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Purification effect and accumulative characteristics of dissolved heavy metals by modified bioretention system

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ABSTRACT

Six bioretention filter columns with different media were designed to explore the effects of media on dissolved heavy metals. The reduction effect of bioretention filter column on heavy metals under different operating conditions and its influencing factors were studied by changing five test parameters (pollutant concentration (PC), discharge ratio (DR), recurrence interval (RI), rainfall duration (RD), and antecedent dry period (ADP)). The correlation between the accumulation characteristics of heavy metals and enzyme activity in the media was analyzed. Results showed that the water reduction rate of column #1 was 27.78%, and other columns were more than 40%. Adding water treatment residue (WTR) and fly ash (FA) into bioretention soil media (BSM) has improved adsorption effect on Cu; adding green zeolite (GZ) and FA into BSM has enhanced adsorption effect on Zn; adding WTR, GZ, and coconut bran into BSM has improved adsorption effect on Cd. Different factors had varying effects on the water reduction and load reduction rates of the bioretention system. The RI had the largest influence on the water reduction rate, followed by the DR, and the RD and ADP were relatively small. The PC and ADP had a greater impact on heavy metals, and the other three factors were relatively small. The accumulation of heavy metals and enzyme activity were detected at different depths of the filler layer before and after the experiment. The accumulation of Cu and Cd in the filler was increasing, while Zn was decreasing, which was related to the excessive accumulation of Zn in the filler before the test. The accumulative of heavy metals did not show a certain regularity with depth. The accumulative characteristics of heavy metals in the media layer were related to the enzyme activity. Among these enzymes, protease, dehydrogenase, and catalase had a substantial correlation with Zn and Cd and had a small correlation with Cu. The correlation between urease and heavy metal content was low.

Keywords: Bioretention; Purification effect; Heavy metal; Accumulative characteristics

1. Introduction

With the continuous development of China's industrial level and the advancement of urbanization, the impermeable area of the city continues to expand, and a large number of impermeable pavements seriously destroy the natural water cycle. On the one hand, the expansion of non-permeable urban area blocks the infiltration channel of rainwater. This expansion leads to the increase in rainwater confluence speed, the advancement of flood peak flow, an increase in rain peak value, and frequent flood disasters. On the other hand, organic and inorganic matter,

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heavy metals, pathogenic bacteria, nitrogen, and phosphorus nutrients deposited on non-permeable pavements are brought into rivers, lakes, reservoirs, and other receiving water bodies along with the confluence of rainfall, thereby causing serious pollution to water resources [1]. Heavy metals are pollutants that are difficult to degrade in the environment and are easily enriched in living organisms. A large number of local and international studies have shown that non-point source pollution caused by rainfall has become one of the main metal pollution sources of surface environmental water [2]. The types and forms of heavy metals in urban rainfall-runoff are complicated, and the contents of Cu, Zn, and Cd are relatively high. Most heavy metals exist in dissolved and particle states [3–6]. Heavy metal content is closely related to factors, such as recurrence interval (RI), rainfall duration (RD), and antecedent dry period (ADP) [7,8]. Therefore, controlling urban rain floods has become an effective way to solve the contradiction between the urbanization process and ecological environment protection.

The low-impact development technology was first implemented in Maryland in the 1990s. The main idea is to minimize human disturbance, mimic the natural hydrological cycle as much as possible, and use the original functions of nature to alleviate a series of environmental problems caused by rainfall. This technology mainly realizes the evaporation, interception, storage, and filtration of rainwater runoff through scattered and small-scale source control, thus achieving effective control of rainwater flooding [9]. Bioretention technology is a low-impact development measure, which has the advantages of low cost, small land occupation, wide application range, and significant ecological and environmental benefits. The degradation mechanism of the technology for rainwater runoff pollutants is mainly through the interception and precipitation of surface medium, the absorption of plant roots, the physical and chemical adsorption of internal media, and the metabolism of microorganisms. Studies have shown that bioretention technology has a removal rate of heavy metals (Cu, Zn, and Cd) of up to 90% [2]. Most heavy metals are removed in the surface of the media, and the contribution of plants to the removal of heavy metals is negligible [10]. Thus, the media play a major role in the removal of heavy metals.

At present, few studies have involved the accumulation of heavy metals in bioretention systems and the long-term problems of possible leaching [11]. The adsorption capacity of bioretention media is limited. After 15–20 y of application, heavy metals accumulate to a certain extent, which may bring ecological risks such as groundwater pollution [10]. From the perspective of mass balance, there are three measures to improve the removal efficiency of heavy metals in bioretention facilities. One is to add a low solubility substance (such as an oxide of Fe or Al) to chelate with metal to reduce the migration rate; One is to periodically remove heavy metal accumulated saturated surface media; The other is to select suitable bioretention plants to promote the absorption of heavy metals and to harvest the plants regularly.

The removal of heavy metals in urban stormwater runoff by the media in the bioretention system plays a major role. Considering the shortcomings of the traditional bioretention soil media (BSM) water purification effect, adding a certain proportion of modifiers to the traditional BSM can improve the purification effect of the system [12–14]. In this study, five common adsorption materials of water treatment residue (WTR), green zeolite (GZ), fly ash (FA), turfy, and coconut bran (CB) were used as modifiers and mixed with BSM in different proportions to improve bioretention media, and simulated water distribution experiments were performed. A short-term simulated water distribution test for heavy metals was conducted approximately half a year before the test [15]. Based on the short-term simulated water distribution test, this experiment further study the regulation effect and accumulative distribution of bioretention systems on heavy metals (Cu, Zn, and Cd), identify the factors affecting the operation of bioretention systems, and identify the correlation between heavy metals and microbial activity. Thus, this study provides a reference for related mechanism research and pollution prevention of heavy metals in bioretention systems.

