International Journal of Coal Science & Technology (2022) 9:7
https://doi.org/10.1007/s40789-022-00480-6

RESEARCH

# Adsorption and desorption of Cd in reclaimed soil under the influence of humic acid: characteristics and mechanisms

**Yonghong Zheng[1,2,3] · Zhiguo Zhang[3] · Yongchun Chen[1,2] · Shikai An[1,2] · Lei Zhang[1] · Fangling Chen[1] · Chengnan Ma[1] · Weiqing CAi[1]**

Received: 30 May 2021 / Accepted: 26 January 2022

**Abstract**

Exogenous humus can change the content and migration activity of cadmium (Cd) in soil. Humic acid (HA) is an important soluble humus component in soil. In order to explore the relationship between cadmium pollution mechanism and ecological environment of humic acid in reclaimed soil, the characteristics of humic acid adsorbing cadmium in alkaline conditions were studied. This study employed reclaimed soil from the Huainan mining area, China. The adsorption and desorption characteristics as well as influence mechanisms on the heavy metal cadmium (Cd) were explored under the influence of HA. The results show that: (1) When Cd concentration was low (0.2–10 mg/L), HA had little effect on Cd adsorption and desorption in reclaimed soil. When the Cd concentration was high (15–80 mg/L), HA had a great influence on the adsorption and desorption of Cd in reclaimed soil. The addition of HA can inhibit the adsorption of Cd by reclaimed soil and effectively improve the desorption capacity of Cd by reclaimed soil. (2) The kinetic curves of Cd adsorption and desorption of reclaimed soil with added HA show that both processes (adsorption and desorption) include two stages: rapid reaction and slow reaction. The adsorption of Cd by reclaimed soil under the influence of HA was 18.18% lower than that of normal reclaimed soil, and the increase of Cd desorption was 50.29%. (3) The factors affecting the adsorption and desorption of Cd in the soil were analyzed with gray theory, and their importance can be ordered as follows: Cd concentration > HA concentration > pH > temperature. Considering the influence of HA, a multi-factor coupling function model of adsorption and desorption of Cd in soil is established. This model provides theoretical guidance for the scientific prediction and evaluation of Cd environmental pollution risks in soil and will be useful for developing a new solution for engineering remediation of high concentration Cd contaminated soil.

**Keywords** Reclaimed soil · Humic acid · Heavy metal · Cadmium · Adsorption · Desorption

## 1 Introduction

Huainan mining area is one of China's main coal production bases and a major engineering construction area (Zhang et al. 2018). The mining of coal resources produces considerable solid waste in the form of coal gangue, resulting in expanding land subsidence areas. Since 2003, Huainan mining area is employing coal gangue filling and soil covering technology to backfill subsidence terrain to the original surface elevation. The recovered subsidence land has been reused since then. However, land reclamation activities have had a considerable impact on the soil quality of the mining area and have resulted in low soil nutrient content, soil densification, and a tendency of soil to harden. The potentially incurred heavy metal pollution, especially cadmium (Cd) pollution, has exceeded the risk screening value of agricultural land soil pollution (Yao et al. 2010; Zhang et al. 2010; Li et al. 2008; Xie et al. 2020). An ecological risk assessment of reclaimed soil from the Huainan coal mine area by Jiang et al. (2013) showed that the potential ecological risk imposed by Cd was highest and was 2.57 times higher than that of unreclaimed areas. Lu et al. (2020) evaluated the ecological risk of reclaimed mining areas by the Nemero

---

✉ Zhiguo Zhang
zzgaust@aust.edu.cn

[1] Huainan Mining (Group) Co. LTD, Huainan 232001, China

[2] National Engineering Laboratory for Protection of Colliery Eco-Environment, Huainan 232001, China

[3] School of Earth and Environment, Anhui University of Science and Technology, Huainan 232001, China

comprehensive pollution index method, and found that reclaimed sites reached alert level.

Humic substances are organic compounds originating from natural organic matter formed by animals, plants, and microbial residues under the action of biological and non-biodegradation and polymerization (Li et al. 2020; Liu et al. 2019). Humus is the most abundant form of organic matter in ecosystems and exerts an important impact on ecological functions such as biogeochemical element cycling (Feng et al. 2018). Humic acid (HA) is an important soluble component of humus in soil, with wide distribution not only in soil, but also in lakes (Ba et al. 2019), coal strata (Madiha et al. 2021), and other environments. HA promotes the formation of soil aggregates (Ahmad et al. 2015), plant root growth (Gholami et al. 2018), soil nitrogen and phosphorus activities (Zhang et al. 2019), and crop yield. HA also plays an important role in global carbon and nitrogen cycles, mineral complexes, plant growth, soil fertility improvement applications, and the prevention of soil degradation (Madiha et al. 2021). HA is a polymer organic compound with colloidal properties in solution. It has large specific surface area, complex surface structure, and numerous functional groups (Ali et al. 2020), including carboxyl, hydroxyl, carbonyl, phenolic, aliphatic, and aromatic structures (Doskočil et al. 2018; Hirakendu et al. 2019; Martina et al. 2018; Hongcheng et al. 2019). HA itself has the characteristics of good adsorption capacity, hydrophilicity, as well as weak acidity and complexation ability (Zhao et al. 2020). HA adsorbed by soil particles adsorbs soil heavy metals through its surface charge and forms a complex with heavy metals through its surface functional groups, which prevent the migration of pollutants. This process is of great significance for reducing or eliminating heavy metal pollution in soil (Besnard et al. 2001). The adsorption of heavy metals by HA is mainly affected by pH, temperature, ionic strength, and ion concentration (Mou et al. 2019; Uddin et al. 2017).

Zou (2018) showed that the content of available Cd decreases with the addition of HA, and over time, Cd gradually transforms to its residual state. Qiu et al. (2020) studied the adsorption characteristics of lead and copper by HA extracted from tropical secondary rain forest soil. The results showed that the adsorption mode was mainly chemical, and the binding ability of HA to lead was higher than that to copper. HA was extracted from humus by the alkali-soluble acid precipitation method. The adsorption characteristics and action mechanism of HA on $Cu^{2+}$, $Pb^{2+}$, and $Cd^{2+}$ were studied and the results showed that the adsorption intensity of HA on heavy metals followed $Cu^{2+} > Pb^{2+} > Cd^{2+}$ (Zhu et al. 2008).

At present, research on soil HA both in China and internationally mainly focuses on the distribution and composition characteristics of HA in soil, the adsorption characteristics of HA on heavy metals in soil, and the influences of vegetation cover and organic fertilizers on HA. However, studies on the adsorption and desorption characteristics, the main influencing factors, and multi-factor coupling model of HA on heavy metal ions in reclaimed soil are rare. In this paper, the adsorption and desorption characteristics of Cd in reclaimed soil under the addition of HA were studied. Typical reclaimed soil samples of Panyi Mine in Huainan mining area are taken as research object, and a multi-factor coupling model of Cd adsorption and desorption in reclaimed soil is established. This model provides theoretical guidance for the scientific prediction and evaluation of the environmental pollution risk of Cd in reclaimed soil and for the application of remediation technologies for alleviating soil Cd pollution.

