Adsorption and Desorption of Cd: Characteristics and Mechanisms in Reclaimed Soil Under the Influence of Dissolved Organic Carbon

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Abstract

Organic acids are widespread in the environment, where they play an important role in the adsorption, desorption, and migration of Cd in soil. This study evaluated the characteristics and mechanisms of Cd adsorption and desorption in reclaimed soil from the Panyi Mine, in the Huainan mining area (China), under the influence of humic acid (HA). The addition of HA inhibited the adsorption of Cd but enhanced its desorption in reclaimed soil. With an increasing concentration of added HA, the adsorption capacity of Cd in the reclaimed soil gradually decreased, while the desorption capacity gradually increased. That is, the adsorption inhibition/desorption promotion effect was stronger under higher concentrations of organic acid. Cd adsorption and desorption dynamics could be described as a logarithmic function of organic acid concentration. Kinetic curves for Cd adsorption and desorption in reclaimed soil under the influence of organic acid showed that both adsorption and desorption involved two stages: a fast reaction stage, followed by a slow reaction stage. The factors influencing the capacity of Cd adsorption and desorption in soil were analyzed by gray correlation analysis, and their resulting rank order was as follows: Cd concentration > HA concentration > pH > temperature. Using linear regression analysis, a multi-factor coupling functional model of soil Cd adsorption and desorption under the influence of DOC was established, in the form of $Y = a + bX_{HA} + cX_T + dX_{PH} + eX_{Cd}$.

1. Introduction

Coal mining has been carried out in the Huainan mining area for 100 years. The large-scale mining of coal resources has inevitably generated substantial amounts of solid waste and coal gangue, but it has also led to land subsidence whose area continues to expand. Since 2003, coal gangue filling and soil covering techniques[1] have been applied in the Huainan mining area to backfill subsided terrain (with coal gangue) up to the original surface elevation, thereby allowing the subsided area to be reused. Yet such reclamation activities have affected the soil quality in the mining area to a certain extent, in that the soil is easily compacted, has a low nutrient content and large volume, and is potentially contaminated by heavy metals. In particular, the content of cadmium (Cd), a heavy metal, often exceeds the agricultural land filter value for soil pollution risk.[2−9]

Dissolved organic carbon (DOC) refers to organic carbohydrates with relatively low molecular weights and simple structures. Accordingly, DOC can be dissolved in water and passed through a 0.45-μm microporous membrane, and it is the most active component of soil organic carbon[10−16] and the main carrier of many trace organic and inorganic pollutants. DOC reacts directly with metal ions in water, soil, and sediment through a series of reactions, such as ion exchange, adsorption, complexation, chelation, flocculation, and precipitation,[17−19] which modulates the adsorption and desorption behaviors of heavy metals in soil. Therefore, changes in the content of DOC are expected to lead to changed contents of heavy metals in soil. Research has shown that DOC in soil can affect the adsorption of heavy metals and improve their mobility in soil.[20] For example, Mahara et al.[21] reported that low-molecular-weight DOC in soil strongly affected the migration and transformation of Cd in the environment, and recently Zhang[22]

uncovered a strong correlation between dissolved heavy metals in the natural environment and the concentration of DOC. Liu[23] had reported that DOC easily adsorbs and binds Cd in the soil: specifically, adding DOC to soil was able to increase the content of soil-exchanged Cd, resulting in a significant positive correlation between soil-exchanged Cd and soil DOC.

Research to date on soil DOC in China and elsewhere has mainly focused on the distribution and composition of DOC in soil, vegetation coverage, and soil fertilization, as well as the adsorption, desorption, complexation, dissociation, precipitation, and dissolution of soil heavy metal ions in the presence of DOC. However, the basic chemical equilibriums along with their corresponding mechanisms, laws, kinetic processes and multi-factor coupling models associated with the interactions between soil DOC and heavy metals have all received relatively less attention from scientists. In this study, reclaimed soil in the subsidence area of Panyi Mine was chosen as the research object. Humic acid (HA), which harbors the largest content of soluble humus, was selected as a representative DOC molecule. The HA was used to prepare DOC solutions at different concentrations, which were then applied to determine the effects of DOC upon the characteristics and kinetics of Cd adsorption and desorption in soil, for which a multi-factor coupling model was sought and developed. The results provide not only fundamental data for evaluating the Cd pollution status of reclaimed soil of coal mines but also a robust scientific method for risk assessment and prediction. This study's findings could also offer guidance for the rational application of organic materials.

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 on 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, the coal gangue is covered by clay with a design thickness of 100 cm. After that treatment, several tree species including poplar, privet, metasequoia, cedar, and Sichuan juniper were planted in the subsidence area. This area lies in a warm temperate semi-humid continental monsoon climate zone. The average annual temperature is 15.3°C, with the highest and lowest temperatures respectively occurring in July and January, while the average annual precipitation is 926 mm.

2.2 Sample collection and pretreatment

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 to collect 0–20 cm of reclaimed soil. Each sample had a mass of at least 1 kg. After removing any impurities, the soil sample was crushed and spread flat on an air-dried soil dish to dry.

Each sample was sieved using the quarter method, ground with an agate mortar, passed through a 100-mesh nylon screen, packed in a Ziploc bag, and then labeled for use.

2.3 Experimental method

As mentioned above, HA was selected as the representative DOC molecule. HA was used to prepare DOC solutions with different concentrations.

2.3.1 Adsorption of Cd in reclaimed soil under the influence of DOC

A given sample of reclaimed soil (1.000 g, 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 having a Cd concentration of 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, followed by the addition of 1 mL of HA solution whose concentration was 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. Finally, the supernatant was passed through a 0.45-μm filter membrane, and one drop of 1% nitric acid was added to the filtrate followed by shaking for the Cd determination. The Cd adsorption capacity (Q_a, in mg/kg) was determined as the difference between the concentration of Cd before and after its adsorption:

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

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 an 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 (60 mg/L).

2.3.2 Desorption of Cd from reclaimed soil under the influence of DOC

The desorption experiment was performed upon completing the adsorption experiment. The reclaimed soil after Cd adsorption was washed once with absolute ethanol to remove any free Cd and placed 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, followed by its covering and shaking at 200 r/min and 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 the Cd determination. The Cd desorption capacity (Q_d) was determined this way:

$$Q_d = \frac{C \times V}{m}. \qquad (2)$$

The Cd desorption rate (W) was calculated as

$$W \ (\%) = \frac{Q_d}{Q_a} \times 100\%. \qquad\qquad (3)$$

2.3.3 Effects of pH on Cd adsorption and desorption in soil

For this, the HA and Cd solutions were respectively set to a fixed concentration of 60 mg/L and 20 mg/L, while the pH of soil samples was adjusted to 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, or 10.5 at 25°C. The specific steps consisted of putting a 1.000-g soil sample (passed through an 18 mesh screen) into a 50-ml centrifuge tube, to which was added 20 ml of $Cd(NO_3)_2$ solution (20 mg/L concentration of Cd) followed by the addition of 1 ml of the HA solution (60 mg/L Cd concentration). The pH value of the sample was adjusted accordingly along the gradient (pH 4.5 to 10.5), with each sample removed at 25°C for 24 h, and then centrifuged (4000 r/min) for 20 min. The ensuing supernatant in the centrifuge tube was filtered through a 0.45-µm membrane. After this filtration, one drop of 1% nitric acid was added to the filtered solution and shaken, the concentration of Cd was then determined. According to the difference in the Cd concentration before and after adsorption, the adsorption capacity was calculated using formula (1).