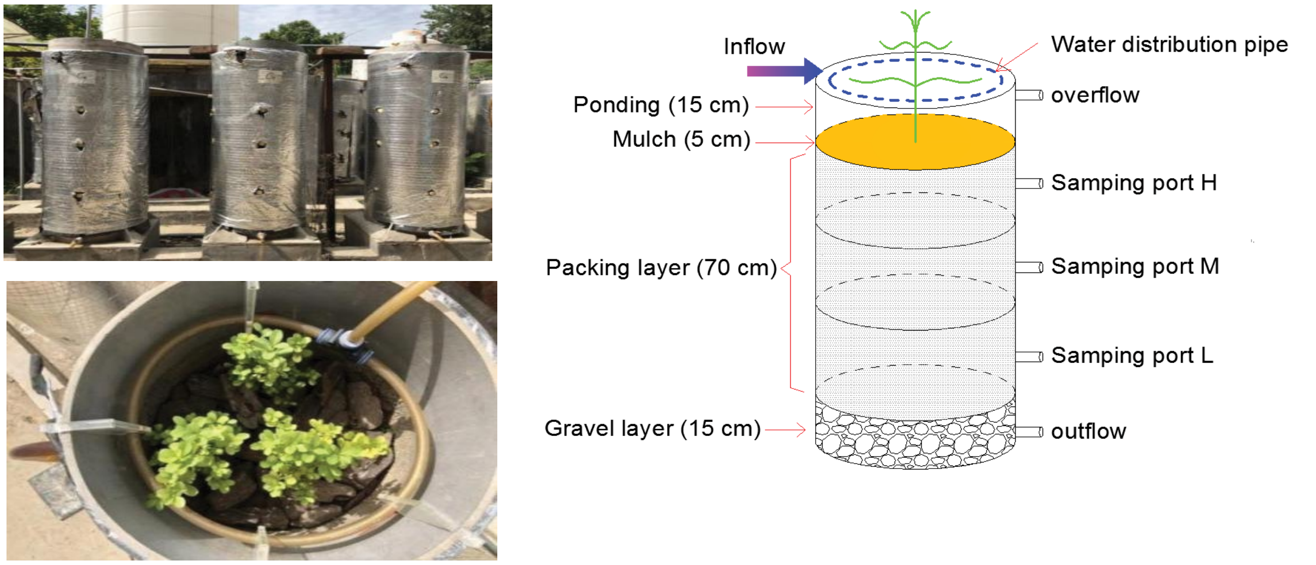
2. Materials and methods

2.1. Device setting

Six media, including BSM, WTR, GZ, FA, turfy, and CB, were used in this study as research objects. The selection and proportion of modifiers were determined by previous adsorption experiments and simulated rainfall experiments [15–17]. The BSM comprised of river sand, soil, and wood chips at a ratio of 65%, 30%, and 5% (mass ratio), respectively. The soil was obtained from the local surface planting soil of Fengxi New City, Xi'an City, Shaanxi Province. The river sand and wood chips were from a local building material market, and the soil was passed through a 2 mm sieve. Six bioretention filter columns were established at the Xi'an University of Technology. The filter column comprised DN400 PVC tube with a thickness of 6 mm, a diameter of 40 cm, and a height of 1.2 m. The columns consisted of gravel layer, packing layer, mulch, and ponding from bottom to top. The gravel layer comprised gravel with a particle size of 12 mm to 35 mm and a height of 15 cm high. The height of the packing layer was 70 cm. The mulch was filled with bark and had a height of 5 cm. The ponding height was 15 cm. The high water tank was used to simulate water distribution. Water outflow and overflow were set at the bottom and top of the filter column, respectively. Three soil extraction ports were set at 10, 30, and 50 cm under the media layer to collect the media. Meanwhile, three boxwood and ryegrass were planted inside the filter column. Live photos are shown in Fig. 1a and the device structure profile is shown in Fig. 1b.

2.2. Simulated water distribution experiment

Five common adsorbent materials, namely, WTR, GZ, FA, turfy, and CB, were mixed with BSM in different proportions to explore the regulation effect and accumulative distribution rule of heavy metals in the modified bioretention system and form five modified media and compare them with BSM. The ratio of media is shown in Table 1. The purification effect of bioretention systems on heavy metals was affected by many factors, including pollutant



(a) Live photos (b) Structure profile

Fig. 1. Test device and site photos.

Table 1
The ratio of six types of fillers

Device number	Media (mass ratio)
1	BSM
2	BSM + 10% WTR
3	BSM + 10% GZ
4	BSM + 10% FA
5	BSM + 5% turfy
6	BSM + 5% CB

Table 2
Simulated water distribution test parameters and level selection

A (PC)/(mg/L)			B	C	D	E
Cu	Zn	Cd	DR	(RI)/a	(RD)/min	(ADP)/d
0.2	0.3	0.05	5:1	0.5	30	3
0.3	0.5	0.1	10:1	1	60	6
0.5	1	0.3	15:1	2	90	9
1	1.5	0.5	20:1	3	120	12

concentration (PC), RI, RD, discharge ratio (DR), and ADP [18,19]. The simulated water distribution experiment aimed to ensure the effects of PC, RI, DR, RD, and ADP on water reduction and heavy metal purification effects under other conditions unchanged. A total of 16 orthogonal experiments were set for the five factors to explore the accumulation and distribution characteristics of heavy metals in modified bioretention fillers and the correlation between heavy metal accumulation and microbial activity combined with the typical rainfall-runoff characteristics of Xi'an City, Shaanxi Province. The test factors and levels were selected as shown in Table 2. The test scheme is shown in Table 3. Simulated water distribution flow was determined according to Eq. (1) [20].

$$i = \frac{16.715 \times \left(1 + 1.1658 \lg P\right)}{\left(t + 16.813\right)^{0.9302}} \tag{1}$$

where P is the RI, and t is the duration of the rainfall in min.

