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Experimental simulation and dynamic model analysis of Cadmium (Cd) release in soil affected by rainfall leaching in a coal-mining area

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Abstract: In order to explore the influence of rainfall on the release of heavy metal Cadmium (Cd) in soil in a coal-mining area, soil column leaching experiments were carried out by simulating 3 types of rainfall (acid rain, normal rainfall, and actual rainfall) with 5 different pH values (4, 5, 6, 6.7, 7), and 65 groups of data about leachate pH value and Cd concentration were obtained respectively. The results indicate the general change rule of Cd concentration in leachate: (1) the easiness of Cd release is negatively correlated to the pH value of leaching solution and positively correlated the leaching amount; (2) leaching solution with lower pH values shows more obvious release stages. Leached by solution with different pH values, the release of Cd in soil ranks as follows: Acid rain group>normal rainfall group>actual rainfall group. In the first stage, the acidity of rainfall has a significant impact on the release of Cd in soil, but in the second stage, the release of Cd is alleviated due to the soil buffering. Among the four dynamic equations to simulate the release of Cd in soil, the modified Elovich equation can describe the process most accurately, with the highest coefficient of determination R^2 of 0.997 5. These results can serve as a reference for further study on the migration, transformation and enrichment of Cd in soil.

Keywords: Rainfall; pH value; Soil; Cd; Dynamic equation

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Introduction

Connected with various components of soil in different ways, cadmium (Cd) takes different binding forms, which determine its mobility and bioavailability. The biological toxicity of Cd is correlated to its total amount, and more to its various chemical forms and their release amount. Major factors affecting Cd concentration in soil solution include pH, organic matter, coexisting ions, moisture, temperature, and mineral com-position (CAO Yan-ling *et al*. 2020; ZHANG Ji-zhou *et al*. 2012; LIU Chun-yang *et al*. 2006; Joseph *et al*. 2019; LIU Jia-li *et al*. 2010; HUANG Yi *et al*. 2007).

As a prominent environmental problem, acid rain can acidify surface and even deep soil, and activate in soil by increasing their mobility, migration distance and bioavailability (WANG Xing-wen, 1993; YANG Ben-hong, 2000; Saleem *et al*. 2018; Doabi *et al*. 2018). Cd accumulating to a certain extent in soil can alter both biological and non-biological system: It can degrade the soil quality as well as the yield and quality of agricultural products; it can pollute surface water and groundwater by surface runoff and leaching, damaging the hydrological environment; it may

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also endanger the physiology and health of human body through direct or indirect contact (RAN Jian-ping, 2013; ZHOU Yong-zhang and SONG Shu-qiao, 2005; ZHOU Jian-jun *et al*. 2014; LIU Jian-gen, 2019; Papale *et al*. 2018; ZHANG Li-hua *et al*. 2008). All the above mentioned will cause great inconvenience to production and life.

The studied coal-mining area is located in the central valley of Sichuan Basin, where occurrence rate of the acid rain is above 50% all the year round, and even reached 83.33% and 80.0% in 2006 and 2007 respectively. In addition, due to the commuting of coal transport vehicles and the spatter of rain and dust along the road, heavy metals are enriched in the surface soil of farmland. With the leaching of acid rain, these heavy metals migrate to the deeper soil layer, impairing the quality of local groundwater, and further polluting the water in a wider range due to the mobility of groundwater. Therefore, it is of great significance to study the effect of rainfall leaching on the release of Cd in soil.

This study adopts the method of indoor soil column dynamic leaching to simulate the release of Cd in soil under different rainfall conditions. It explores the characteristics of Cd release under various pH values, and the correlation between the concentration of Cd in leachate and the amount and pH value of leaching solution. The study can provide a more detailed basis for the research on the effect of rainfall on the release of Cd in soil.

1 Materials and methods

1.1 Experiment materials

The soil in this experiment was collected from the surface layer of farmland beside the highway near Hongyue Coal Mine Co., Ltd in Wutongqiao District, Leshan City, Sichuan Province. It was sampled in a quincunx pattern with a depth of 0~20 cm. After it was air-dried, and the impurities such as roots and stones were removed, the soil was mashed into fine particles and screened through a 2 mm sieve to ensure it was fully mixed. After all the preparations it was then put into bags for use.