After completing the adsorption experiment, the corresponding desorption experiment was likewise carried out. To do this, soil samples that had adsorbed a certain amount of Cd were washed with anhydrous ethanol (washed once) and maintained at constant temperature (25°C) for 1 h. Next, 20 ml of 0.01 mol/L NaNO3 solution was added and the pH value of a sample adjusted accordingly (pH gradient of 4.5 to 10.5, as used above), then each tube was shaken at 25°C for 24 h and centrifuged for 20 min. The supernatant in the samples' centrifuge tube was filtered by a 0.45-µm membrane, and this filtrate was then shaken after adding to it one drop of 1% nitric acid. The concentration of Cd was determined. The desorption amount of Cd was calculated using formula (2).

2.3.4 Effect of temperature on Cd adsorption and desorption in soil

To each soil sample, the 60 mg/L HA solution and 20 mg/L Cd solution were added. Under the condition of pH 7.5, the temperature of the samples was adjusted to 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, or 40°C.

Specifically, a 1.000-g soil sample (first passed through an 18 mesh screen) was put into a 50-ml centrifuge tube, to this was added 20 ml of $Cd(NO_3)_2$ solution (20 mg/L Cd), and then 1 ml of the HA solution (60 mg/L Cd) was added to each centrifuge tube. The samples were removed at the eight different temperatures (5°C to 40°C gradient) under constant temperature oscillation (200 r/min) for 24 h and centrifuged (4000 r/min) for 20 min. The supernatant in the centrifuge tube was passed through a 0.45-µm membrane. After this filtration, one drop of 1% nitric acid was added to the filtered solution and shaken, after which the concentration of Cd was determined. According to the difference in the Cd concentration before and after adsorption, the adsorption capacity was calculated using formula (1).

The corresponding desorption experiment was carried out after the completion of the just-described adsorption experiment. The soil that had adsorbed a certain amount of Cd was washed with anhydrous ethanol to remove the free Cd (washed once). The soil was placed at 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, or 40°C for 1 h. Then 20 ml of 0.01 mol/L NaNO3 solution was added to each sample, and these removed in a constant temperature oscillator (200 r/min) for 24 h and centrifuged (4000 r/min) for 20 min. The supernatant in the centrifuge tube was filtered through a 0.45-μm membrane, and the filtrate was shaken after adding to it one drop of 1% nitric acid. The concentration of Cd was determined. The desorption amount of Cd was calculated using formula (2).

2.4 Data processing

SPSS 24.0 software was used for the statistical analysis of the data, Origin8.0 software was used for drawing the figures, and MATLAB mathematical software was used to compile the corresponding calculation program for the gray correlation[40] analysis. According to the statistics for Cd adsorption capacity, desorption capacity, and various factors, 74 samples were analyzed, for which the order number was m = 4 (HA concentration, Cd concentration, temperature, and pH value) P= 0.5. Using the MATLAB calculations, the gray correlation degree of HA concentration, Cd concentration, temperature, and pH value are listed in Table 1. To establish the best adsorption and desorption model as function of HA concentration, Cd concentration, pH value, and temperature (at a 95% confidence interval), these four predictors were entered into a multiple linear regression (but with no interaction terms). In this model, the response variable Y is the adsorption capacity of Cd in the solution, X_{HA} is the concentration of HA, X_{Cd} is the concentration of Cd in the solution, X_T is the solution temperature, and X_{PH} is the pH of the solution.

3. Results And Discussion

3.1 Characteristics and mechanism of isothermal Cd adsorption under the influence of HA

As Fig. 1 shows, as the concentration of Cd in the equilibrium solution increased, the adsorption capacity of reclaimed soil for Cd gradually increased. When the Cd concentration was low (i.e., 0.2−10 mg/L), the amount of adsorbed Cd was similar in the presence and absence of HA. Thus, under low Cd concentrations, HA has little effect on the ability of reclaimed soil to adsorb Cd. By contrast, when the Cd concentration was 15−80 mg/L, the presence of HA significantly reduced the adsorption of Cd by the reclaimed soil, and the amount of adsorbed Cd decreased as the concentration of added Cd increased. Thus, adding HA significantly inhibits the adsorption of Cd by reclaimed soil. Notably, the high organic acid concentration (60 mg/L) produced a stronger effect than did adding the low concentration (10 mg/L). Studies have shown that different DOC components can affect the migration of organic and inorganic pollutants in soil.[12,24−27] We know that HA contains a variety of active groups. In particular, HA harbors 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.[28−31] These sites compete with the reclaimed soil to adsorb Cd, thereby reducing the ability of the soil to readily adsorb Cd. 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 the soil.[32−35] Furthermore, HA, which is rich in anionic groups, such as phenolic, hydroxyl, and carboxyl groups, precedes Cd at occupying the soil seat sites via soil surface adsorption,[36−37] thereby reducing the Cd adsorption capacity of reclaimed soil. This interpretation of results is consistent with other findings indicating that DOC has a significant inhibitory effect on Cd adsorption in soil.[38]

3.2 Characteristics and mechanism of isothermal Cd desorption under the influence of HA

As seen in Fig. 2, with an increased concentration of Cd in the equilibrium solution, the Cd desorption capacity of reclaimed soil gradually increased as well. When the Cd concentration was low (0.2−10 mg/L), the amounts of desorbed Cd were similar irrespective of HA. Thus, under low Cd concentrations, HA negligibly affects the ability of reclaimed soil to desorb Cd. However, when the Cd concentration was 15−80 mg/L, the presence of HA significantly increased the desorption of Cd in the reclaimed soil, and the amount of desorbed Cd increased as the concentration of added Cd increased. Due to the differing physical and chemical properties of reclaimed soils, HA had different effects on desorption capacity. Using a high organic acid concentration (60 mg/L) produced a larger effect than did a low concentration (10 mg/L).

The desorption rate of Cd from reclaimed soil increased upon the addition of HA (Fig. 3). The Cd desorption rate of reclaimed soil increased, on average, by 5.71% and 3.21% upon the addition of high (60 mg/L) and low (10 mg/L) concentrations of HA, respectively. The adsorption process of Cd is one dominated by chemical bonding and electrostatic attraction; the activation energy required for adsorption is low, while the adsorption affinity is high. Unlike that, the desorption process of Cd is an ion exchange process. Organic ligands contained in organic acids can form soluble organometallic complexes with Cd, thereby reducing the adsorption of Cd in reclaimed soil. Moreover, the protons in HA can activate Cd in reclaimed soil and this also promotes its desorption.[39]

3.3 Kinetics and mechanism of Cd adsorption and desorption under the influence of HA

As depicted in Fig. 4, when compared with the normal (untreated) reclaimed soil, Cd adsorption was significantly reduced in the soil containing HA. Under the influence of HA, Cd adsorption was reduced by 17.06−18.80% (average: 18.18%). These results demonstrate that HA is capable of changing the migration behavior of Cd in the reclaimed soil by affecting its adsorption.