2.3. Data analysis

In this test, the entire process of simulated water distribution was monitored from the time when the water outlet and overflow were available. The water outlet and overflow amount were monitored every 5 min, and the water quality of the water outlet and overflow was monitored every 15 min, recorded, and analyzed. The water sample was filtered through a 0.45 μm membrane, and then the content of heavy metals (Cu, Zn, and Cd) was detected by atomic absorption spectroscopy (Analytik Jena, Germany). The water reduction, concentration removal, and load reduction rates of the bioretention system were calculated according to Eqs. (2)–(4), respectively. The packed layers were sampled at 10, 30, and 50 cm before and after the simulated water distribution test. The urease, protease, dehydrogenase, and catalase activities were determined by indophenol blue colorimetry, copper salt colorimetry, 2,3,5-triphenyl tetrazolium chloride, and volume method, respectively. The theoretical and the actual accumulative changes of heavy metals in the filler were calculated according to Eqs. (5) and (6), respectively.

$$R_V = \frac{V_{\text{in}} - V_{\text{out}} - V_{\text{over}}}{V_{\text{in}}} \times 100\% \tag{2}$$

$$R_c = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \tag{3}$$

Table 3
Simulated water distribution test scheme

No.	Factor A (PC)	Factor B (DR)	Factor C (RI)	Factor D (RD)	Factor E (ADP)	Water distribution flow/L
1	A_1	B_1	C_1	D_1	E_1	5.001
2	A_1	B_2	C_2	D_2	E_2	19.445
3	A_1	B_3	C_3	D_3	E_3	43.488
4	A_1	B_4	C_4	D_4	E_4	70.738
5	A_2	B_2	C_1	D_3	E_4	13.932
6	A_2	B_1	C_2	D_4	E_3	11.366
7	A_2	B_4	C_3	D_1	E_2	41.633
8	A_2	B_3	C_4	D_2	E_1	45.381
9	A_3	B_3	C_1	D_4	E_2	22.132
10	A_3	B_4	C_2	D_3	E_1	10.732
11	A_3	B_1	C_3	D_2	E_4	52.530
12	A_3	B_2	C_4	D_1	E_3	23.978
13	A_4	B_4	C_1	D_2	E_3	25.243
14	A_4	B_3	C_2	D_1	E_4	23.117
15	A_4	B_2	C_3	D_4	E_1	30.705
16	A_4	B_1	C_4	D_3	E_2	16.698

Note: 1, 2, 3, and 4 represent the four levels of each influencing factor.

$$R_L = \frac{C_{\text{in}}V_{\text{in}} - C_{\text{out}}V_{\text{out}} - C_{\text{over}}V_{\text{over}}}{C_{\text{in}}V_{\text{in}}} \times 100\% \tag{4}$$

$$M_t = T_{\text{in}} - T_{\text{out}} - T_{\text{over}} \tag{5}$$

$$M_a = \int_0^H \omega M \text{d}h \tag{6}$$

$$M_{\text{in(water)}} - M_{\text{over(water)}} - M_{\text{out(water)}} - M_{\text{others}} = M_{\text{end(media)}} - M_{\text{start(media)}} \tag{7}$$

where R_v is the water reduction rate of the device, %; R_c is the concentration removal rate of the device, %; R_L is the load reduction rate of the device, %; $V_{\text{in/out/over}}$ is the inflow/outflow/overflow, L; $C_{\text{in/out/over}}$ is the inflow/outflow/overflow concentration, mg/L; $T_{\text{in/out/over}}$ is the inflow/outflow/overflow load for bioretention systems, mg; $M_{t/a}$ is the theoretical/actual bioretention filler heavy metal change, mg; M is the mass of the filler, Kg; ω is the amount of change in heavy metals per unit mass of filler; $M_{\text{in/out/over(water)}}$ is the inflow/outflow/overflow pollutants mass in water, mg; $M_{\text{start/end(media)}}$ is the start/end of the mass of the pollutant mass in the media, mg; M_{others} is the effect of plant roots and microorganisms on heavy metals in the media, mg.

3. Results and discussion

3.1. Water/heavy metal reduction effect

The changes in water reduction and average water reduction rates in 16 tests of six columns are shown in Fig. 2. The experimental results indicated that the water reduction rates of the six bioretention columns fluctuated in the range of 13.80%–48.82%, 19.50%–64.77%, 22.60%–84.26%, 17.80%–90.25%, 20.93%–74.33%, and 15.81%–87.48%. The average water reduction rates of the columns #1–#6 were 27.78%, 44.78%, 43.51%, 44.88%, 41.47%, and 42.6%. The average water reduction rate of column #1 was small compared to others. The reason may be that the water holding capacity of a single filler was lower than others. The water reduction effects of the columns #2–#6 were not much different and greater than 40%. Therefore, the incorporation of a certain amount of modifier in the BSM could enhance the water holding capacity of the filler, thereby increasing the water reduction rate of bioretention system. Fig. 2a shows that as the test changes, the water reduction trend of different bioretention columns was the same, and the water reduction rate of the same filter column was considerably varied in different tests. This finding was closely related to the test conditions. The water reduction rate of different filter columns in the same test was different and related to the type of media.

The concentration and average concentration removal rates of the three heavy metals of Cu, Zn, and Cd in six bioretention columns in 16 orthogonal experiments are shown in Fig. 3. As shown in Fig. 3a, the Cu concentration removal rate of the six experimental columns fluctuated within the range of –105.32%–96.67%, –4.55%–97.11%, –34.42%–96.72%, –1.06%–98.22%, –16.57%–99.33%, and –45.40%–95.83%. The average concentration removal rate of Cu in column #1 (BSM) was 43.06%, which was the lowest among the six columns. Columns #2 (BSM + 10% WTR) and #4 (BSM + 10% FA) had the highest removal rates of Cu at 64.67% and 63.85%, respectively. Fig. 3b shows that the six experimental columns had a large amount of negative removal rate for the concentration purification of Zn. The

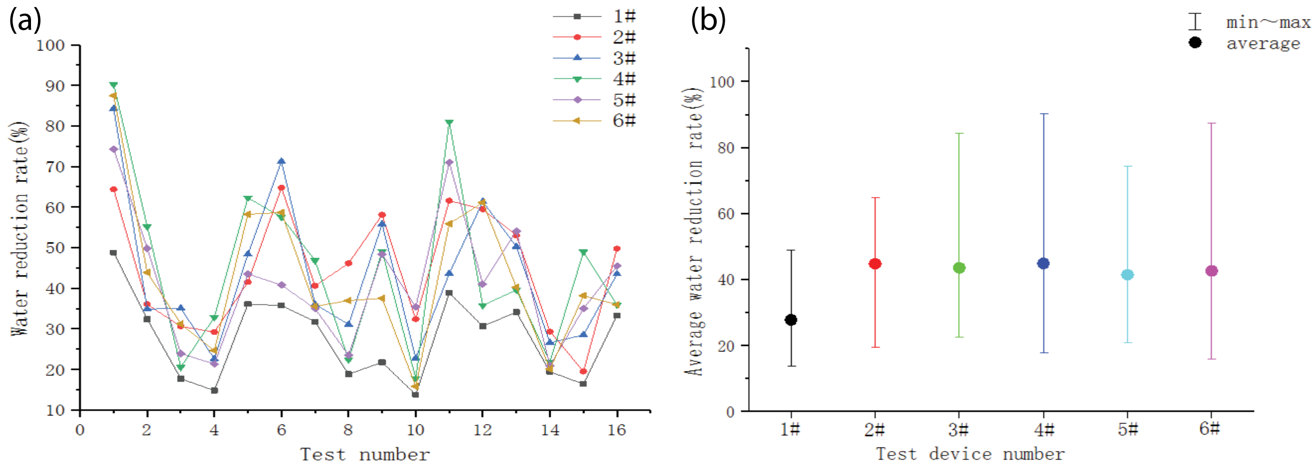


Fig. 2. Water reduction effect. (a) Water reduction effect in 16 trials and (b) average water reduction rate of the device.

