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Original Research

Modified Media for Heavy Metals and COD Removal from Urban Stormwater Runoff Using Pilot Bioretention Systems

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Abstract

The media and structural optimization in bioretention systems play important roles in removing pollutants from urban stormwater runoff. Ten bioretention basins were constructed by adding water treatment residual (WTR), green zeolite, flyash, and coconut bran to traditional bioretention soil (65% sand + 30% soil + 5% sawdust, by mass), respectively, through mixing or layering. The steady infiltration rates of modified media were 3.25~62.78 times those of plant soil. The peak flow reduction rates of plant soil (1#) and flyash (7#) basins were significantly high, ranging from 78.09% to 92.91% (median = 86.52%) and 88.01% to 96.85% (median = 93.62%).The outflow concentrations of Cu and Zn were superior to Class II limitation (1.0 mg·L^{-1}) in surface water environmental quality standards in China. The outflow concentration was inferior to Class V for COD and Cd. COD load reduction rate decreased with the increase of the recurrence interval and discharge ratio, which increased with the increase of inflow concentration. Although load reduction rate of heavy metal Cd increased with the increase of these three influencing factors, the reduction rate of Zn and Cu in heavy metals occurred without certain regularity. The median loading reduction rates of COD were the highest for layered media structure bioretention basins (6# and 8#). The heavy metal load reduction rates of 3#~6# (mixed or layered media structure, adding 10% WTR as modifier) and 8# (layered media structure, adding 10% fly ash as modifier) were higher than other basins, and the median load reduction rate was mostly above 80%.

Keywords: bioretention; modified media; stable infiltration rate; concentration; loading

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Introduction

Rainfall runoff from urban impermeable surfaces is a key polluter of urban waterways, contributing pollutants such as suspended solids (SS), biodegradable organic matter (BOD_5 and COD), organic micropollutants, nutrients, and heavy metals [1-2]. Among them, heavy metals have such characteristics as persistent pollution, wide area and difficult management. Therefore, heavy metal pollution has a relatively harmful effect on the environment and the entire ecosystem, and it has become one of the hot spots.

One emerging stormwater management philosophy is low impact development (LID) [3]. LID aims to return the developed watersheds to pre-development hydrological conditions (i.e., to mimic natural water cycles or achieve hydrological neutrality) [4]. Stormwater quality regulations are another major driver for the adoption of LID, as some controls have also been implemented to improve water quality. Bioretention basins utilize soil retention to remove pollutants and allow for infiltration. However, pollutants infiltrating into soil and groundwater may cause subsurface contamination. Meanwhile, toxic metal accumulation requires periodic replacement of topsoil, making operation and maintenance more complex and costly [5]. The heavy metal purification mechanisms on urban runoff for bioretention technology often include surface media interception, limited plant absorption/uptake and internal media physical adsorption [6-7]. Studies have shown that most heavy metals are removed in the 0~20 cm planting soil, and the concentration of heavy metals decreases with increasing depth of the medium [8]. Zgheib et al. [9] found that the concentration of particulate Pb, Cd, Cu and Zn in urban storm runoff accounted for 97%, 83%, 67% and 52% of the total, respectively, and the dissolved proportions of Zn are highest in these four heavy metal ions. Zhao et al. [10] conducted a study on road sediments, and they found that heavy metals accounted for more than 80% of the total heavy metals in sediments sized less than 250 μm in stormwater runoff, and heavy metals accounted for more than 70% in sediments whose particle size was less than 44 μm.

The main influencing factors of heavy metal removal by bioretention technology include rainfall runoff concentration, rainfall duration, rainfall intensity and bioretention medium types, medium height and configurations. In addition, the biological reactions would be significantly affected by the drying and wetting regimes, since the bioretention system is operated intermittently in practice [11]. Blecken et al. [12] examined the impact of this design modification on heavy metal treatment. The results show that submerged zone (SZ) and carbon source have a significant impact on metal treatment. In particular, the removal of Cu

Table 1. Component characteristics of the media.