## 2 Materials and methods

### 2.1 Study area

The Panyi Mine Reclamation Area is located approximately 1.0 km east of the Panyi Mine, in the Panji District, Huainan City, China. A coal gangue hill is located at the southern side of the reclamation area. This reclamation area was formed by the filling and rolling of coal gangue into the coal mining subsidence area. Coal gangue is covered by clay with a design thickness of 100 cm. This region belongs to the warm temperate semi-humid continental monsoon climate zone. The soil types are sandy ginger loess and silty clay, and the parent material is loess ancient river sediment (Zheng et al. 2013, 2020). The average annual temperature is 15.3 °C, with the highest and lowest temperatures occurring in July and January, respectively, and the average annual precipitation is 926 mm.

### 2.2 Collection and analysis of samples

#### 2.2.1 Sample collection

Three sampling lines were established in the Panyi Mine Reclamation Area. Along each line, a sampling point was established every 5 m, for a total of 60 sampling points. At each sampling point, a soil heavy metal sampler was used and the top 0–20 cm layer of reclaimed soil was collected. Reclaimed wasteland was selected as control and soil samples were collected, with each sample not less than 1 kg. The study area and sampling profile of reclaimed soil are shown in Fig. 1.

#### 2.2.2 Sample conditioning

After removing impurities, soil samples were crushed and paved on a soil drying plate where they were dried naturally, and then screened by the four-point method. Samples were

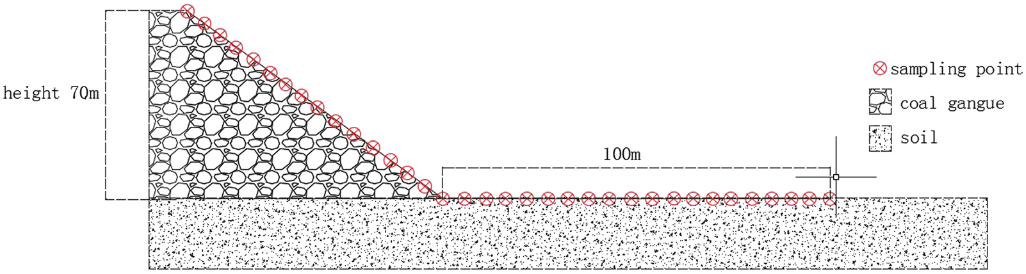

**Fig. 1** Sampling profile

ground by an agate bowl, and passed through 10 mesh, 18 mesh, and 60 mesh nylon screens. Samples were packed in a bag and labeled for further tests.

### 2.2.3 Sample analysis and test

To determine the level of Cd in reclamation soil samples, an atomic absorption spectrophotometer (American PE company AA800) was used. The physical and chemical indicators of reclaimed soil were tested by soil agrochemical analysis methods (Bao 2000).

## 2.3 Experimental method

### 2.3.1 Isothermal adsorption and desorption of Cd in reclaimed soil with added HA

A given sample of reclaimed soil (1.000 g, which was passed through an 18-mesh screen) was weighed and placed in a 50 mL centrifuge tube. Then, 20 mL of a $Cd(NO_3)_2$ solution with a Cd concentration of either 0, 0.2, 0.4, 0.6, 0.8, 1, 1.5, 2, 2.5, 3, 4, 5, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, or 80 mg/L was added to the centrifuge tube. This was followed by the addition of 1 mL of HA solution with a concentration of 10 mg/L. The centrifuge tube was immediately capped, shaken at 200 r/min at a constant temperature of 25 °C for 24 h, and then centrifuged at 4000 r/min for 20 min. The supernatant of the centrifuge tube was filtered through a 0.45 um filter membrane, and the filtrate was shaken with one drop of 1% nitric acid to determine the concentration of Cd. The adsorption capacity of Cd was calculated according to the difference between Cd concentrations before and after adsorption.Add 60 mg/L HA solution and no HA solution adsorption control experiment. Equation (1) was used for calculating the adsorption capacity $Q_a$of Cd:

$$Q_a = \frac{(C_0 - C) \times V}{m} \tag{1}$$

where $C_0$is the concentration of Cd in the initial solution (mg/L), $C$ is the concentration of Cd in the equilibrium solution at adsorption equilibrium (mg/L), $V$ is the initial volume of liquid added (mL), and $m$ is the mass of the sample (g). A control experiment was simultaneously carried out with an HA solution of 60 mg/L.

The desorption experiment was performed upon completion of the adsorption experiment. The reclaimed soil sample after Cd adsorption was washed once with absolute ethanol (to remove any free Cd) and was left to settle at a constant temperature (25 °C) for 1 h. Next, 20 mL of $NaNO_3$ solution (0.01 mol/L) was added to the soil, and the sample was covered and subjected to shaking at 200 r/min at 25 °C for 24 h. The solution was then centrifuged at 4000 r/min for 20 min. Finally, the supernatant was filtered through a 0.45 μm membrane, and one drop of 1% nitric acid was added to the filtrate followed by shaking for Cd determination. The Cd desorption capacity ($Q_d$) was determined via Eq. (2):

$$Q_d = \frac{C' \times V}{m} \tag{2}$$

where $Q_d$ is the equilibrium desorption amount of Cd (mg/kg), $C$, is the concentration of Cd in the filtrate after desorption (mg/L).

The Cd desorption rate ($W$) was calculated according to Eq. (3):

$$W = \frac{Q_d}{Q_a} \times 100\%. \tag{3}$$

### 2.3.2 Adsorption and desorption kinetics of Cd in reclaimed soil under HA addition

A total of 1.000 g of soil sample (passed through an 18-mesh sieve) was weighed, placed in a 50 mL centrifuge tube, and 20 mL Cd $(NO_3)_2$ solution was added with a Cd concentration of 30 mg/L. Then, 1 mL HA solution with a Cd concentration of 60 mg/L was added to each centrifuge tube and shaken at 25 °C and 200 r/min. Samples were taken at 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 22, and 24 h and centrifuged at 4000 r/min for 20 min. The supernatant in the centrifuge tube was filtered through a 0.45 um filter membrane, and the filtered solution was shaken with one drop of 1% nitric acid to determine the Cd concentration. According to the difference between Cd concentration before and after adsorption, the Cd adsorption amount was calculated according to Equation (1). The control experiment was conducted without HA addition.