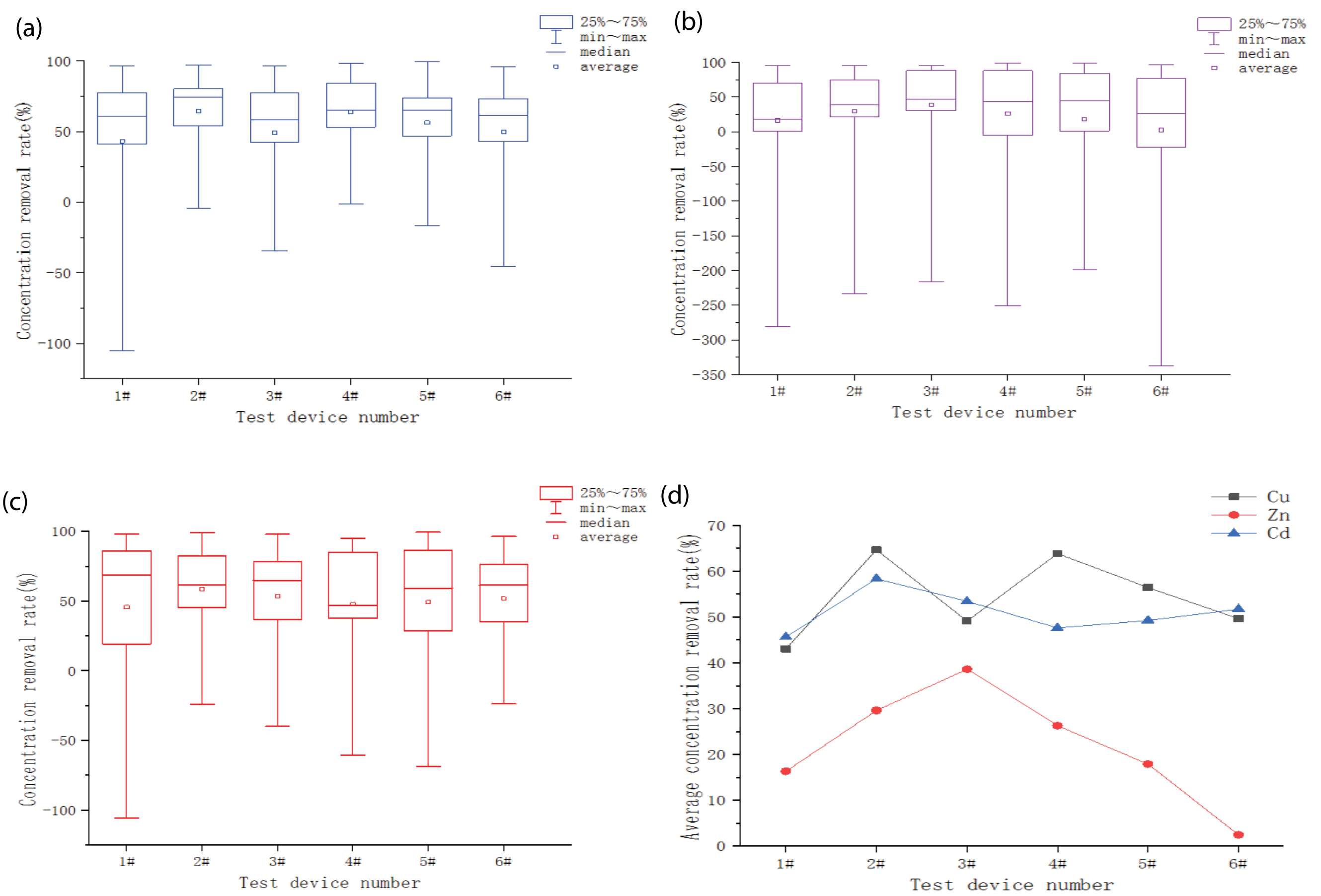


Fig. 3. Concentration purification effect. (a) Cu concentration removal rate, (b) Zn concentration removal rate, (c) Cd concentration removal rate, and (d) average concentration removal rate.

average concentration removal rate of Zn for column #1 (BSM) was 16.35%, which was lower than that of columns #2 (BSM + 10% WTR), #3 (BSM + 10% GZ), #4 (BSM + 10% FA), and #5 (BSM + 5% turfy), and the removal rates were 29.60%, 38.61%, 26.28%, and 17.90%, respectively. The average concentration removal rate of column #6 (BSM + 5% CB) was low. As shown in Fig. 3c, the Cd concentration removal rate of the six columns fluctuated within the range of –105.97%–98.25%, –24.15%–99.06%, –39.91%–98.00%, –60.44%–94.85%, –68.69%–99.44%, and –23.83%–96.41%.