The adsorption process of Cd in the reclaimed soil containing HA was the same as in that lacking it. Adsorption began with a fast adsorption stage, lasting just 0−0.5 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. Under the influence of HA, the Cd adsorption rate was 71.36%, corresponding to a reduction of 15.04% relative to the normal reclaimed soil. These results further demonstrate that HA can inhibit the adsorption of Cd in reclaimed soil.

Under the influence of HA, the Cd desorption capacity in reclaimed soil first decreased and then increased over time, revealing two desorption stages (Fig. 5): a fast reaction stage spanning 0 to 2 h at the beginning of the experiment, followed by a slow reaction stage spanning 2.5 to 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, attaining equilibrium after approximately 12 h. Including HA significantly increased the desorption capacity of Cd in reclaimed soil; HA increased the Cd desorption capacity by 28.51–72.98% (average: 50.29%). These results demonstrate that HA can alter the migration activity of Cd in reclaimed soil by affecting the desorption of Cd.

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

3.4.1 Correlation analysis

According to Table 1, the rank order of influencing factors of Cd adsorption and desorption is Cd concentration > HA concentration > pH > temperature. These results indicate that among the considered factors that could influence the adsorption and desorption of Cd, its concentration was the decisive factor, followed by the HA concentration, pH value, and temperature.

Table 1
Correlations of influencing factors of coal gangue weathering matter and soil.

	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

3.4.2 Multiple regression analysis

Two linear models were built to explain the adsorption and desorption of Cd based on the Cd concentration, HA concentration, pH, and temperature coupling showed an excellent fit to the data. Furthermore, the relative error (dX [%]) between the predicted and measured values were analyzed by applying the established linear coupling-function model. Doing so shows that it can reliably predict the changes in soil Cd adsorption and desorption under the influence of multiple factors (Table 3).

Table 2 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 3 Comparison of observed and predicted values of the multiple linear regression model.

Type	Relative error dx (%)
Cd adsorption capacity of soil	$-2.97 \sim 1.74$
Cd desorption capacity of soil	$-3.01 \sim 3.20$

Therefore, 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 verify the characteristics of Cd adsorption and desorption in the Huainan reclamation area (and perhaps other similar to it).

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

In this paper, MATLAB 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 $Y = -32.176-2.024X_{HA} + 1.325X_T + 18.352X_{PH} + 14.974X_{Cd}$, the 3D diagrams were drawn, as shown in Figs. 6−9.

Figure 6 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 7 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 8 shows that when the pH value is 7.5, increasing the HA concentration decreases the adsorption capacity of Cd in soil; conversely, with an increased Cd concentration or temperature, the adsorption capacity of Cd is also increased. Figure 9 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 $Y = 36.368 + 0.047X_{HA} - 0.590X_T - 3.556X_{PH} + 2.373X_{Cd}$, the 3D diagrams were drawn, as shown in Figs. 10–13.

Figure 10 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 11 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 12 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. 13 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

The effects of organic acids on Cd adsorption and desorption dynamics in reclaimed soil are complicated. In this study, the addition of humic acid (HA) inhibited the adsorption of Cd in the reclaimed soil of a coal mine. Further, HA strengthened the process of Cd desorption in the same reclaimed soil. The adsorption and desorption kinetics of Cd in reclaimed soil were significantly affected by time, which could be divided into two stages: an initial fast reaction stage that was followed by a slow reaction stage. The factors influencing the Cd adsorption and desorption capacity in soil were investigated by gray correlation analysis, which revealed their rank order: Cd concentration > HA concentration > pH > temperature. By using regression methods, a multi-factor coupling function model of soil Cd adsorption and desorption under the influence of DOC was established: $Y = a + bX_{HA} + cX_T + dX_{PH} + eX_{Cd}$. Hence, this model may be used to predict and verify the characteristics of Cd adsorption and desorption. It could also be applied to improve the Cd migration ability in soil by manipulating the levels of four influencing factors in combination with phytoremediation technology to achieve the goal of removing Cd pollution from soil entirely.

Declarations

Acknowledgments:

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Figures
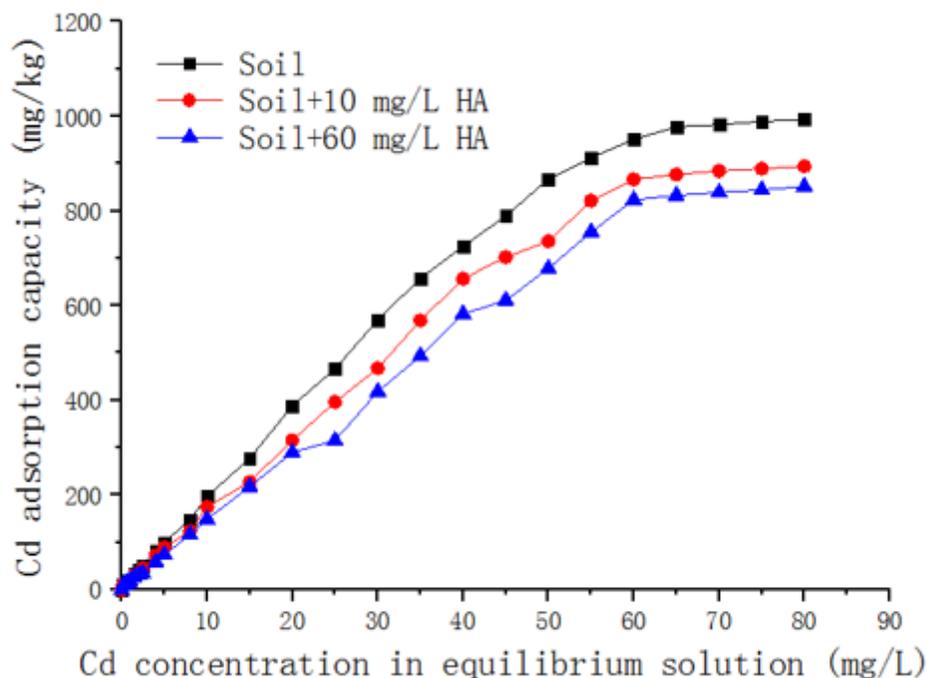
Figure 1