The desorption kinetics experiment was carried out after the completion of the adsorption experiment. Soil that had absorbed Cd was washed once with anhydrous ethanol to remove free Cd and placed at constant temperature (25 °C) for 1 h. Then, 20 mL of 0.01 mol/L $NaNO_3$ solution was added, and the solution was covered and subjected to shaking at 25 °C (200 r/min). The solution was removed at 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 22, and 24 h and centrifuged at 4000 r/min for 20 min. The supernatant in the centrifuge tube was filtered through a 0.45 um filter membrane, and the filtered solution was shaken with one drop of 1% nitric acid to determine the concentration of Cd. The Cd desorption amount was calculated according to Equation (2).

HA used in the experiment was extracted and purified from HA (Anhui Cool Bioengineering Co., Ltd., purity of 70%). The extraction and purification method followed the recommendation of the International Humic Acid Association (Wen et al. 1982; Liu et al. 2016).

### 2.4 Quality control

The wavelength of the instrument is 228.8 nm, and the minimum detection limit is 0.002 μg/L. In order to control the accuracy of the instrument and the quality of the analysis and testing of the samples, the determination results of the soil samples adopt the national soil effective component analysis standard material (GBW07461) for quality control. The standard substance was tested 3 times and the relative standard deviation (RSD) was calculated. The results showed that the average value of standard substance Cd was within the given range of certificate (0.049 ± 0.003 mg), and the relative standard deviation was 1.2%–2.3%, indicating that the method had high precision and good reproducibility, which could meet the requirements of analysis and test.

Three portions of 1.000 g soil samples were weighed and added with 1 mg/L, 2 mg/L and 5 mg/L Cd standard solution for standard addition recovery experiment. The results showed that the recovery rate was between 93% and 104%, and the quality of analysis and detection was effectively guaranteed.

### 2.5 Data processing

SPSS 24.0 software was used for the statistical analysis of data, Origin 8.0 software was used for visualizing data, and MATLAB 2014B software was used to compile the corresponding calculation program for gray correlation analysis.

## 3 Results and discussion

### 3.1 Physical and chemical properties of reclaimed soil

The results in Table 1 show that reclaimed soil had an average pH of 7.92 (weakly alkaline). The salt content ranged between 0.74–1.06 g/kg (average of 0.82 g/kg), which was higher than the soil control point value. According to the second soil survey nutrient classification standard of China (National Soil Survey Office 1992), an organic matter content between 0.53 and 3.88% (average of 1.06%) is at a relatively deficient level. Alkaline nitrogen content of 18.79–56.88 mg/kg (average of 38.14 mg/kg) is at a deficient level. The available potassium content was 81.51–148.02 mg/kg (average of 127.28 mg/kg), which is a medium level. The content of available phosphorus was 2.83–6.59 mg/kg (average of 5.78 mg/kg), which is a relatively low level. Overall, nutrient levels in soil from the Panyi Mine reclamation area are relatively low, and to improve plant growth conditions and better promote plant growth, soil should be fertilized. Soil pollutants in the reclamation area mainly originate from the migration and enrichment of salt and heavy metals because of the storage of coal gangue (Zhang et al. 2018).

**Table 1** Physical and chemical properties of reclaimed soil

| Statistical analysis | pH | Organic matter (%) | Alkaline hydrolysis nitrogen (mg/kg) | Rapidly available potassium (mg/kg) | Available phosphorus (mg/kg) | Salt content (g/kg) |
|---|---|---|---|---|---|---|
| Maximum value | 8.46 | 3.88 | 56.88 | 148.02 | 6.59 | 1.06 |
| Minimum value | 6.76 | 0.53 | 18.79 | 81.51 | 2.83 | 0.74 |
| Mean value | 7.92 | 1.06 | 38.14 | 127.28 | 5.78 | 0.82 |
| Deviation | 0.36 | 1.08 | 8.27 | 16.26 | 1.56 | 0.11 |
| Control point | 7.86 | 0.85 | 47.13 | 122.40 | 6.27 | 0.53 |

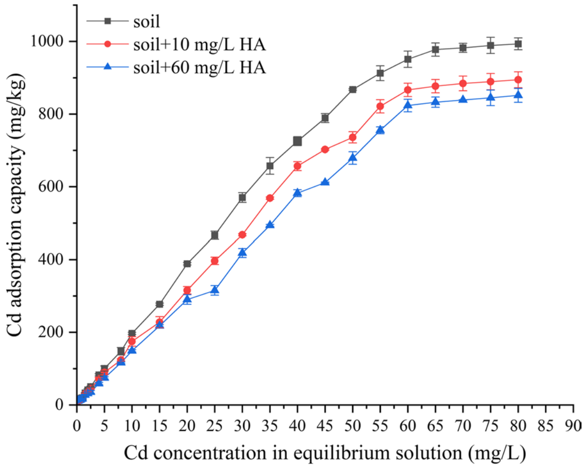

**Fig. 2** Cd adsorption capacity versus the Cd concentration in solution in the presence and absence of HA

## 3.2 Characteristics and mechanism of isothermal Cd adsorption under HA addition

Figure 2 shows the isothermal adsorption line of Cd for reclaimed soil under the addition of HA. The concentration of Cd in the equilibrium solution increased, and the adsorption capacity of reclaimed soil for Cd increased gradually. At a low Cd concentration (i.e., 0.2–10 mg/L), the amount of adsorbed Cd was similar regardless of whether HA was present or absent. Thus, under low Cd concentrations, HA had little effect on the ability of reclaimed soil to adsorb Cd. By contrast, at a Cd concentration of 15–80 mg/L, HA presence significantly reduced the adsorption of Cd by reclaimed soil, and the amount of adsorbed Cd decreased with increasing concentration of added Cd. Thus, HA addition significantly inhibits the adsorption of Cd by reclaimed soil. Notably, high HA concentration (60 mg/L) had a stronger effect than low concentration (10 mg/L). HA has abundant benzene rings, carboxyl groups, alcoholic hydroxyl groups, phenolic hydroxyl groups, and amino groups, all of which can undergo exchange, adsorption, and chelation reactions with various heavy metals (Ma et al. 2020; Xu et al. 2008; Huang 2020). These sites compete with reclaimed soil for the adsorption of Cd, thereby reducing the Cd amount soil adsorbed. The ionization of $H^+$ in the oxygen-containing functional groups of HA reduces the pH of the reclaimed soil solution, thereby changing the metal solubility and further reducing the Cd adsorption capacity of soil (Li et al. 2018; Yang 2018; Yan 2019; Jagadamma et al. 2014). Furthermore, HA, which is rich in anionic groups (e.g., phenolic, hydroxyl, and carboxyl groups) occupies the soil seat sites quicker than Cd via soil surface adsorption (He et al. 2020; Izosimova et al. 2020), thereby reducing the Cd adsorption capacity of reclaimed soil. This interpretation of results is consistent with previous findings, indicating that HA exerts a significant inhibitory effect on Cd adsorption in soil (Bi et al. 2018).