Considering that the soil was near the mining area and extreme circumstances could happen, the experiment used sulfuric acid and nitric acid to acidify the collected rainwater in terms of the specific conditions of local acid rain. According to the statistics of the ion component of annual precipitation in Leshan city, the annual average concentration ratio of sulfate and nitrate in precipitation is 3:2 (ZHENG Tian, 2012). With this ratio, 3 groups of leaching solution with 5 different pH values were prepared, namely distilled water as solvent with different pH values of 4, 5, 6 and 7 respectively, and untreated rainwater with pH value of 6.7 (pH=6.7). Among them there are a total of 3 groups, in which the solutions with pH=4 and pH=5 were regarded as acid rain simulation group, pH=6.7 as actual rainfall simulation group, pH=6 and pH=7 as normal rainfall simulation group, 3 groups in total.

Transparent acrylic pipes were selected as the leaching pipe in the experiment, and the whole soil column was filled with 3 layers, *i.e.* quartz sand, soil and quartz sand from top to bottom, so as to ensure the uniform infiltration of rain water and prevent the accumulation of leachate at the bottom. The 5 soil columns in the experiment were filled according to the actual compaction of surface soil, and were numbered pH=4, pH=5, pH=6, pH=6.7, and pH=7 respectively.

Fig. 1 Experimental apparatus

1.2 Experiment and sampling method

According to the amount of local rainfall and requirements of sampling frequency, the flow rate was set at 0.56 mL·min^{-1}; 0.4 L of leaching solution with pH of 4, 5, 6, 6.7 and 7 were respectively added to each titration bucket at each time and each leaching process lasted 12 h, after which the soil was left in the natural state for another 12 h. This process fully simulated the alternate dry and wet state of the soil.

The leachate was sampled every 6 h in the early stage of the experiment with a total of 4 times, and then every 12 h.

1.3 Testing method

The pH value of the leachate was measured on site with a handheld portable pH meter to ensure the accuracy of the data. The concentration of Cd in the leachate was determined by graphite furnace atomic absorption spectrophotometer. The leachate of each group was gaged twice for an average value in order to ensure the accuracy of data.

1.4 Data processing

Excel and Origin software was used in data organization, processing and chart production.

2 Results and discussion

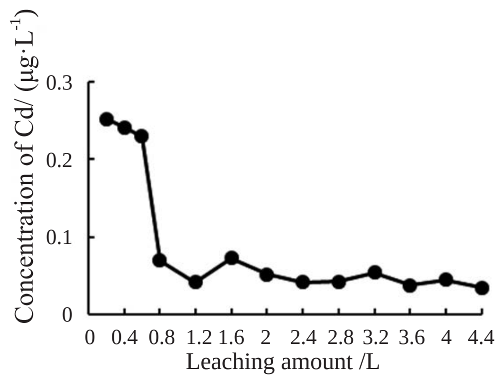
2.1 Characteristics of Cd release in soil leached by solution with different pH values

2.1.1 The general change rule of Cd concentration in leachate

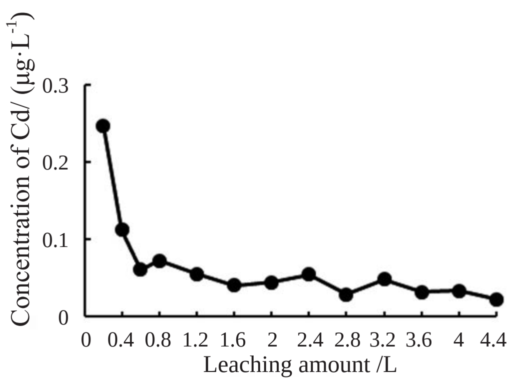
As revealed by Fig. 2(a)-Fig. 2(e), the overall trend is that the concentration of Cd in the leachate gradually declines in the process. Under the conditions of simulated rainfall, Cd in the soil is leached from the soil column as the leaching proceeds. In this experiment, the leaching effect of rainfall on Cd in the soil can be broadly divided into two stages:

(1) The rapid leaching stage: The concentration of Cd in the leachate was relatively large at the initial stage of the leaching. Also, the smaller the initial pH value of the leaching solution was, the greater the concentration of Cd in the leachate became, which suggests the initial pH value of the leaching solution had a significant effect on the release of Cd in soil. High as the concentration of Cd in the leachate was at this stage, its duration was short. The inflection point of Cd concentration in the leachate of columns pH=4, pH=5, pH=6, pH=6.7 and pH=7 appeared when the total leaching amount reached 0.8 L, 0.6 L, 1.6 L, 0.8 L and 1.2 L respectively. Among them, the concentration of Cd in the leachate of the column pH=4 maintained 3 high points, an obvious mark of stages. The other groups all showed a rapid decline, indicating that the pH value of leaching solution had a significant impact on the release of Cd in soil.