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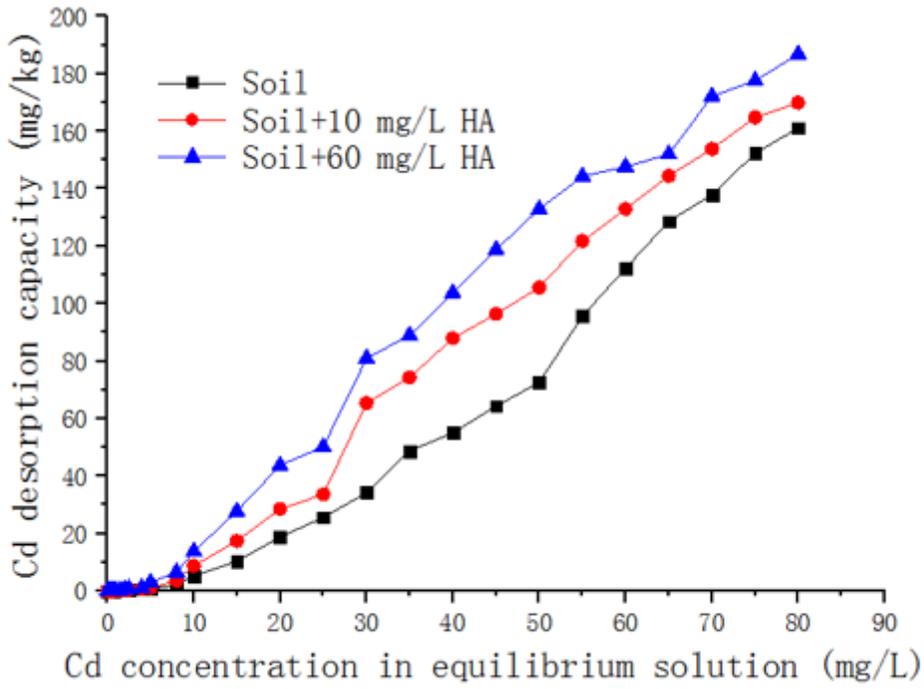
Figure 2

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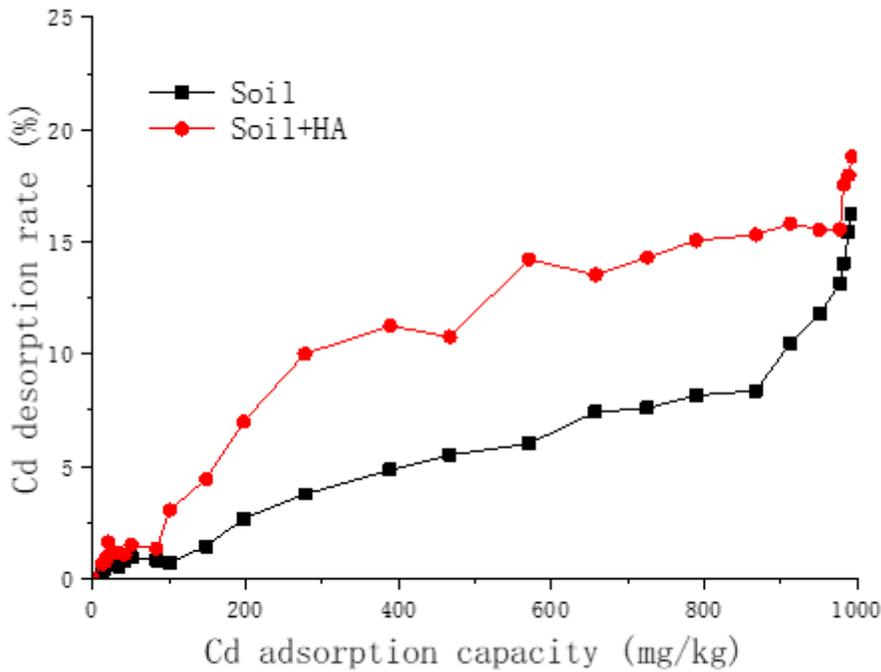
Figure 3

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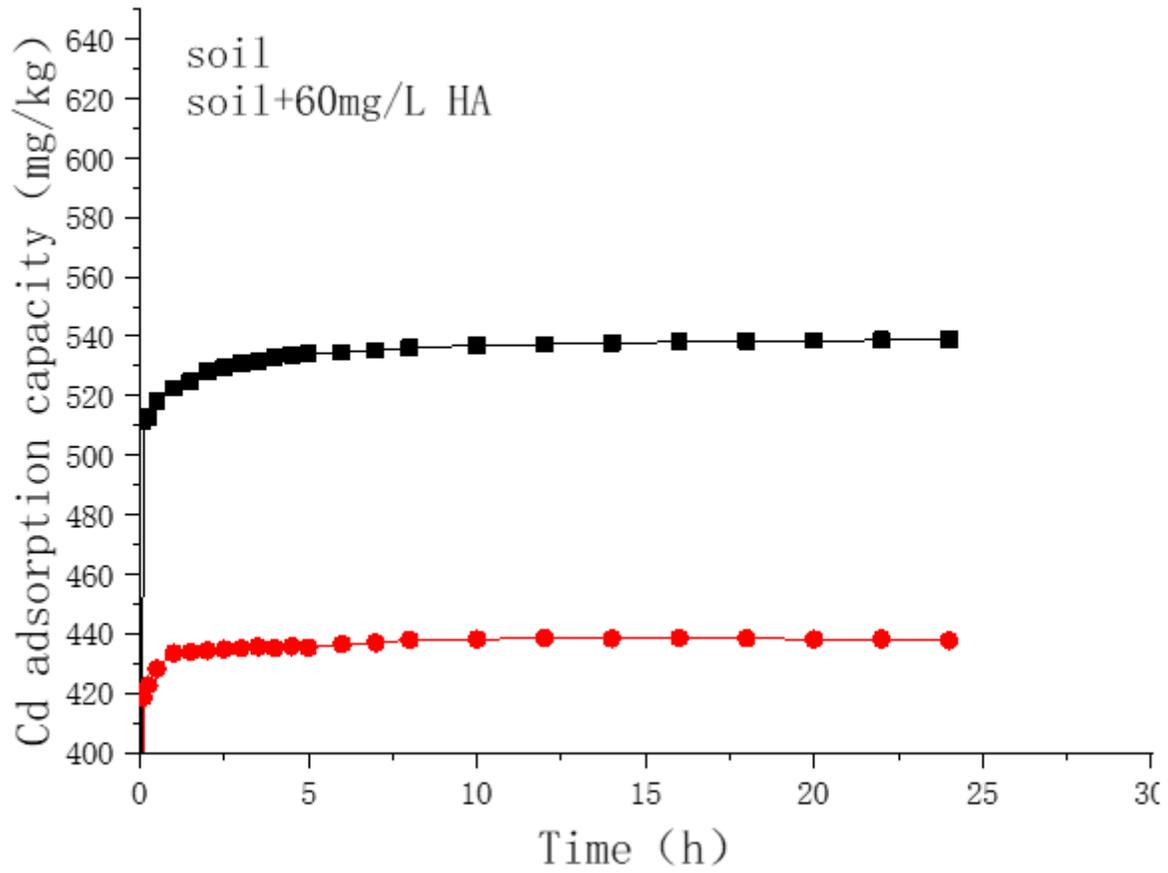
Figure 4