## 3.3 Characteristics and mechanism of isothermal Cd desorption under the addition of HA

As shown in Fig. 3, with increasing concentration of Cd in the equilibrium solution, the Cd desorption capacity of reclaimed soil gradually increased. At a low Cd concentration (0.2–10 mg/L), the amounts of desorbed Cd were similar irrespective of whether HA was present. Thus, under low Cd concentrations, HA did not noticeably affect the ability of reclaimed soil to desorb Cd. However, at a Cd concentration of 15–80 mg/L, HA presence significantly increased the desorption of Cd in reclaimed soil, and the amount of desorbed Cd increased with increasing Cd concentration. Because of the differences in physical and chemical properties of reclaimed soils, HA exerted different effects on the desorption capacity of soil. The desorption capacity of HA at different concentrations on Cd was also largely different. With increasing HA concentration, heavy metals were increasingly released from soil (Gao et al. 2011; Huang et al. 2012; Liu et al. 2016). Using a high HA concentration (60 mg/L) produced a larger effect than a low concentration (10 mg/L).

The desorption rate of Cd from reclaimed soil increased after HA addition (Fig. 4). The Cd desorption rate of reclaimed soil increased by 3.21% on average under the influence of HA. The adsorption process of Cd is dominated by chemical bonding and electrostatic attraction. The activation energy required for adsorption is low, while the adsorption affinity is high. By contrast, the desorption process of Cd is an ion exchange process. Organic ligands contained

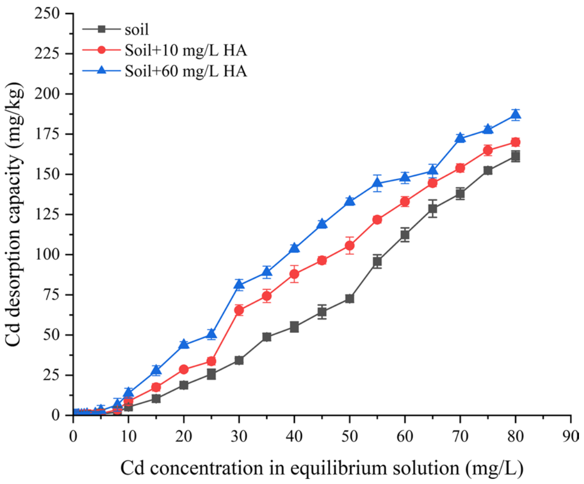

**Fig. 3** Cd desorption capacity versus Cd concentration in solution in the presence and absence of HA

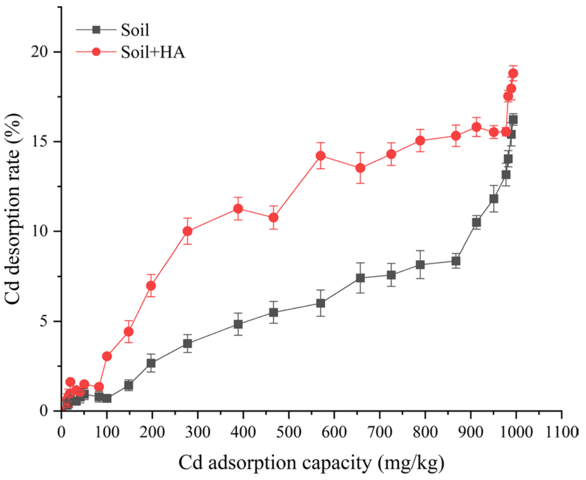

**Fig. 4** Cd desorption rate versus Cd adsorption capacity for reclaimed soil in the presence and absence of HA

in organic acids can form soluble organometallic complexes with Cd, thereby reducing Cd adsorption in reclaimed soil (Hu et al. 2013; Kou et al. 2019). Moreover, protons in HA can activate Cd in reclaimed soil which further promotes its desorption (Xu et al. 2015).

### 3.4 Kinetics and mechanism of Cd adsorption and desorption under HA addition

The adsorption kinetics curve and desorption kinetics curve of Cd in soil with added HA are shown in Figs. 5 and 6, respectively.

As depicted in Fig. 5, the adsorption process of Cd in HA containing reclaimed soil was the same as in soil without HA addition. Adsorption began with a fast adsorption stage, which lasting only 0–1 h, followed by a slow adsorption stage lasting 1–12 h. In the fast absorption stage, the adsorption capacity of Cd in reclaimed soil increased rapidly. In the slow absorption stage, the adsorption rate of Cd continued to increase, but the increase rate was slow. Compared with the adsorption of Cd on normal reclaimed soil, the adsorption rate also became slow, and the adsorption equilibrium was basically reached after 12 h. when compared with normal (i.e., untreated) reclaimed soil, Cd adsorption was significantly reduced in HA containing soil samples. Under the influence of HA, Cd adsorption was reduced by 17.06%–18.80% (average of 18.18%). These results demonstrate that HA can change the migration behavior of Cd in the reclaimed soil by affecting its adsorption.