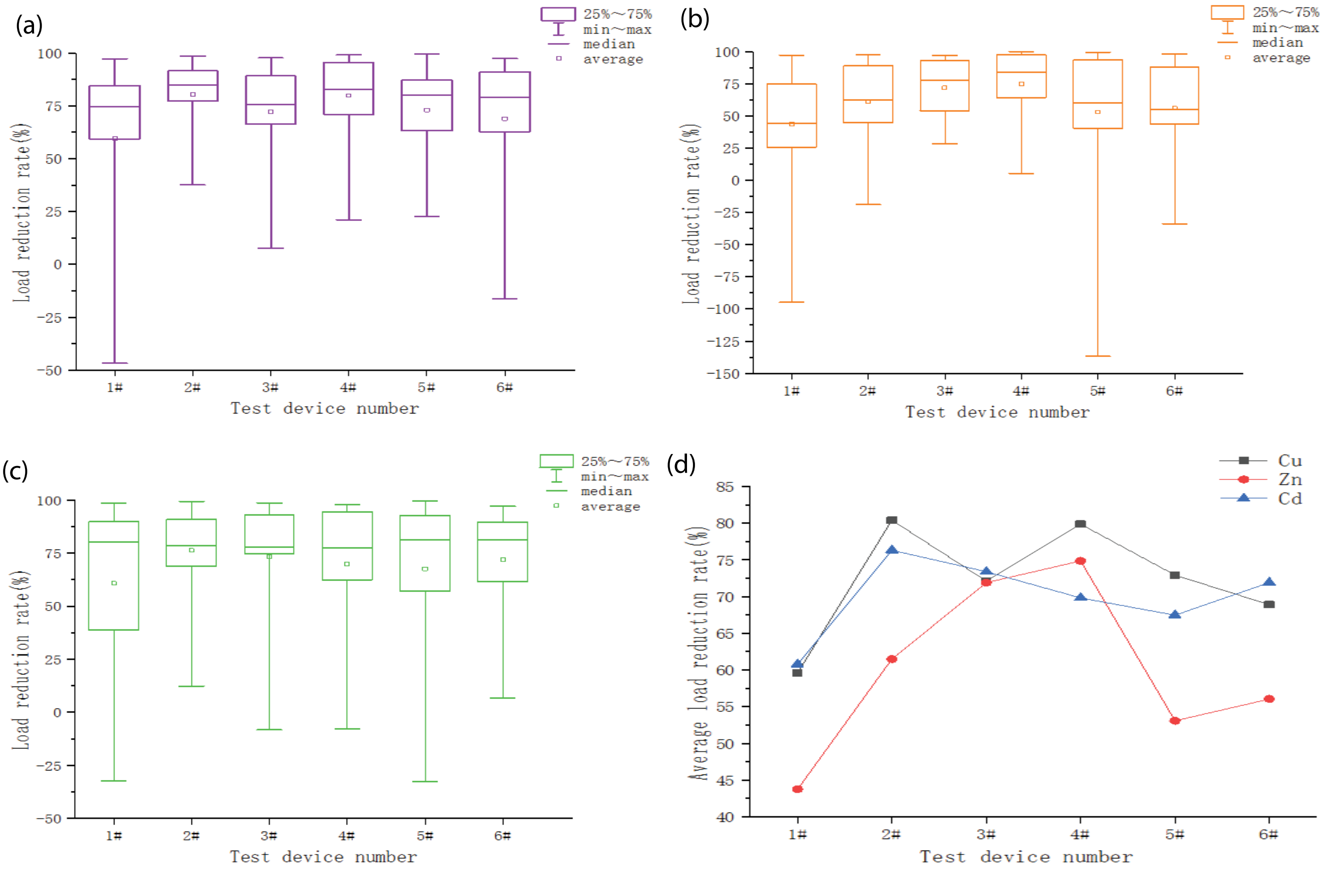


Fig. 4. Effect of load reduction. (a) Cu load reduction rate, (b) Zn load reduction rate, (c) Cd load reduction rate, and (d) Average load reduction rate.

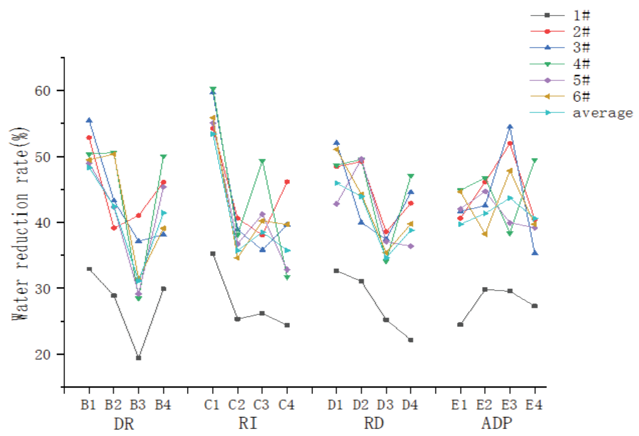


Fig. 5. Trend chart of water reduction rate.

The average concentration removal rate of columns #2–#6 was higher than that of column #1 (BSM), and the removal rates were 58.39%, 53.44%, 47.64%, 49.25%, and 51.73%.

The load and average load reduction rates of each column are shown in Fig. 4. Results showed that the load reduction rates of six bioretention columns for Cu fluctuated within the range of –46.71%–97.22%, 37.65%–98.42%, 7.66%–97.65%, 21.02%–99.09%, 22.75%–99.49%, and –16.19% –97.42%. The fluctuation range of columns #2 (BSM + 10% WTR), #4 (BSM + 10% FA), and #5 (BSM + 5% turfy) was relatively small. The average load reduction rate of columns #2–#6 for Cu was higher than that of column #1 (BSM). The average load reduction rate of columns #2 (BSM + 10% WTR) and #4 (BSM + 10% FA) was relatively high at 80.41% and 79.87%, respectively. The load reduction rate of Zn in six bioretention columns fluctuated within the range of –94.81% –97.22%, –18.88%–97.59%, 28.33%–97.07%, 5.40%–99.97%, –136.80%–99.54%, and –33.77%–98.14%. The fluctuation rate of the column #4 (BSM + 10% FA) was relatively small. The average load reduction rates of Zn for the six columns were 43.75%, 61.48%, 71.90%, 74.86%, 53.08%, and 56.04%. The load reduction rates of Zn for columns #3 (BSM + 10% GZ) and #4 (BSM + 10% FA) were relatively high. The load reduction rates of six columns for Cd fluctuated in the range of –32.33%–98.49%, –32.33%–98.49%, 12.26%–99.37%, –8.29% –98.59%, –7.81%–97.78%, –32.69%–99.64%, and 6.72%–96.98%. The average load reduction rates of the six columns for Cd were 60.76%, 76.32%, 73.40%, 69.82%, 67.47%, and 71.92%. The reduction rates of columns #2 (BSM + 10% WTR) and #3 (BSM + 10% GZ) were relatively high but the fluctuation was small. Through the analysis of the water quality purification results of 16 orthogonal tests, the concentration removal and load reduction rates of columns #2–#6 show superior effects to those of the column #1 (BSM).