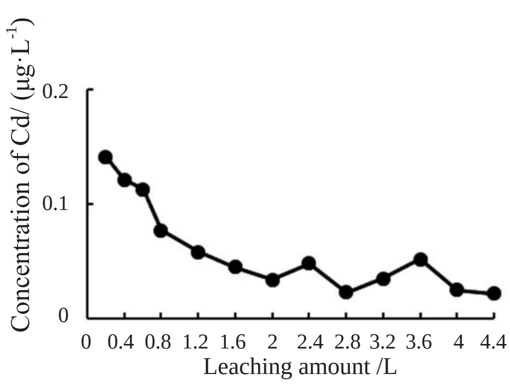
(2) The slow release stage: The concentration of Cd in the leachate was relatively small, and showed a trend of wavy decline with the increase of the leaching amount. When the leaching amount was the same and exceeded 1.2 L, despite different initial pH values of the leaching solution, the differences of Cd concentration among the 5 groups of leachates were relatively small, all falling between 0.006 $\mu g \cdot L^{-1}$ and 0.030 $\mu g \cdot L^{-1}$. Under this circumstance, the pH value of the leaching solution had a smaller effect on the release of Cd in soil.



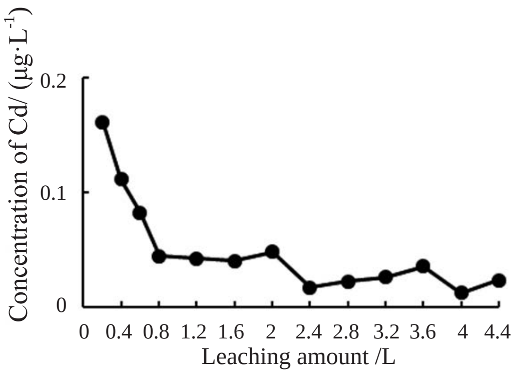
(a) pH=4



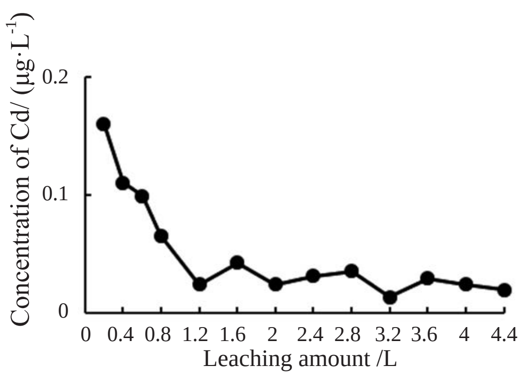
(b) pH=5



(c) pH=6



(d) pH=6.7



(e) pH=7

Fig. 2 Changes of Cd concentration in leachate with different pH

2.1.2 Cd release in soil leached by solution with different pH values

In this experiment, with the same rainfall pH value, the cumulative leaching loss of Cd in the soil rose with the increase of leaching amount. With the same leaching amount, the cumulative leaching loss of Cd is higher in the soil leached by solution with lower pH and vice versa (Fig. 3). Also, the total leaching loss of Cd is negatively correlated with the pH value of rainfall (Fig. 4). Specifically, when the pH value of the leaching solution was 4, the cumulative leaching loss of Cd increased significantly at a rate of 0.05 μg per 0.2 L as the leaching amount rose from 0 to 0.6 L, and then went up at about 0.02 μg per 0.2 L. When the pH was 5, the cumulative leaching loss of Cd increased greatly at a rate of 0.04 μg per 0.2 L as the leaching amount grew from 0 to 0.4 L, and then rose gradually at 0.01~0.02 μg per 0.2 L. When the pH was 6, 6.7 and 7, the cumulative leaching loss of Cd in the soil increased steadily in the whole process at a rate of 0.01~0.025 μg per 0.2 L; since the pH values of 6.7 and 7 were close, their variation curves of cumulative leaching loss of Cd in the soil roughly coincided.