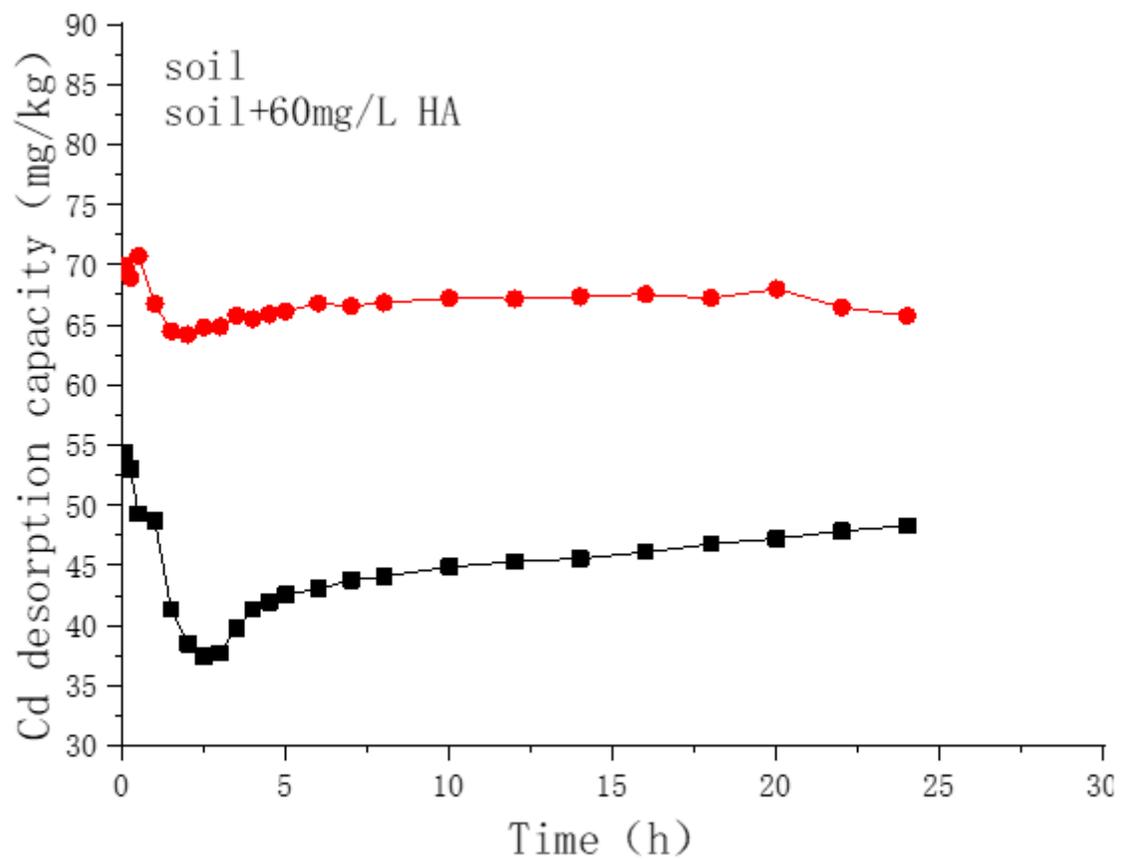Kinetic curves of Cd adsorption in reclaimed soil in the absence and presence of HA.