After comprehensive evaluation, columns #2 (BSM + 10% WTR), #3 (BSM + 10% GZ), and #4 (BSM + 10% FA) devices have improved water quality control effects.

3.2. Analysis of influencing factors

Different conditions had a certain impact on the water reduction rate. The water reduction of the six filter columns under different factors was analyzed, and the results are shown in Figs. 5 and 6. Fig. 5 shows that the optimal operating condition of the column #1 (BSM) was $B_1C_1D_1E_2$, $B_1C_1D_1E_3$ for column #2 (BSM + 10% WTR), $B_1C_1D_1E_3$ for column #3 (BSM + 10% GZ), $B_2C_1D_2E_4$ for column #4 (BSM + 10% FA), $B_1C_1D_2E_2$ for column #5 (BSM + 5% turfy), and $B_2C_1D_1E_3$ for column #6 (BSM + 5% CB). The optimal operating condition of the average water reduction rate of the six filtration columns was $B_1C_1D_1E_1$. The range analysis of the influencing factors of the water reduction rate of different filter columns is shown in Fig. 6. The results indicated that the RI had the largest influence on the water reduction rate, followed by the DR, and the RD and ADP were relatively small. In addition, with the change in the single condition factor, the water reduction rate of the six filter columns did not show evident synchronicity. Column #1 (BSM) had the lowest water reduction rate compared with that of other filter columns. Therefore, BSM mixed with different proportions of modifiers can improve the water reduction rate of bioretention systems to a certain extent. This improvement may be related to the addition of modifiers, which can change the water retention performance of media.

The purification effect of heavy metals was affected by many aspects. The influence of PC, DR, RI, ADP, and RD on the load reduction rate of heavy metals (Cu, Zn, and Cd) was explored through the simulated water distribution experiment of the bioretention system. Based on the range analysis of the reduction effect of heavy metals in 16 tests, the degree of influence of various factors on heavy metal reduction and the best-operating conditions were determined as shown in Table 4 and Fig. 7. Columns #1–#2 was most affected by PC and RD, followed by RI and ADP, and DR was the smallest. Columns #3–#6 was most affected by PC and ADP, and the 3 other factors were relatively small. The optimal test conditions of columns #1–#6 were obtained by comparing the load reduction efficiency of different factors and levels. The optimal test conditions for columns #1 (BSM), #2 (BSM + 10% WTR), and #5 (BSM + 5% turfy) were $A_3B_4C_3D_2E_1$, $A_3B_4C_4D_2E_1$, and $A_3B_1C_3D_2E_1$, respectively, and for the other 3 columns were $A_3B_1C_1D_2E_1$. For the optimal test conditions of 6 columns, A_3, B_1, C_1, D_2, and E_1 appeared 6, 4, 3, 6, and 6 times, respectively. The optimal setting levels that correspond to the six factors were 0.5 mg/L for Cu, 1 mg/L for Zn, 0.3 mg/L for Cd, 5:1, 0.5a, 60 min, and 3 d. In practical projects, bioretention facilities (device DR and type of media) can be reasonably designed according to the quality of incoming water and local climatic conditions to alleviate heavy metal pollution caused by non-point source pollution.

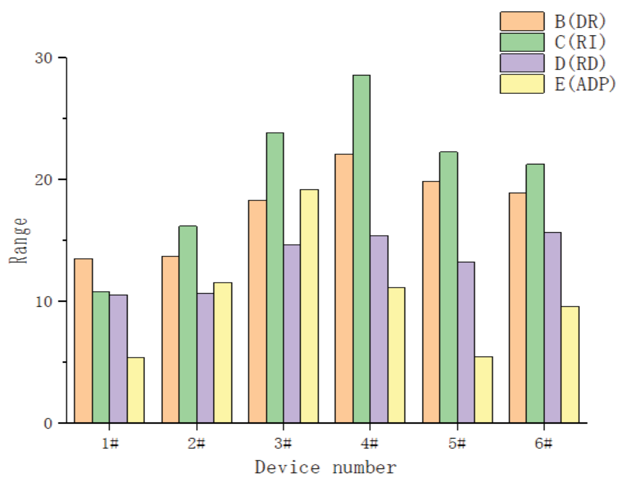


Fig. 6. Comparison of range among the four factors.

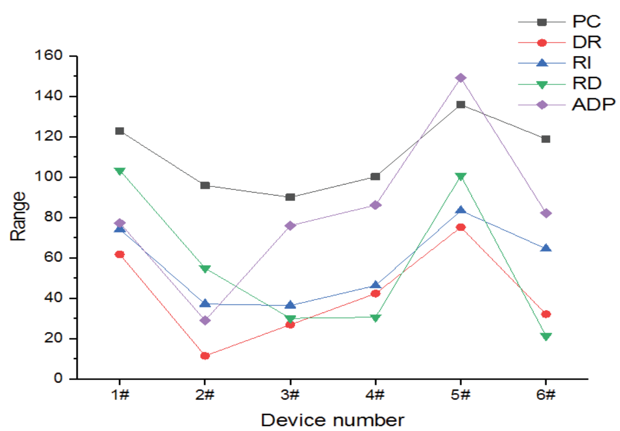


Fig. 7. Comparison of range among the five factors.

Table 4
Range of the five factors and optimal test condition in different media

Device number	Range/A	Range/B	Range/C	Range/D	Range/E	Optimal test condition
#1	122.8	61.66	74.11	103.27	77.2	$A_3B_4C_3D_2E_1$
#2	95.78	11.43	37.08	54.81	28.95	$A_3B_4C_4D_2E_1$
#3	89.96	26.83	36.37	29.99	75.91	$A_3B_1C_1D_2E_1$
#4	100.12	42.29	46.24	30.56	86.08	$A_3B_1C_1D_2E_1$
#5	135.79	75.11	83.33	100.65	149.09	$A_3B_1C_3D_2E_1$
#6	118.85	32.06	64.41	21.24	82.1	$A_3B_1C_1D_2E_1$

