of the adsorption of heavy metals on lime soil can be used to study the exothermic, spontaneous or endothermic nature of heavy metal adsorption on the interface between the adsorbate and adsorbent [44]. The positive values of $\Delta S^0$ suggested an increase in randomness at the solid/solution interface [45]. The positive value obtained for $\Delta H^0$ indicates the endothermic nature of heavy metal adsorption, which demonstrates that this process consumes energy [46]. Therefore, the process was a spontaneous and entropy-driven process. The negative value of $\Delta G^0$ showed the feasibility and spontaneity of heavy metal adsorption onto the soil sample [47]. Therefore, the adsorption capacities were enhanced with increasing temperature, which may be due to the endothermic reaction. The adsorption capacity of heavy metals in soil was more easily adsorbed on the surface of soil particles with an increase in temperature, and there was no obvious desorption phenomenon due to the increase in temperature, which may be caused by stable chemical adsorption during the whole process. The adsorption capacities of heavy metals in the soil material fluctuated with increasing temperature; however, there was no significant increase or decrease. This may be because the adsorption has reached a balance (the binding sites of the surface and inner pores of the soil particles have been filled). Both adsorption and desorption were promoted with increasing temperature, which showed that the adsorption amount of heavy metals in lime soil did not obvious increase.

### Table 5. Thermodynamic parameters for adsorption of heavy metals on soil sample.

|      | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (J mol$^{-1}$K$^{-1}$) | $\Delta G^0$ (kJ/mol) |
|------|-----------------------------|-----------------------------------|-----------------------|
|      | 303.150 K | 308.150 K | 313.150 K | 318.150 K | 323.150 K |
| As   | 40.172   | 136.474  | −0.571   | −1.160   | −0.566   | −0.688   | −0.757   |
| Cu   | −1.309   | −1.792   | −0.397   | −0.678   | −0.512   | −0.303   | −0.093   |
| Zn   | −6.377   | 18.945   | −0.898   | −2.099   | 0.937    | 1.974    | −0.577   |
| Pb   | −30.558  | −97.157  | −1.168   | −1.941   | −1.074   | −1.051   | −1.752   |
| Cr   | 2.188    | 5.157    | −0.434   | −0.559   | −0.521   | −0.605   | −0.358   |
| Cd   | $1.081 \times 10^{-5}$ | 5.081   | −4.212   | −3.563   | −3.420   | −2.347   | −3.424   |
| Hg   | $2.153 \times 10^{-4}$ | 78.417   | −0.571   | −1.160   | −0.566   | −0.688   | −0.757   |

The adsorption capacities were enhanced with increasing temperature, which may be due to the endothermic reaction.
change with increasing temperature. The reason why the adsorption capacity of heavy metals in the soil material decreased with increasing temperature may be that adsorption was an exothermic reaction. The increase in temperature was an inhibiting factor for the total amount of heavy metals adsorbed in the soil sample, or it may be that after the adsorption reached a certain temperature, the adsorption process was changed from chemical adsorption to physical adsorption (the desorption rate of heavy metals from soil was greater than the adsorption rate).

3.6. Effect of pH and Electrolyte on Adsorption of Heavy Metals by Lime Soil

The adsorption capacities of Cr decreased with increasing pH, which may be caused by the unique physical properties of Cr. The adsorption capacities of Cu, Zn, Hg and Cd increased with increasing pH, which may be because the increase in pH effectively reduced the concentration of H\(^+\) in the solution. However, soil colloids with a negative charge and heavy metal ions with a positive charge can more effectively increase the adsorption capacity of soil colloids for heavy metal ions; therefore, the adsorption capacities of heavy metal ions increased with increasing pH value. Surprisingly, the capacities of Pb and As were saturated at the beginning of adsorption (Figure 9a). Generally, an increase in pH can promote the adsorption of several heavy metals and inhibit the adsorption of Cr; however, its mechanism still needs to be further investigated. The maximum adsorption capacities of heavy metals in the soil sample were reached at pH = 8.00, which may be related to the physical and chemical properties of the soil material. It was found that the slow adsorption processes emerged at pH < 7.00, implying that the adsorption process of heavy metals in the soil sample was slow under acidic conditions. In contrast, the fast adsorption stage occurred at pH > 7.00, indicating that the adsorption process of heavy metals in the soil was fast under alkaline conditions. The influence of pH on the adsorption of heavy metals by soil particles was generally shown in the following four aspects: the influence on the solubility of heavy metals in solution [48], the influence on the adsorption characteristics of the natural colloid surface in solid particles [49], control of various adsorption reactions on the surface of solid particles, and the increase in pH, which promoted an increase in the adsorption point of the soil colloid since soil colloids generally have a negative charge [50].