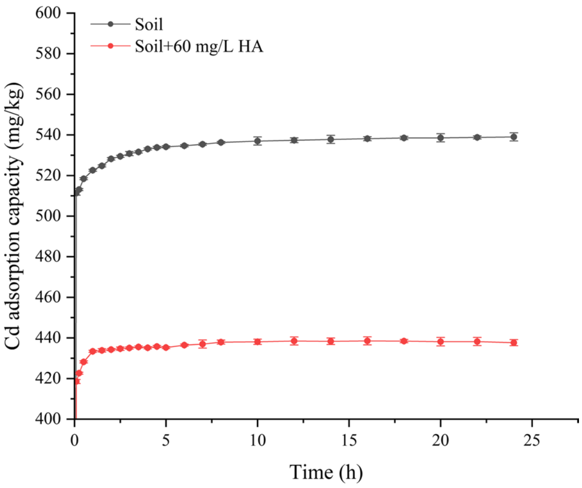

**Fig. 5** Kinetic curves of Cd adsorption in reclaimed soil in the absence and presence of HA

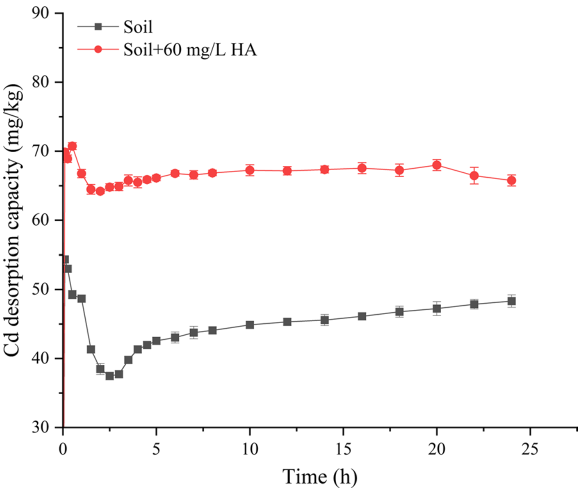

**Fig. 6** Kinetic curves of Cd desorption from reclaimed soil in the presence and absence of HA

Under the influence of HA, over time, the Cd desorption capacity in reclaimed soil first decreased and then increased, showing two distinct desorption stages (Fig. 6): a fast reaction stage at the beginning of the experiment (0–2 h), followed by a slow reaction stage (2–12 h). Within the first 2 h, the desorption capacity diminished rapidly, reaching its lowest value at 2 h. In the subsequent slow reaction stage, the desorption capacity increased slowly, and reached equilibrium after approximately 12 h. Addition of HA significantly increased the desorption capacity of Cd in reclaimed soil. HA addition increased the Cd desorption capacity by 28.51%–72.98% (average of 50.29%). These results demonstrate that HA addition alters the migration activity of Cd in reclaimed soil by affecting the desorption of Cd.

### 3.5 Function model of adsorption and desorption of Cd under HA addition

The results of regression analysis show that the logarithmic function model ($Y = a\ln X + b$) achieves the best match,

**Table 2** Logarithmic function model of HA concentration ($Y$) and adsorption desorption quantity

| Dynamic process | Functional equation | $R^2$ | $N$ |
|---|---|---|---|
| Adsorption model | $Y=-28.3\ln X+610.26$ | 0.9943 | 27 |
| Desorption model | $Y=5.5037\ln X+34.855$ | 0.9532 | 27 |

and can thus be used to describe the relationship between HA concentration and Cd adsorption and desorption. In this model, a and b reflect the differences of HA behavior in reclaimed soil, and the function model reflects the relative strength of adsorption and desorption ability of HA for Cd in reclaimed soil. The specific function model is shown in Table 2.

The established logarithmic function model is suitable for describing the Cd adsorption and desorption in reclaimed soil under the addition of HA. By changing the values of a and b, the Cd adsorption and desorption amount of reclaimed soil under the influence of different concentrations of HA can be calculated.

## 3.6 Multi-factor coupling model of Cd adsorption and desorption in soil

As soil is a complex open multi-phase system, due to differences in soil-formation effects, soil types, particle fractions, and texture components differ widely; thus, many factors affect the adsorption and desorption of Cd. The effects of HA concentration, Cd concentration, pH value, and temperature on the adsorption and desorption mechanism of Cd in soil were studied. Using the grey correlation analysis method, the significant influencing factors were identified, and a multi-factor coupling model suitable for coal gangue weathering-soil system in coal mine reclamation area was established.

### 3.6.1 Grey relational analysis

According to the results of Cd adsorption, desorption, and various factors of reclaimed soil obtained experimentally, 60 samples were analyzed. The number of sorting sequences was $m=4$ (HA concentration, Cd concentration, temperature, and pH value). The resolution coefficient was set as $\rho=0.5$. The grey correlation degrees of HA concentration, Cd concentration, temperature, and pH value were calculated by MATLAB 2014B and results are listed in Table 3. The rank order of influencing factors of Cd adsorption and desorption follows: Cd concentration > HA concentration > pH > temperature. These results indicate that among considered factors that influence the adsorption and desorption of Cd, Cd concentration was the decisive factor, followed by HA concentration, pH value, and temperature.

**Table 3** Correlations of influencing factors of coal gangue weathering matter and soil

| Dynamic process | Correlation degree | | | |
|---|---|---|---|---|
| | HA | Cd | Temperature | pH |
| Soil adsorption | 0.7199 | 0.8762 | 0.6369 | 0.7033 |
| Soil desorption | 0.7666 | 0.9184 | 0.6922 | 0.7562 |

### 3.6.2 Multiple regression analysis

The multiple linear regression model is a linear regression model with multiple explanatory variables, which is commonly used for identifying the linear relationship between explanatory variables and multiple explanatory variables. In the 95% confidence interval, the multiple linear regression method (Enter) between the four factors of HA concentration, Cd concentration, pH, and temperature was used to establish the best adsorption model. In the function model, $Y$ is the adsorption amount of Cd in solution, $X_{\mathrm{HA}}$ is the concentration of HA, $X_{\mathrm{Cd}}$ is the concentration of Cd in solution, $X_{\mathrm{T}}$ is the solution temperature, and $X_{\mathrm{pH}}$ reflects the acidity and alkalinity of the solution. The function model is shown in Table 4. The fitting effect of this soil adsorption–desorption model is very good. In addition, the established function model (Eq. (4)) was used to predict and calculate the relative error between the predicted value and the measured value.

$$\text{relative error}(\%)=\frac{\text{predicted value}-\text{measured value}}{\text{predicted value}}\times 100\% \tag{4}$$

The result indicates that the function model predicts the changes of Cd adsorption and desorption under the influence of multiple factors well, as shown in Table 5.

The adsorption and desorption of Cd in soil is determined by the Cd concentration, HA concentration, pH value, and temperature. The above model can be used to predict and confirm the characteristics of Cd adsorption and desorption in the Huainan reclamation area (and other areas with similar soil conditions).

### 3.6.3 Three-dimensional (3D) diagrams of the multi-factor coupling function model

In this paper, MATLAB 2014B software was used to draw the 3D graphs of each multi-factor coupling model, because this can more clearly and intuitively describe the relationships between the adsorption or desorption capacity for Cd and various factors influencing in soil. According to the multi-factor coupling model $Y=-32.176-2.024X_{\mathrm{HA}}+1.325X_{\mathrm{T}}+18.352X_{\mathrm{PH}}+14.974X_{\mathrm{Cd}}$, the 3D diagrams were drawn, as shown in Figs. 7, 8, 9 and 10.