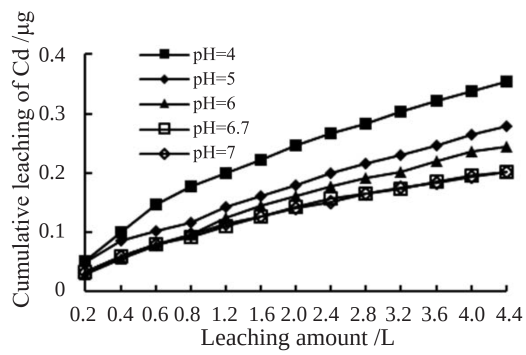


Fig. 3 Changes of Cd cumulative leaching loss in solution with different pH

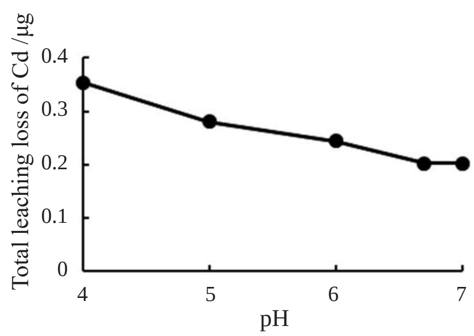


Fig. 4 Changes of total amount of Cd leaching loss in solution with different pH

2.2 Kinetic models of Cd release in soil leached by solution with different pH values

In studies on simulating the release of heavy metals in soil, fitting the data to kinetic equations is a broadly adopted method. Some commonly used mathematical models of metal release from environmental samples include the first-order kinetics equation, the double constant rate equation, the parabola equation and the modified Elovich equation (SU Guang-ming *et al*. 2013). In this experiment, the cumulative leaching loss of Cd and the leaching amount were fitted to the above four equations respectively, and the results are shown in Table 1. In the significance test of the coefficient of determination R^2 of the fitted results (Table 1), the first-order kinetics equation is outshone by the other three, indicating that under the condition of rainfall, Cd release in soil is not a simple linear process, but a process affected by many factors such as the reaction rate and diffusion factor. In comparison, the parabolic equation, the double constant rate equation and the modified Elovich equation can better describe the release process of Cd. Notably, the R^2 of the modified Elovich equation reaches 0.997 5, marking the highest accuracy. The accuracy of equations describing the kinetic process of Cd release in soil ranks as follows: The modified Elovich equation>the double constant rate equation>the parabolic equation>the first-order kinetics equation.

Table1 Kinetic fitted results of Cd release in soil under simulated rainfall conditions

Subject	First-order kinetics equation $y=ax+b$			Parabolic equation $y=a+bx+cx^2$				Double constant rate equation $y=ax^b$			Modified Elovich equation $y=a-b*\ln(x+c)$			
pH	a	b	R^2	a	b	c	R^2	a	b	R^2	a	b	c	R^2
4	0.062 9	0.099 5	0.925 1	0.061 4	0.118 6	-0.012 5	0.970 5	0.174 5	0.480 5	0.983 7	0.160 7	-0.118 4	0.210 2	0.992 0
5	0.050 2	0.069 7	0.974 8	0.052 0	0.076 0	-0.005 8	0.990 9	0.127 9	0.517 3	0.997 3	-0.040 1	-0.175 6	1.572 0	0.994 6
6	0.048 1	0.049 8	0.956 8	0.025 5	0.083 6	-0.008 0	0.989 5	0.105 2	0.579 0	0.993 6	0.042 1	-0.121 5	0.713 1	0.997 4
6.7	0.037 1	0.054 7	0.943 4	0.032 8	0.069 1	-0.007 2	0.987 4	0.098 5	0.498 4	0.993 4	0.070 1	-0.082 2	0.457 0	0.997 5
7	0.036 2	0.056 4	0.936 8	0.034 8	0.067 6	-0.007 1	0.981 1	0.099 4	0.485 1	0.990 9	0.081 2	-0.074 5	0.338 0	0.996 0

Note: X is the leaching amount, L; Y is the cumulative leaching loss of Cd, μg.

2.3 Buffering effect of soil on leaching and release behavior of Cd

2.3.1 Buffering effect of soil on leaching

In the experiment, the pH value of the leachate changed with the leaching amount, as shown in Fig. 5. From a lateral perspective, the pH value of the leachate remained above 7.0 in the whole process, with a significant increase after the solution passed through the soil column. When the leaching amount was 0.2~0.6 L, the pH value of the leachate increased; when 0.6~2.0 L, the pH value showed a slight decline; when over 2 L, the pH value climbed; when more than 2.8 L, it remained stable. From the beginning to the end, the pH value of the leachate fluctuated, because the cation exchange capacity (CEC) of the soil allowed the H^+ flowing in to neutralize with the negative charges on the surface of the soil colloid, and it provoked a substitution reaction with the base ions. These displaced ions came into the leachate, leading to the upsurge of the pH value in the initial stage. When adsorption of the H^+ in the soil reached saturation with the continuous influx of simulated acid rain, part of the H^+ flowed directly into the leachate, decreasing its pH value. Subsequently, the H^+ flooding into the soil sample reacted with the aluminum on the surface of the crystal lattice and generated exchangeable aluminum, resulting in the consumption of H^+, the loss of aluminum and also the rise of the pH value of the leachate, which eventually stabilized (LUO Ying, 2016).