Figure 9b exhibits the change in adsorption capacities followed by the different electrolyte concentrations (10\(^{-5}\), 10\(^{-4}\), 10\(^{-3}\), 10\(^{-2}\) and 10\(^{-1}\) mol/L). The adsorption capacities of heavy metals increased with increasing electrolyte concentrations, which may be due to the promotion of the ion activity of heavy metals in the electrolyte. Several heavy metals showed the phenomenon of decreasing first and increasing later with the increase in NaNO\(_3\) concentration, which may be because the inert electrolyte was neutralized by the external negative charge of the soil, reducing the affinity towards heavy metals and the adsorption capacity of heavy metals. Generally, there are three approaches for a soil to adsorb heavy metals: the activity of free heavy metal ions will change because of the effect of ions or the pH by forming ions [51]; inert electrolytes will dissociate into anions and cations, and cations will compete with excessive heavy metal ions or heavy metal ions for adsorption [52]; inert electrolytes will affect the electrostatic point on the surface of the soil colloidal particles since the soil colloid is charged [53].
the influence on the adsorption characteristics of the natural colloid surface in solid particles [49], control of various adsorption reactions on the surface of solid particles, and the increase in pH, which promoted an increase in the adsorption point of the soil colloid since soil colloids generally have a negative charge [50].

Figure 9b exhibits the change in adsorption capacities followed by the different electrolyte concentrations (10$^{-5}$, 10$^{-4}$, 10$^{-3}$, 10$^{-2}$ and 10$^{-1}$ mol/L). The adsorption capacities of heavy metals increased with increasing electrolyte concentrations, which may be due to the promotion of the ion activity of heavy metals in the electrolyte. Several heavy metals showed the phenomenon of decreasing first and increasing later with the increase in NaNO$_3$ concentration, which may be because the inert electrolyte was neutralized by the external negative charge of the soil, reducing the affinity towards heavy metals and the adsorption capacity of heavy metals. Generally, there are three approaches for a soil to adsorb heavy metals: the activity of free heavy metal ions will change because of the effect of ions or the pH by forming ions [51]; inert electrolytes will dissociate into anions and cations, and cations will compete with excessive heavy metal ions or heavy metal ions for adsorption [52]; inert electrolytes will affect the electrostatic point on the surface of the soil colloidal particles since the soil colloid is charged [53].

Figure 9. Adsorption capacities of heavy metals adsorbed on the soil at different pH values (a) and NaNO$_3$ concentrations (b).

4. Conclusions

Topsoil samples collected from Lixisol of Guizhou Province were selected in this study, and the adsorption behavior of heavy metals on the soil samples was explored by indoor simulation. The contents of Cu, Zn, Cd, Cr, Pb, Hg and As in the soil material were 10.8 mg/kg, 125 mg/kg, 0.489 mg/kg, 23.5 mg/kg, 22.7 mg/kg, 58.3 mg/kg and 45.4 mg/kg, respectively. The soil pH values increased with the increase of CaCO$_3$ concentration in the soil, and the fluctuation of the soil pH values was weak after the CaCO$_3$ concentration reached 100 g/kg. The adsorption of lime soil increased by approximately 10 mg/kg on average, and the desorption capacity decreased by approximately 300 mg/kg on average. The desorption of all heavy metals in this study did not change with increasing clay content.

Pseudo-second-order kinetics were more suitable to describe the adsorption kinetics of heavy metals on the soil sample, as evidenced by the higher $R^2$ value. Furthermore, the Freundlich model can better describe the adsorption process of As on lime soil. The process of As, Cr, Cd and Hg adsorption onto the soil material was spontaneous and entropy-driven. Additionally, the process of Cu and Pb adsorption onto the soil sample was spontaneous and enthalpy-driven. It was found that the slow adsorption processes occurred at pH < 7.00, implying that the adsorption process of heavy metals in the soil was slow under acidic conditions. In contrast, the fast adsorption stage occurred at pH > 7.00, indicating that the adsorption process of heavy metals in the soil was fast under alkaline conditions. Generally, the adsorption and desorption of heavy metals in polluted soil increased and decreased,
respectively, with increasing CaCO$_3$ content. The effect of calcium carbonate on the accumulation of heavy metals in soil was greater than that of clay.

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