Figure 5

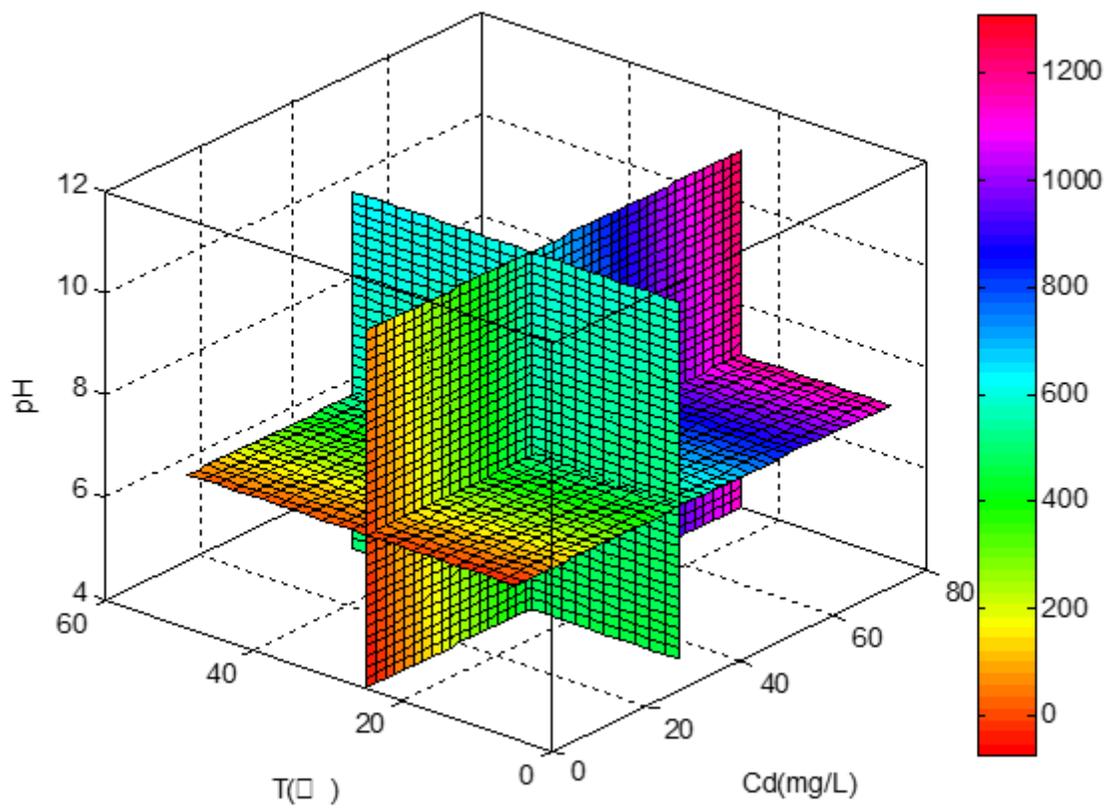Kinetic curves of Cd desorption from reclaimed soil in the presence and absence of HA.
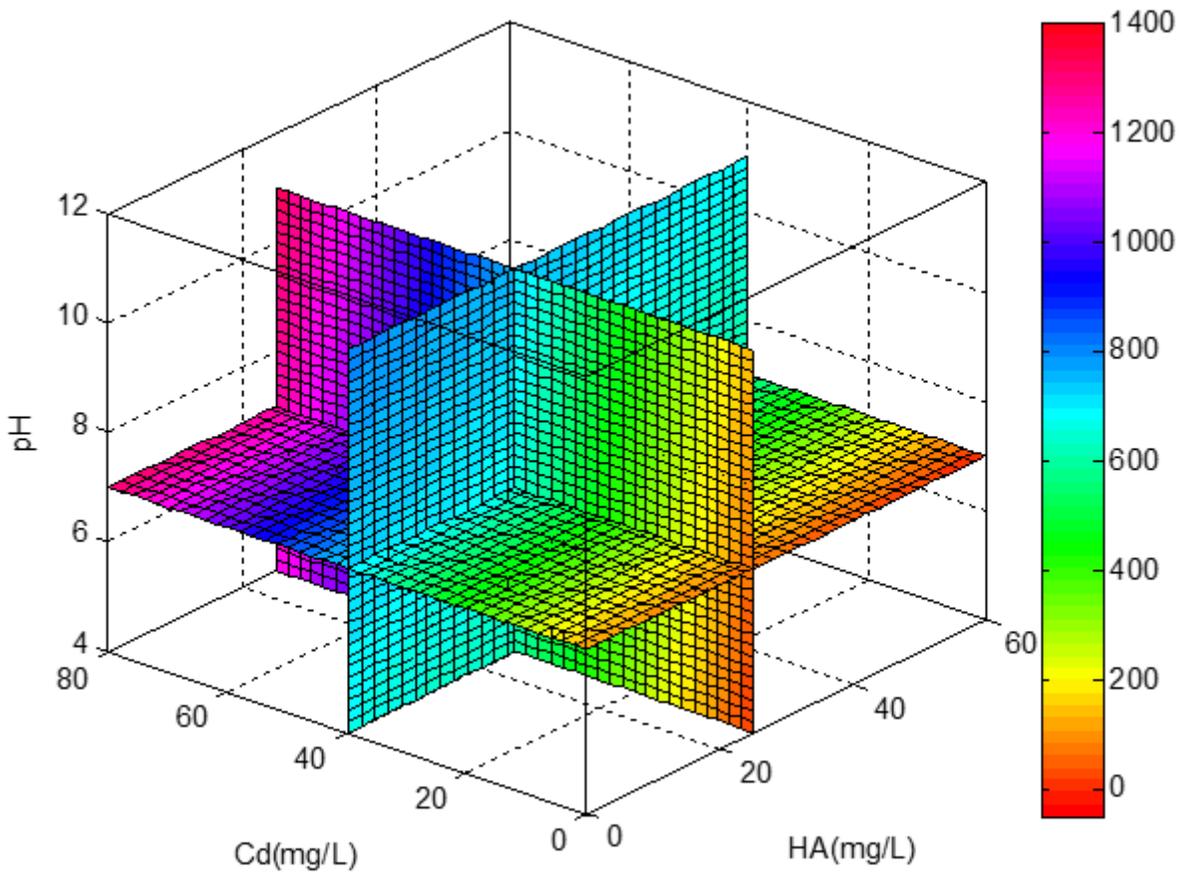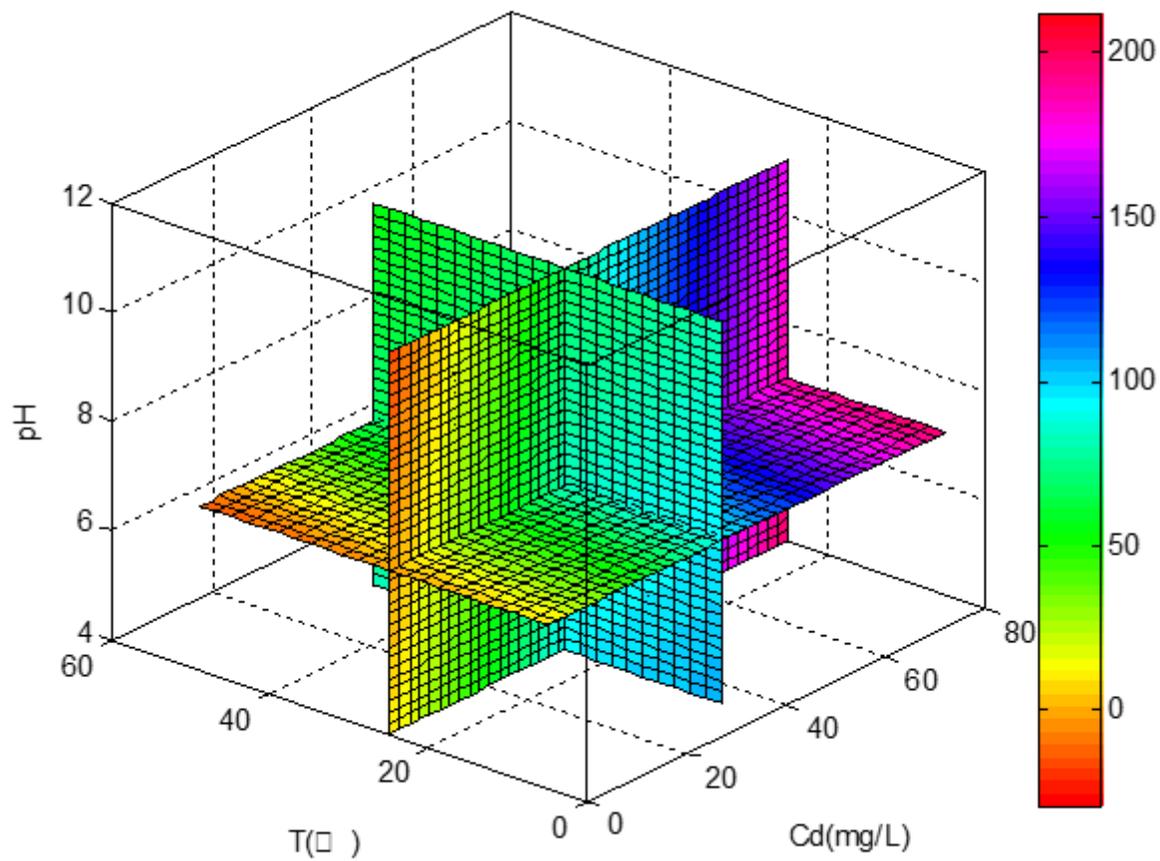
Figure 6