**Table 4** Multi-factor coupling model for the adsorption and desorption of Cd in coal gangue weathering matter and soil

| Sample | Type | Multiple linear regression model | $R^2$ | F | *P* |
|---|---|---|---|---|---|
| Soil | Adsorption model | $Y=-32.176-2.024X_{HA}+1.325X_T+18.352X_{pH}+14.974X_{Cd}$ | 0.991 | 914.00 | 0 |
| | Desorption model | $Y=36.368+0.047X_{HA}-0.590X_T-3.556X_{pH}+2.373X_{Cd}$ | 0.987 | 672.90 | 0 |

**Table 5** Comparison of observed and predicted values of the multiple linear regression model

| Type | Relative error (%) |
|---|---|
| Cd adsorption capacity of soil | –2.97 – 1.74 |
| Cd desorption capacity of soil | –3.01 – 3.20 |

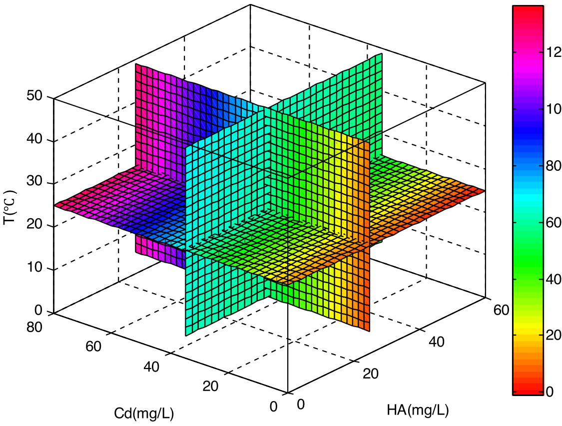

**Fig. 9** The coupling of HA, Cd, and *T* at pH = 7.5

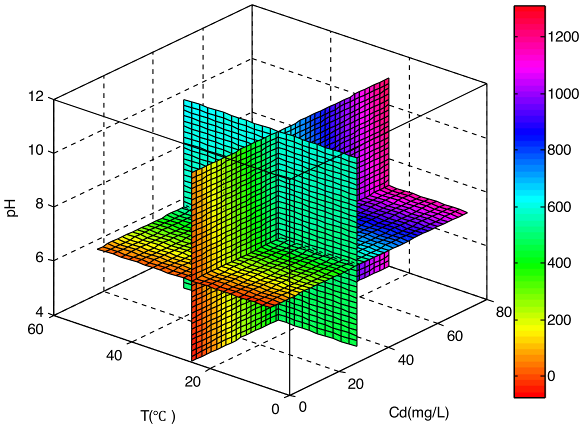

**Fig. 7** The coupling of *T*, pH, and Cd at HA = 60 mg/L

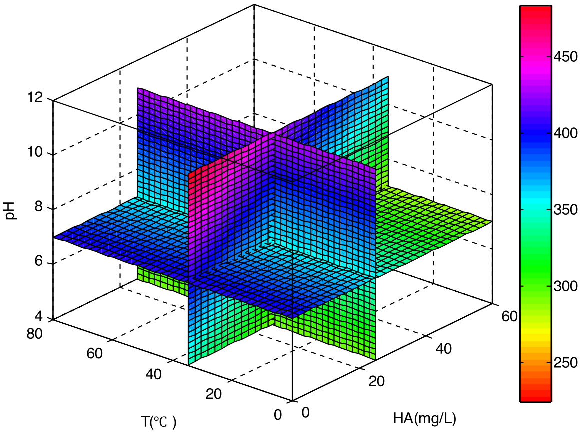

**Fig. 10** The coupling of HA, *T*, and pH at Cd = 20 mg/L

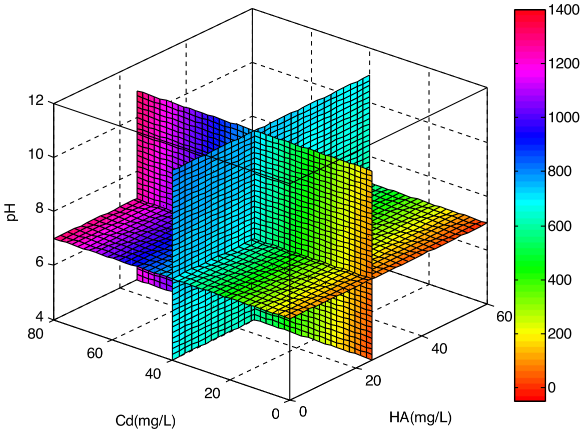

**Fig. 8** The coupling of HA, pH, and Cd at *T* = 25 °C

Figure 7 shows that when the HA concentration is 60 mg/L, the adsorption capacity of Cd is strengthened by an increasing Cd concentration; with a greater pH value, the adsorption capacity of Cd is also enhanced; further, with a higher temperature, the adsorption capacity of Cd is enhanced as well. Figure 8 shows that when the temperature is 25 °C, with an increasing HA concentration, the adsorption capacity of Cd decreases; however, with an increased Cd concentration, the adsorption capacity of Cd is augmented; similarly, with an increased pH value, the adsorption capacity of Cd is also augmented. Figure 9 shows that when the pH value is 7.5, increasing the HA concentration decreases