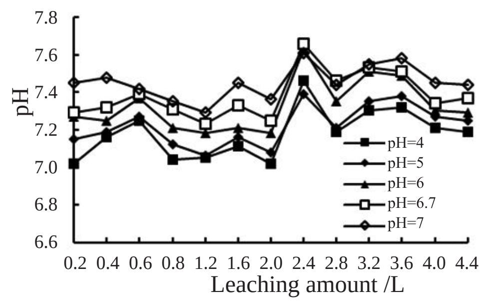


Fig. 5 Curve of pH value change of leachate with leaching amount

In this experiment, from a longitudinal perspective, the overall trend is that the pH value of the leachate increases with the initial pH of the leaching solution. According to the statistics in Table 2, the pH value of the solution can even surge from 4 to 7 after it passes through the soil column; the pH value of the leachate ranges from 7.02 to 7.66, and mainly falls between 7.05 and 7.65, with each pH gradient increase of 0.01~0.20. The standard deviation and mean square deviation of the pH value of the leachate in each group are less than 0.15, and the coefficient of variation less than 2%; the coefficient of variation of all the experiment results is only 2.11%, indicating the stability of the pH value of the leachate, which fluctuates slightly around 7.31. It can be seen that the acidity of the soil itself have a great influence on the pH value of the leachate passing through it. The pH value of the soil is estimated to be 7.8, suggesting that the tested soil has a strong buffer capacity to the acid leaching solution. HUANG Yi (2007) utilized simulated acid rain with a pH value of 4.0 to conduct leaching tests on paddy soil and yellow soil respectively in urban area of Chengdu. The pH values of the leachate were 6.32~6.53 and 6.18~7.12 respectively, denoting that the release of Cd in the soil was accompanied by the release of OH^-. In the study on the influence of simulated acid rain on the release of Cd in purple soil, it was found that all the leachate was weakly alkaline, whose pH value was higher than that of the simulated acid rain. As the leaching proceeded, the pH value of the leachate decreased in the middle (LI Hong-ling, 2006).

Table 2 Mathematical statistics of pH value of leachate

Soil column	Number	Maximum pH	Minimum pH	Average pH	Standard deviation	Mean square deviation	Coefficient of variation (%)
pH=4	13	7.46	7.02	7.18	0.128	0.133	1.78
pH=5	13	7.39	7.06	7.22	0.105	0.109	1.45
pH=6	13	7.63	7.18	7.33	0.135	0.140	1.84
pH=6.7	13	7.66	7.23	7.38	0.119	0.124	1.61
pH=7	13	7.61	7.29	7.45	0.087	0.090	1.17
Results	65	7.66	7.02	7.31	0.154	0.155	2.11

2.3.2 Analysis of release behavior of Cd in soil

In conclusion, the release behavior of Cd could be: At the early stage of the leaching, the adsorption of soil colloid is hindered by a large number of hydrogen ions flowing in. These ions compete with the Cd ions at the adsorption site, seriously impairing the adsorption effect of soil colloid on the latter. The Cd ions then flow with the acid rain into the leachate, resulting in the high concentration of Cd at beginning. In the second stage, the concentration of Cd in the leachate decreases slowly due to the redox potential (Eh) of the soil. When the column is flooded, the soil is in the reduced state under the comprehensive action of biology, chemistry and physics, and the Fe^{3+} is reduced to Fe^{2+}, Mn^{4+} to Mn^{2+}, and SO_4^{2-} to S^{2-}. The generated insoluble sulfides such as iron sulfide and manganese sulfide react with Cd ions and precipitate, thus reducing the activity of Cd. Therefore, the concentration of Cd in the leachate is extremely low with a slow decline rate (LUO Ying, 2016; LEI Liang-qi, 2019).

3 Conclusions

Based on the above results and discussion, it can be concluded that:

(1) Precipitation and the pH value of rainfall are important factors affecting the release of Cd in soil. The release rate of Cd, the total release amount of Cd and the easiness of the Cd to migrate in the soil are positively correlated to the precipitation and negatively correlated to the rainfall pH values.

(2) According to the kinetic model analysis, the release of Cd in soil under rainfall conditions is a process influenced by multiple factors, such as the reaction rate and diffusion factor.

(3) According to the kinetic model analysis, the release of cadmium in soil under rainfall conditions is a process influenced by multiple factors, such as the reaction rate and diffusion factor.

(4) The release of Cd is not a simple linear process, but a process with obvious stages correlated to the physical and chemical properties of the soil, such as the permeability, pH and Eh.

Long-term and large-scale acid rain in the studied area will boost the activity of Cd in the soil and increase the concentration and content of Cd in the groundwater, severely degrading the quality of the groundwater environment, which deserves sufficient attention in order to avoid irreversible damages.

Ackonwledgements

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