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

Figure 7

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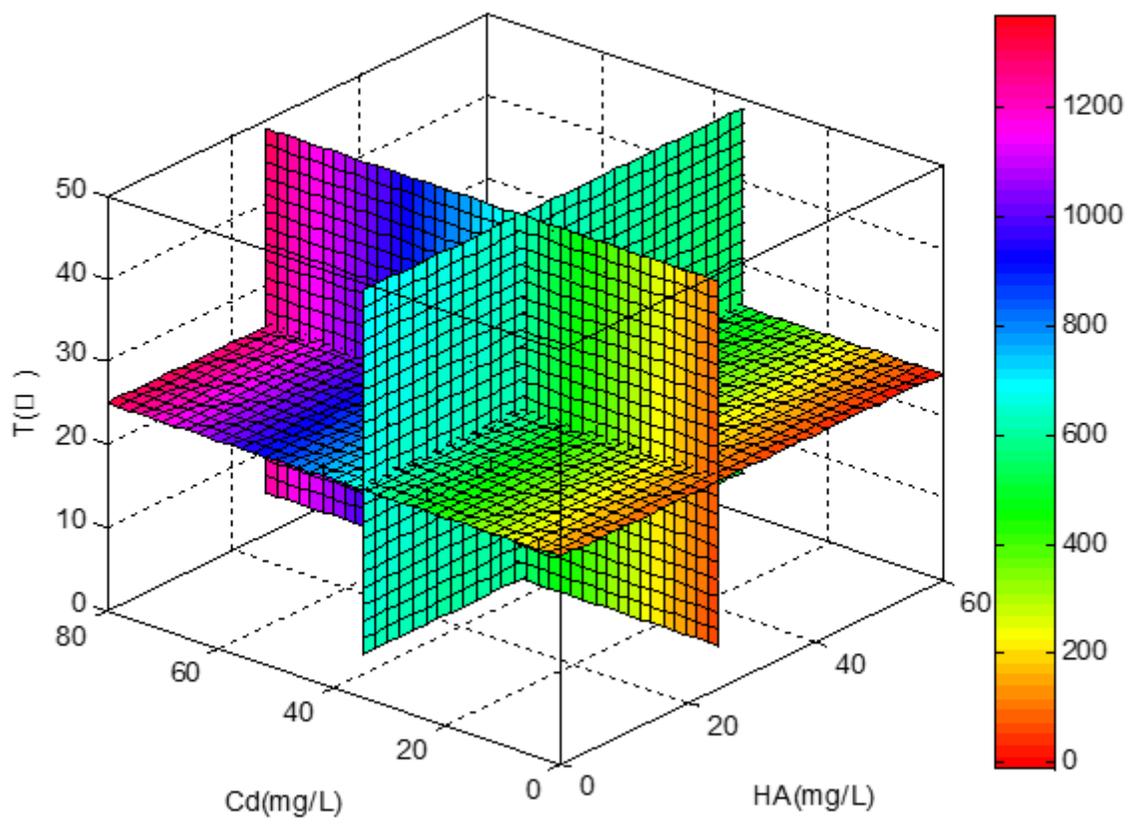
Figure 8

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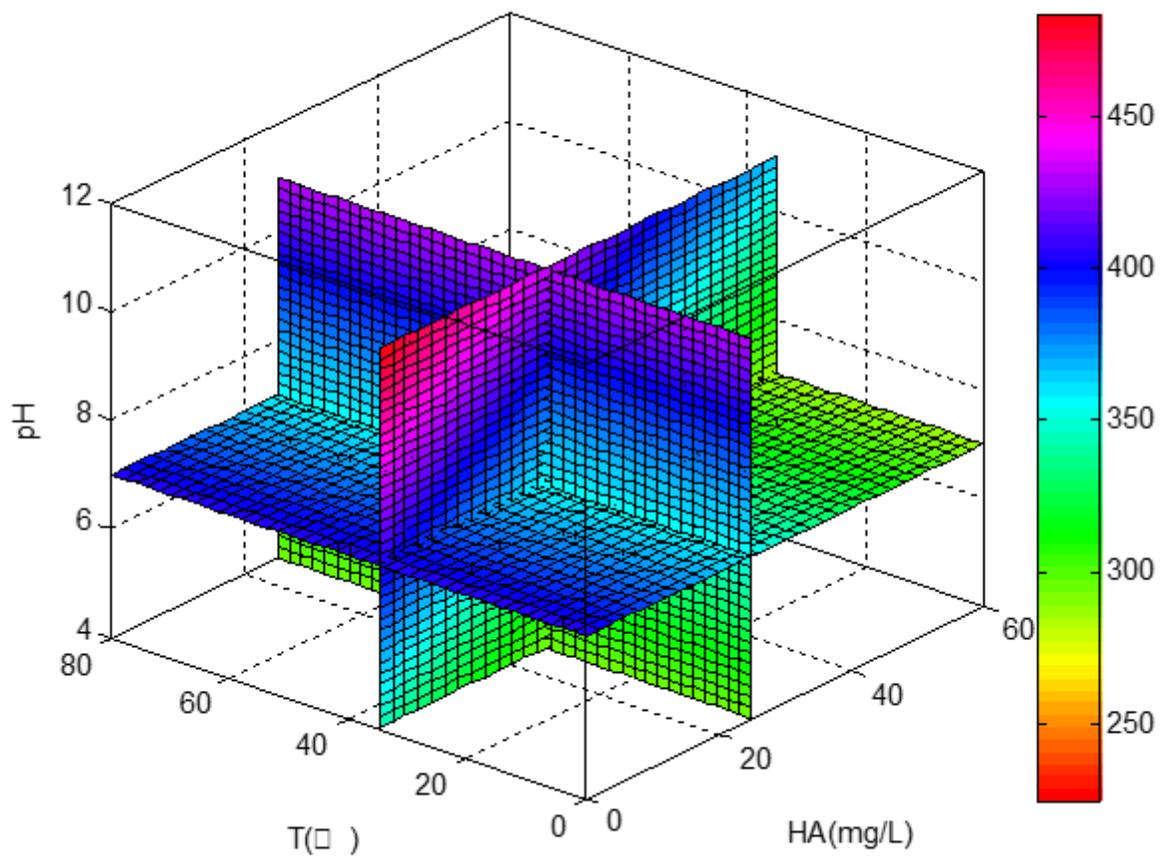
Figure 9

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

Figure 10
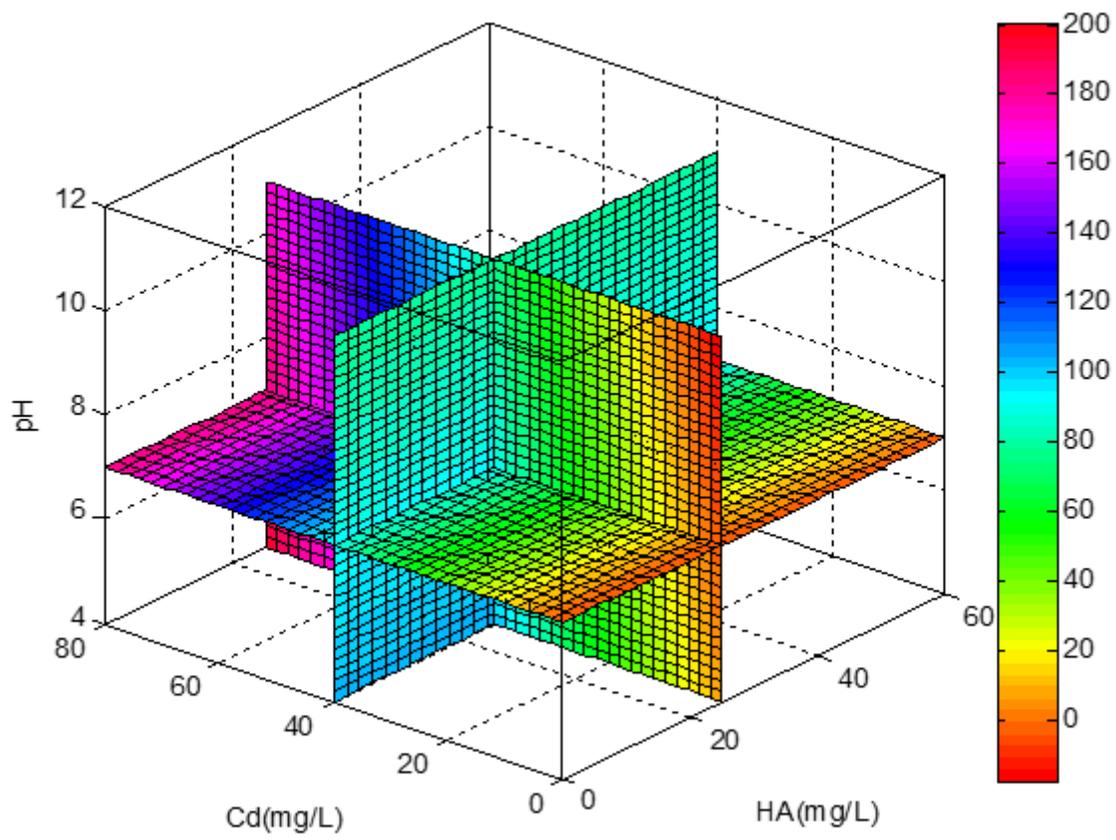
The coupling of T, pH, and Cd at HA = 60 mg/L.