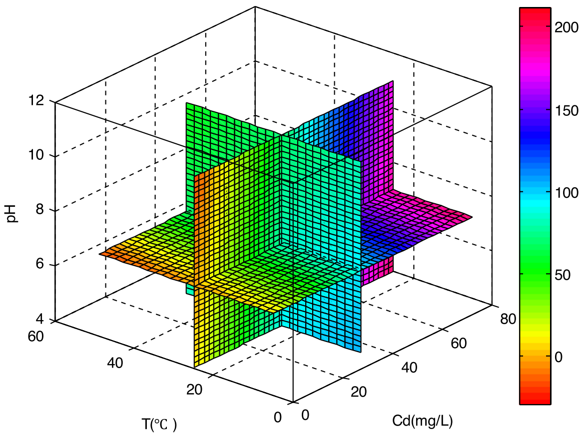

Fig. 11 The coupling of *T*, pH, and Cd at HA = 60 mg/L

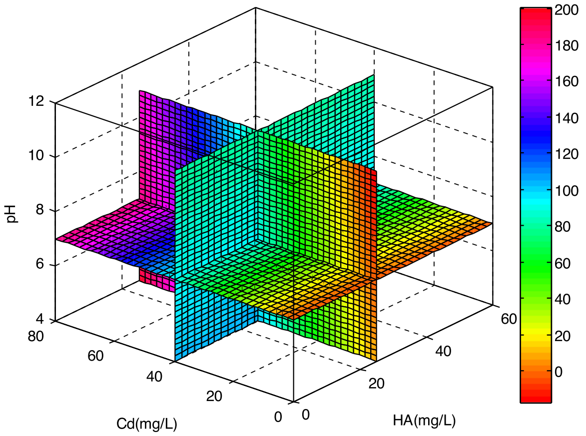

Fig. 12 The coupling of HA, pH, and Cd at *T* = 25 °C

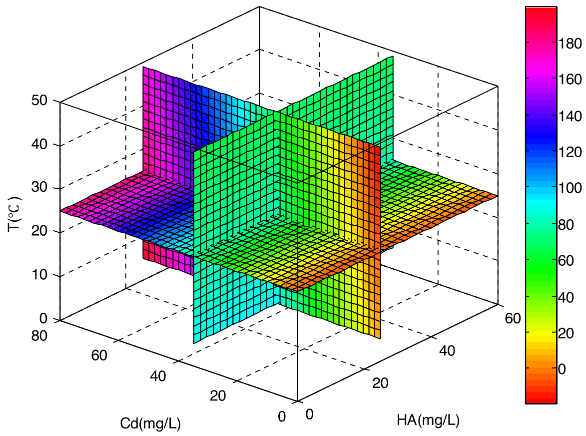

Fig. 13 The coupling of HA, Cd, and at pH = 7.5

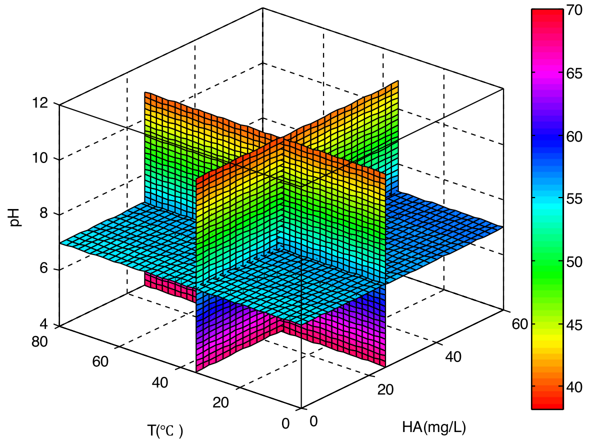

Fig. 14 The coupling of HA, *T*, and pH at Cd = 20 mg/L

the adsorption capacity of Cd in soil; conversely, with an increased Cd concentration or temperature, the adsorption capacity of Cd is also increased. Figure 10 shows that when the Cd concentration is 20 mg/L, the adsorption capacity of Cd decreases with as the HA concentration increases; but with a greater pH value or higher temperature, the adsorption capacity of Cd increases.

According to the multi-factor coupling model $Y = 36.368 + 0.047X_{\mathrm{HA}} - 0.590X_{\mathrm{T}} - 3.556X_{\mathrm{PH}} + 2.373X_{\mathrm{Cd}}$, the 3D diagrams were drawn, as shown in Figs. 11, 12, 13 and 14.

Figure 11 shows that when HA concentration is 60 mg/L, the desorption of Cd increases with an increasing Cd concentration; but with a rising pH or temperature, the desorption of Cd decreases. Figure 12 shows that when the temperature is 25 °C, the desorption of Cd is enhanced by increasing concentrations of HA or Cd, whereas with a greater pH value, the desorption of Cd is diminished. Figure 13 shows that when the pH value is 7.5, the desorption of Cd increases with an increasing HA concentration; likewise, with an increase in the Cd concentration, the desorption of Cd also increases; however, with a rising temperature, the desorption of Cd decreases. Finally, Fig. 14 shows that when the concentration of Cd is 20 mg/L, the desorption of Cd increases with an increasing HA concentration, whereas with either an increase in the pH value or temperature, the desorption of Cd decreases.

## 4 Conclusions

(1) The addition of HA (a representative of humic substances) can inhibit the adsorption of Cd by reclaimed soil and improve Cd desorption. These effects are stronger under high concentrations of HA compared with low concentrations of HA. The adsorption and desorption kinetics of Cd by reclaimed soil under the addition of HA has two stages:

a rapid reaction stage and a slow reaction stage. Both stages tend to be balanced after 12 h.

(2) The influencing factors of Cd adsorption and desorption in reclaimed soil can be ranked as follows: Cd concentration > HA concentration > pH > temperature. The results of regression analysis were used to establish a multi-factor coupling function model of Cd adsorption and desorption in reclaimed soil under the influence of HA. This model can be used for quantitatively predicting the Cd adsorption and desorption characteristics of soil in Huainan reclamation area. This model has practical significance for the prevention and remediation of heavy metal pollution, not just in this area, but also in other areas with similar soil conditions.

(3) Cd mobility in soil can be improved by adjusting the content of HA in soil, and Cd removal can be achieved in combination with phytoremediation technology. For example, Cd hyperaccumulators can be planted on contaminated soil, and Cd desorption and dissolution can be enhanced by regulating HA concentration. Plants absorb Cd through roots and transfer it to other plant organs where it accumulates. Centralized harvesting treatment could be conducted to completely remove Cd pollution from soil.

**Acknowledgements** This research was supported by the National Natural Science Foundation of China (No. 51904014), the Natural Science Research Project of University in Anhui Province (No. KJ2018A0072), and the Postdoctoral Foundation of Anhui Province (No. 2019B337). The authors appreciate the constructive comments from an anonymous reviewer.

## References

Ahmad I, Ali S, Khan KS, Hassan FU, Ijaz SS, Bashir K et al (2015) Use of coal derived humic acid as soil conditioner for soil physical properties and its impact on wheat crop yield. Int J Biosci 6:81–89

Ali J, Li Y, Wang X, Zhao J, Xi N, Zhang Z et al (2020) Climate-zone-dependent effect mechanism of humic acid and fulvic acid extracted from river sediments on aggregation behavior of graphene oxide. Sci Total Environ 721:137682

Ba C, Zhang Y, Yang F, Kong M, Zhang Z, Tang Z, Gu S (2019) Changes of humic acid in the process of decomposition of *Myriophyllum spicatum*. China Environ Sci 39(3):1226–1236

Bao (2000) Soil and agricultural chemistry analysis. China Agricultural Press, Beijing

Besnard E, Chenu C, Robert (2001) Influence of organic amend-ments on copper distribution among particle-size and density fraction sin Champagne vineyard soils. Environ Pollut 112(3):329–337

Bi D, Deng Y, Meng F, Wei J, Wang H, Yuan G (2018) Humic nanoparticles for remediation of Cd-contaminated soils. Chin J Environ Eng 12(05):1295–1302

Doskočil L, Burdíková-Szewieczková J, Enev V, Kalina L, Wasserbauer J (2018) Spectral characterization and comparison of humic acids isolated from some European lignites. Fuel 213:123–132

Feng P, Zhang Y, Tian S et al (2018) Availiability and influencing factors of trace elements in humus layer of broad-leaved *Pinus koraiensis* Forest in Northeast China. J Shenyang Univ (natl Sci) 30(5):361–365

Ghani MJ, Akhtar K, Khaliq S, Akhtar N, Ghauri MA (2021) Characterization of humic acids produced from fungal liquefaction of low-grade Thar coal. Process Biochem 107:1–12

Gholami H, Raouf Fard F, Saharkhiz MJ, Ghani A (2018) Yield and physicochemical properties of inulin obtained from Iranian chicory roots under vermicompost and humic acid treatments. Ind Crop Prod 123:610–616

He J, Lu H, Zhang N (2020) Advanced research on application of humic acid in haevy metal contanminated soil remediation. Humic Acid 2:38-42+55

Hirakendu B, Sudeshna S, Iyer AM, Mehzabin VP, Rakesh KS (2019) Humic acid coated cellulose derived from rice husk: a novel biosorbent for the removal of Ni and Cr. J Water Process Eng 32:100892