3.3. Analysis of accumulative distribution characteristics

3.3.1. Vertical accumulative characteristics

The removal mechanism of heavy metals through bio-retention systems includes filler adsorption, plant root absorption, and microbial action [21]. Among these mechanisms, packing adsorption plays a major role. The samples were obtained from different depths of the packing layer (10, 30, and 50 cm) before and after the test to detect the content of heavy metals, and the results are shown in Fig. 8. The figure showed that the accumulation of Zn in each layer of columns #1–#6 was negative during the test, and the accumulative amount of Cd was positive. The accumulative amount of Cu in each layer of columns #3 (BSM + 10% GZ), #5 (BSM + 5% turfy), and #6 (BSM + 5% CB) was positive. The accumulation of Zn in each layer of the various columns drastically fluctuated during the experiment, and the fluctuation of the accumulative amount of Cd was small. This was related to the high inflow concentration of Zn and the low inflow concentration of Cd. During the test, the accumulative amount of Cu in columns #1–#6 packing was positive. The average accumulative amount of each metal in columns #1–#6 before and after the test was Zn > Cu > Cd and Cu > Zn > Cd, respectively. The average Cd accumulative amount of each device before and after the test was the smallest. The average accumulation of Zn before the test was the largest but was constantly precipitated during the test. The average accumulation of Cu after the test was the largest. This finding may be attributed to the considerably high Zn accumulation in the media packing layer before the test was extremely high, while the accumulation of Cd and Cu was relatively low. The

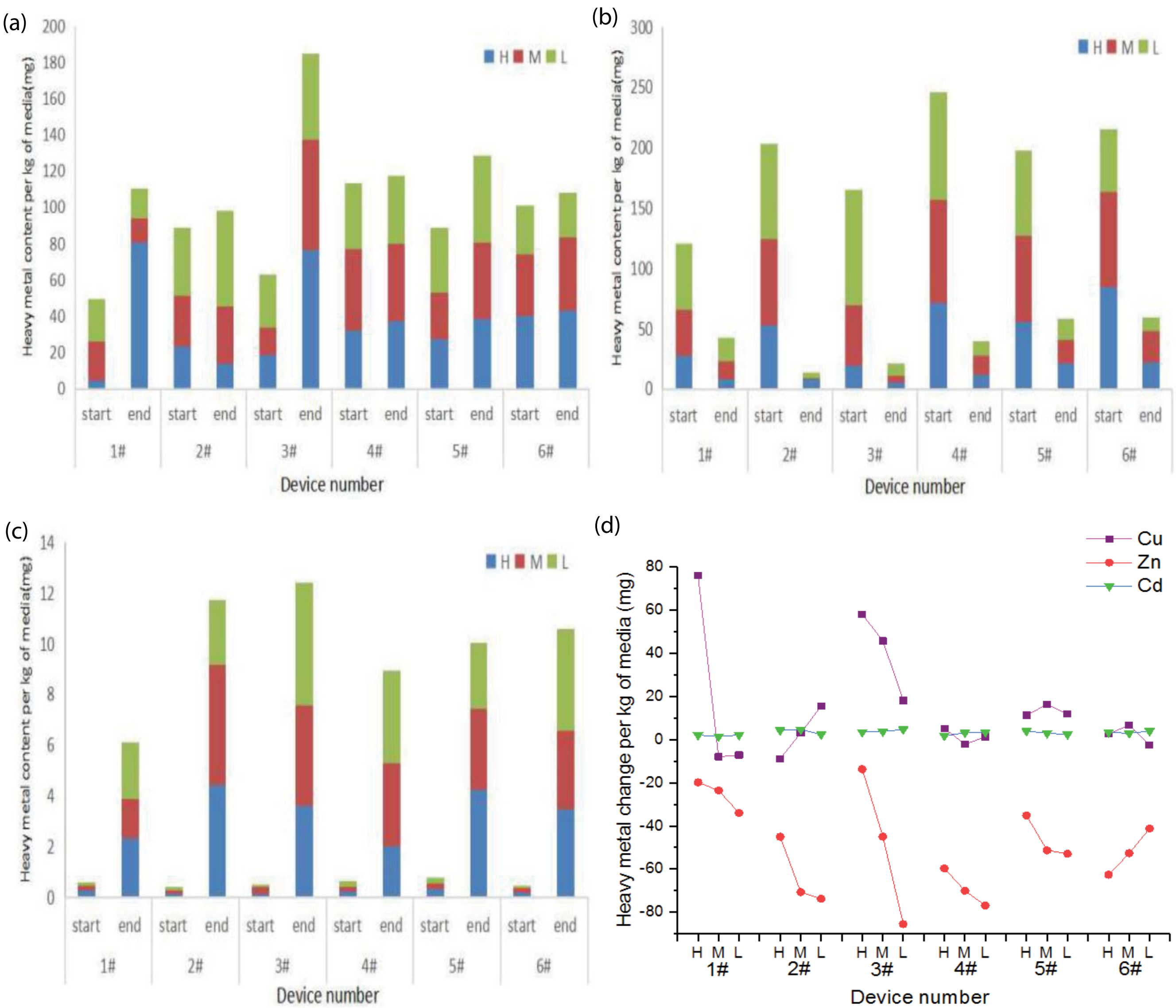


Fig. 8. Content of heavy metals in the media. (a) Cu content at different depths before and after the test, (b) Zn content at different depths before and after the test, (c) Cd content at different depths before and after the test, and (d) Changes of heavy metals at different depths of the filler before and after the test.

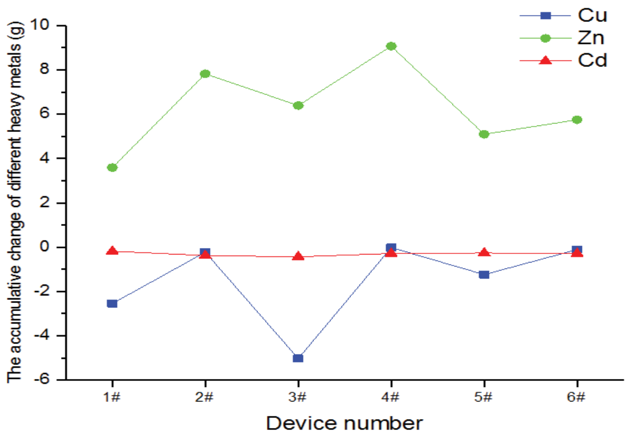


Fig. 9. Accumulative changes in heavy metals caused by other factors during the test.

accumulative amount of heavy metals in each device did not show significant stratification as the depth changed.