Figure 11

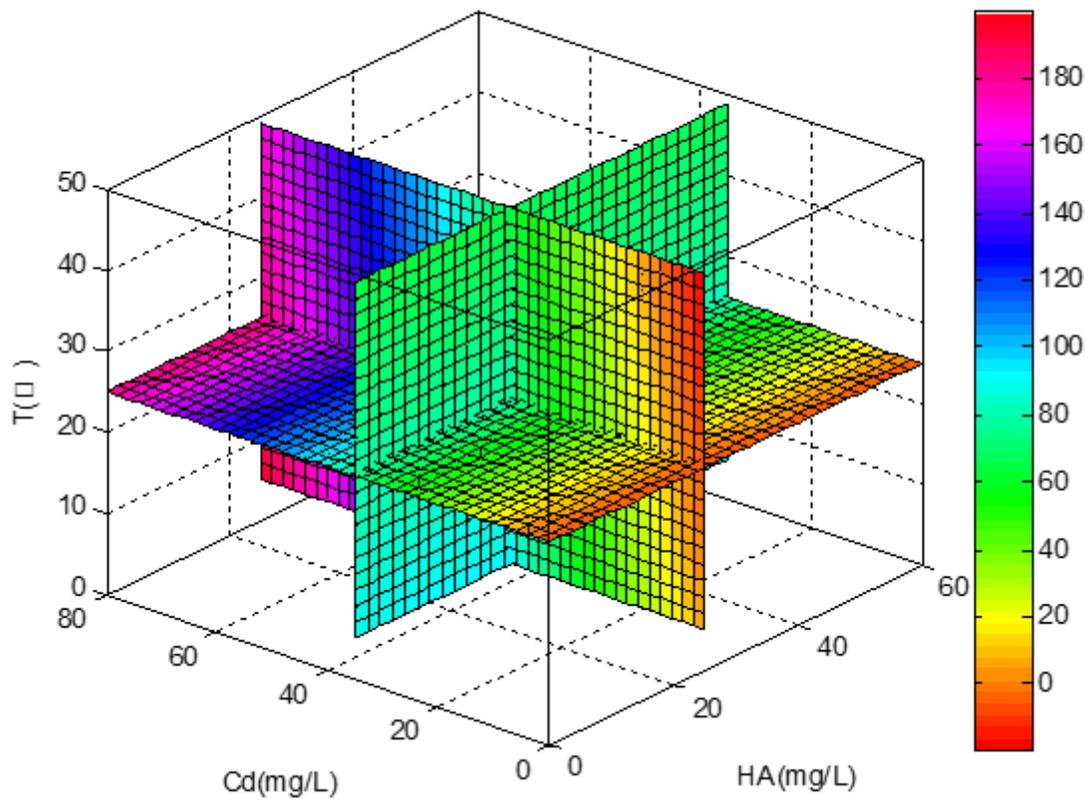The coupling of HA, pH, and Cd at T = 25°C.
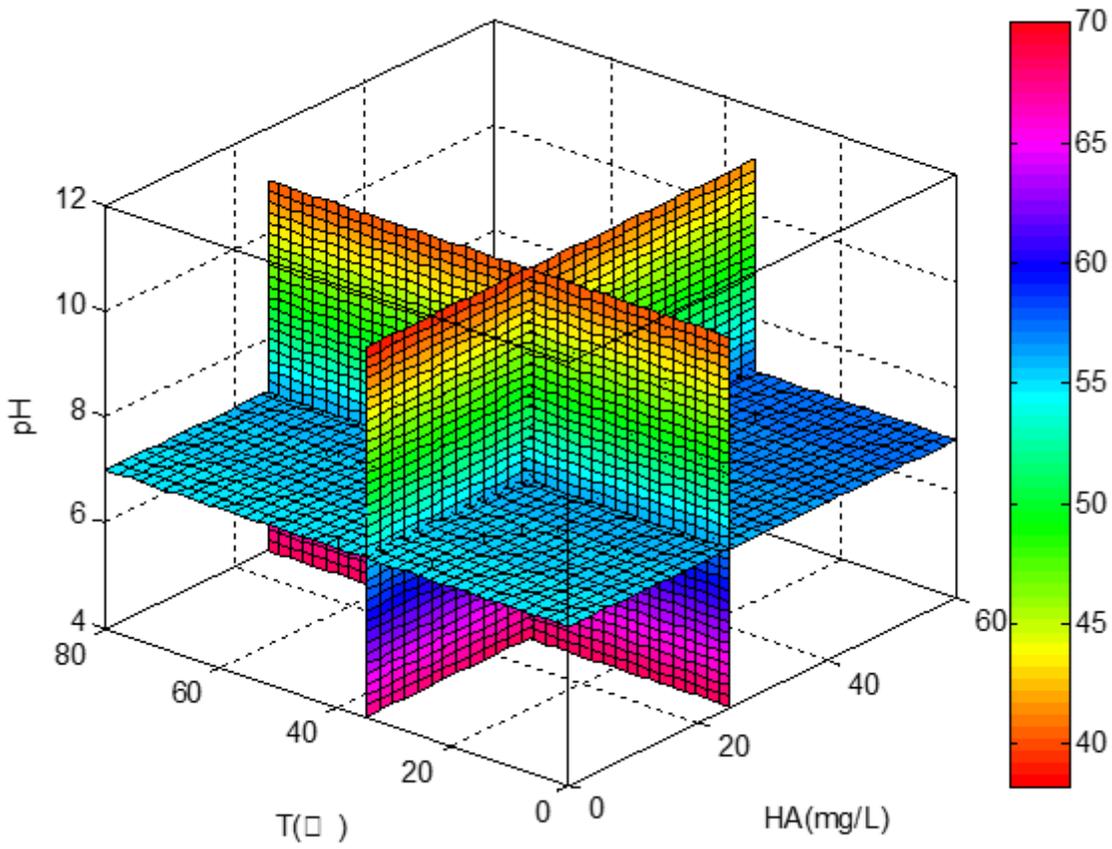
Figure 12

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

Figure 13

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