Hongcheng B, Shiqiang W, Zhenmao J, Mingjing H, Biying Y, Gaoyun L (2019) Pb(II) bioavailability to algae (*Chlorella pyrenoidosa*) in relation to its complexation with humic acids of different molecular weight. Ecotoxicol Environ Saf 167:1–9

Hongwei Li, Shilong Y, Longpeng C (2008) Evaluation of soil heavy metal pollution in Xinji Mining Area of Huainan. Min Saf Environ Protect 35(1):36–37

Hu J (2013) Effect of typical organic ligands on the adsorption of Cd to natural biofilms. Jilin University

Huang J (2020) Effects of organic acids on Cd migration and accumulation in soil-rice systems. Central South University of Forestry and Technology, Hunan

Huang S, Zhang R, Zhang J, Pan R (2012) Effects of physical and chemical characteristics of soils on the adsorption of Cd. J Irrig Drain 31(1):19–22

Izosimova Y, Tolpeshta I, Gurova I et al (2020) Sorption of Cu2+ ions by bentonite modified with Al Keggin cations and humic acid in solutions with pH 4.5. Minerals 10(12):1121

Jagadamma S, Maye MA, Zinn YL (2014) Sorption of organic carbon compounds to the fine fraction of surface and subsurface soils. Geoderma 213(1):79–86

Jiang P, Fang F, Zheng J, Lin Y, Deng Z, Wu L (2013) Distribution and potential ecological risk assessment of soil heavy metals in reclaimed land in huainan coal mine. Bull Soil Water Conserv 33(6):161–165

Junjie Li, Jun Z, Li Yu (2018) An exploration and analysis on the impact of dissolved organic matter on the activity of heavy metals in soil. South China Agric 12(13):62–64

Kou L, Zhao K, Cao J, Jin B, Zhou B (2019) The fitting model of low molecular weight organic acid extracts heavy metals in soil. Acta Sci Circum 39(7):2260–2268

Liu M, Wang C, Wang F, Xie Y (2019) Maize (Zea mays) growth and nutrient uptake following integrated improvement of vermicompost and humic acid fertilizer on coastal saline soil. Appl Soil Ecol 142:147–154

Martina K, Michal K, Jirí S, Marcela L (2018) The transport of metal ions in hydrogels containing humic acids as active complexation agent. Colloids Surf A Physicochem Eng Asp 557:116–122

Mou H, Jiang Q, Wu C, Liang X, Huang J, Chen W, Ao T (2019) Study on the adsorption characteristics of cadmium by five soil colloids. J Sichuan Univ (natl Sci Edn) 56(6):1125–1130

Office NSS (1992) China soil survey technology. Agricultural Press, Beijing

Uddin MK (2017) A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem Eng J 308:138

Wen Q (1982) Soil organic matter research method. Agricultural Publishing House, Beijing, pp 234–247

Wu Pingxiao D (2008) A study of heavy metal adsorption on montmorillonite/humic acid complexes. Acta Petrologica Et Mineralogica 27(3):221–226

Xie C, Qin Y, Chao L et al (2020) Applied research on the numerical simulation of Cu and Cd transport laws in a metal mining area. Amer Inst Phys Adv 10(11):2158–3226

Xin L, Sheng D, Changlong Li et al (2016) Effects of reclamation years on humus composition and humic acid structural characteristics of paddy soil. Acta Pedol Sin 53(1):137–145

Xu R, Li X, Shun L (2015) Washing kinetics and mechanism of removing Pb and Cd from the contaminated soil with the organic acids. J Saf Environ 15(3):261–266

Yan A (2019) Adsorption characteristics and mechanism of heavy metals by soil humus. Jiling Agricultural University

Yang Y (2018) Characteristic effect of two organic acids on adsorption-desorption $Zn^{2+}$, $Cd^{2+}$ in tea plantation soil aggregates. Sichuan Agricultural University

Yao D, Meng J, Zhang Z (2010) Heavy metal pollution and potential ecological risk in reclaimed soils in Huainan mining area. J Coal Sci Eng (china) 16(3):316–319

Yong Q, Tian L, Qingjie Z (2020) Characteristic of adsorption of $Pb^{2+}$ and $Cu^{2+}$ onto soil humic acids from tropical rainforest. Hainan Province Ecol Sci 39(01):78–84

Yongfei Ma, XieGuanlei LZ (2020) On the principle of humic acid restoration and food safety. China Food Saf Mag 16:55–57

Yongqiang Lu, Chen Fu, Jing Ma et al (2020) Effects of heavy metals on soil microbial community in reclaimed mining area. Environ Sci Technol 43(3):21–29

Yushuang Li, Siyao L, Xueying S et al (2020) Effect of humic acid on degradation kinetics and microbial activity of DnBP in soil. J Shenyang Univ (natl Sci) 32(2):115–122

Zhang H, Zhou J (2011) Effect of dissolved organic matter on the environmental behaviors of heavy metals in soils. Ecol Environ Sci 20(4):652–658

Zhang Z, Yao D, Zheng Y et al (2010) The phytoremediation potential of six compositae plants to soil pollution of heavy metal in coal mine collapse and reclaimed area. J China Coal Soc 16(3):316–319

Zhang Z, Hu Y, Zheng Y, Chen X (2018) Effect of coal gangue stockpiling on spatial distribution characteristics and main factors of soil salinity. J China Coal Soc 43(4):1118–1126

Zhang S, Yuan L, Li W, Lin Z, Li Y, Hu S et al (2019) Effects of urea enhanced with different weathered coal-derived humic acid components on maize yield and fate of fertilizer nitrogen. J Integr Agric 18:656–666

Zhao M, Huang Z, Wang S, Zhang L, Wang C (2020) Experimental and DFT study on the selective adsorption mechanism of Au(III) using amidinothiourea-functionalized UiO-66-NH2. Microporous Mesoporous Mater 294:109905

Zheng Y, Zhang Z, Yao D, Chen X (2013) Characteristics of temporal-spatial distribution and enrichment of heavy metals in coal mine reclaimed soil. J China Coal Soc 38(8):1476–1483

Zheng Y, Zhang Z, Chen Y et al (2020) Study on effect and evaluation of tree species on reclamation soil fertility quality in coal mining area. Coal Sci Technol 48(4):156–168

Zhu L, Zhang J, Yu Y et al (2008) Characteristics and affecting factors of humic acid adsorbing heavy metals $Cu^{2+}Pb^{2+}Cd^{2+}$. J Agro-Environ Sci 27(6):2240–2245

Zou C (2018) Effects of humic acids from weathered coal sources on the speciation and bioavailability of cadmium in paddy soils. Zhejiang Agriculture & Forestry University, Zhejiang