3.3.2. Mass distribution of heavy metals

The accumulative changes in heavy metals in bioretention systems primarily depended on influent loading, effluent loading, plant root uptake, and microbial activity. Heavy metals were difficult to be degraded and removed in the soil. Excessive concentrations may lead to the re-precipitation of heavy metals, which will have a serious impact on the ecological environment and human health [22,23]. The removal of heavy metals by the bioretention system is mainly through media adsorption, but the microbial action should not be underestimated. During the test, the contributions of heavy metal removal, such as microbial metabolism and plant absorption, were indirectly evaluated by monitoring the influent and effluent loads and the actual heavy metal in the filler layer. According to the material balance, the amount of heavy metal load change in the packing layer of the bioretention column is shown in Eq. (7). The changes in the accumulation of heavy metals caused by other effects during the test were analyzed, as shown in Fig. 9. $M_{\text{others}} > 0$ and $M_{\text{others}} < 0$ indicated that other effects respectively result in the heavy metal reduction and augmentation in the packing layer of the column. Fig. 9 shows that the effect of Cu and Cd in the six columns was negative for other reasons, and the effect of Zn on the six columns was positive. The effects of other factors on Zn and Cu were relatively different in various columns, and the effect on Cd was small. The removal of Zn from the packing layer by the other functions in columns #1–#6 was 3.59, 7.82, 6.39, 9.07, 5.09, and 5.75 g. Column #4 (BSM + 10% FA) was the largest, and column #1 (BSM) was the smallest. The removal of Cu from the packing layer by the other functions in columns #1–#6 was –2.54, –0.22, –5.03, –0.01, –1.24, and –0.11 g. The column #4 (BSM + 10% FA) was the largest, and the column #3 (BSM + 10% GZ) was the smallest. The removal of Cd from the packing layer by the other functions in columns #1–#6 was –0.18, –0.38, –0.43, –0.28, –0.26, and –0.29 g. The column #1 (BSM) was the largest, and columns #2 (BSM + 10% WTR) and #3 (BSM + 10% GZ) were the smallest. The principle of material balance indicated that many factors affect the accumulation of heavy metals in the bioretention packing layer. The contribution of other effects (microbial activities and plant root absorption) to heavy metal removal was evaluated by comparing the measured changes in the inflow/outflow load and the heavy metals in the packing layer. The specific reasons and the proportion of each part to be removed need further verification.

Table 5
Pearson correlation of enzymes and heavy metals in media

Content difference	Cu	Zn	Cd	Summation
Urease	0.15	−0.173	0.144	−0.107
Protease	−0.355	0.7	−0.71	0.539
Dehydrogenase	0.369	−0.829	0.888	−0.657
Catalase	−0.376	0.848	−0.92	0.674

3.3.3. Enzyme activity analysis

The change of enzymes in soil media is the result of microorganisms and plant life activities [24]. Heavy metal species and content have a certain impact on biological activity. A low concentration of heavy metals promotes microbial activity, and excessive concentration shows toxic effects on microorganisms. Catalase decomposes hydrogen peroxide to prevent soil poisoning and is used as a biological indicator for heavy metal (Cu, Zn, and Cd) contamination [25,26]. Proteases, dehydrogenase, and urease have also been used as biological indicators in certain polluted environments [27–29]. Therefore, studying the activity of enzymes in bioretention media is of considerable importance for indirect evaluation of the accumulation of heavy metals in bioretention systems.

Soil enzyme activity is affected by heavy metals. Detection of soil enzyme activity can indirectly evaluate soil pollution by heavy metals [27,30]. Yang et al. [30] showed that catalase was positively correlated with heavy metals. Shen et al. found that Zn was inversely related to urease activity [28]. Pearson correlation analysis was conducted on the enzyme activity and heavy metal content by monitoring the four enzyme activities (urease, protease, dehydrogenase, and catalase) and heavy metals (Cu, Zn, and Cd) in the bioretention packing layer. When the correlation coefficient (r) is equal to 0.8–1, it indicated that the enzyme had a very strong correlation with heavy metals; 0.6–0.8 was a strong correlation; 0.4–0.6 was a general correlation; 0.2–0.4 was a weak correlation; 0–0.2 was very weak or no correlation. Table 5 showed that a certain correlation exists between enzyme and heavy metal. Urease had little correlation with heavy metals. Protease, dehydrogenase, and catalase were weakly related to Cu. The correlation of protease, dehydrogenase, and catalase was relatively high with Zn and Cd. The sum of the three heavy metals had a high correlation with protease, dehydrogenase, and catalase with Pearson correlation coefficients of 0.539, –0.657, and 0.674, respectively. Therefore, protease, dehydrogenase and catalase activities have some guiding significance for indirect evaluation of heavy metals (Cu, Zn, and Cd) pollution in bioretention systems.

4. Conclusions

Through the bioretention simulation water distribution test, the water/heavy metal reduction effect, influencing factors, and accumulative rules of bioretention facilities under different operating conditions were studied, and the following conclusions were drawn.

- The mixing of BSM with different ratios of adsorbents can improve the heavy metals reduction rate of bioretention systems to a certain extent. Columns #2 (BSM + 10% WTR), #3 (BSM + 10% GZ), and #4 (BSM + 10% FA) has better control effect on the heavy metals. Different factors have different effects on heavy metals reduction rate of bioretention system. The PC and ADP have a greater impact on heavy metals, and the other three factors are relatively small. In practical engineering, bioretention system should be designed reasonably according to Climatic conditions and runoff pollution levels. The accumulation of heavy metals (Cu, Zn, and Cd) in the filler has a certain correlation with the enzyme activity (protease, dehydrogenase, catalase). In the future, the effects of microorganisms on heavy metals and their influencing factors can be further explored.
- In bioretention systems, the degradation of heavy metals by fillers plays a major role. A high concentration of heavy metals has a great influence on the purification effect of the bioretention system and can shorten its service life and cause serious pollution to groundwater. Therefore, it is necessary to manage the bioretention system on a regular basis. At present, there is a lack of understanding of the degradation mechanism of heavy metals in bioretention systems. It is of great significance to study the migration and transformation mechanism of heavy metals in fillers, microorganisms, and plants.

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