No.	Media	ρ (g/mL)	BET (m^2/g)	CEC (cmol/kg)	OM(%)	Porosity (cm^3/g)
1	Soil	1.121	20.837	19.44	0.03	0.0300
2	BSM	1.116	4.991	34.45	7.55	0.0096
3	WTR	0.953	28.433	9.31	10.3	0.0215
4	Green zeolite	1.054	16.871	27.50	6.98	0.0510
5	Flyash	1.008	1.381	23.23	2.66	0.0066
6	Coconut bran	0.092	0.811	13.62	4.65	0.0026

Note: ρ is the filling density for particles; BET is the specific surface area, m^2/g; CEC represents the cation exchange capacity.

Table 2. Pilot plant structure.

No.	1#	2#	3#	4#	5#	6#	7#	8#	9#	10#
Ponding	15cm									
Mulch	Pine bark 5cm									
Media	Soil 70 cm	BSM 70 cm	BSM + WTR mixing 70 cm	BSM + WTR mixing 70 cm	BSM + WTR mixing 70 cm	BSM + WTR layering 70 cm	BSM + Fly ash mixing 70 cm	BSM + Fly ash layering 70 cm	BSM + Gz mixing 70 cm	BSM + Cb mixing 70 cm
GDL	10 cm									
SZH	0	0	0	150mm	350mm	0	0	0	0	0

Note: SZH is the submerged zone height, mm; GDL is the gravel drainage layer. BSM and WTR, Fly ash, Green zeolite (Gz) mixed ratio of 9: 1, BSM and coconut bran(Cb) mixed ratio of 19: 1, by mass.

was improved significantly, and Zn and Pb removal was enhanced slightly. From a quality balance standpoint, there are three measures that can be taken to improve the removal efficiency of heavy metals for bioretention facilities. Firstly, Fe or Al oxide compound could be added to the bioretention media to chelate with metal, reducing the migration rate of heavy metals. Another method is to replace shallow surface media that heavy metal accumulation saturates regularly. The other methods such as selected appropriate bioretention plants to promote the absorption of heavy metals and plants should be regularly harvested to remove heavy metals.

In this paper, the media in the bioretention systems were designed to have high metal removal potential and high permeability. 10 bioretention systems were constructed by (i) mixing efficient modifiers with traditional bioretention soil to form four modified media for bioretention and (ii) setting different configurations (i.e., layered or mixing media, different submergence area heights). These procedures were undertaken to (1) develop modified media for improving bioretention basin hydrologic performance; (2) evaluate the improvement of heavy metals and COD removal by modified media; and (3) identify the relationship between the removal effect of bioretention system and hydrologic/hydraulic elements (e.g., recurrence interval, contribution area ratio, and steady infiltration rate).

Materials and Methods

Media Preparation

Soil was collected from local topsoil using a 2 mm sieve. To improve soil infiltration capacity, water retention capacity, and organic quality, sand and wood chips were separately added to get traditional bioretention media (BSM). The test local river sand and soil were mixed at a ratio of 7:3 (by mass). The mixture contained 49.0% sand, 5.5% clay, and 45.5% silt; then, 5% (by mass) wood chips were added to the mixture to increase the organic content and water-holding capacity of the media. WTR, green zeolite, coconut bran, and fly ash were used as modifiers and mixed with BSM in different proportions to form modified mixed media. Fig. 1 shows the SEM images and physical photos of the media. The media characteristics were shown in Table 1, and the particle sizes were as follows: soil (<2mm), zeolite (3-6 mm), BSM and WTR (<6 mm), and fly ash and coconut bran (<1 mm). The specific surface areas were: soil (20.837 m^2/g), BSM (4.991 m^2/g), WTR (28.433 m^2/g), green zeolite (16.871 m^2/g), flyash (1.381 m^2/g), coconut bran (0.811 m^2/g).

Device Setting

Ten pilot-scale bioretention systems were constructed in the outdoor field of Xi′an University of Technology. Each tank has the following dimensions: length 2.0 m × width 0.5 m × depth 1.05 m. The construction involved 15 cm ponding depth, 5 cm mulch, 70 cm media, and 15 cm gravel layer from top to bottom. The mulch was pine bark, and *Buxus sinica* and *Lolium perenne* L. were planted. Geotextile was laid between the media and the gravel layers. A perforated drain (DN75) was placed on the bottom of the system. Each device artificial packing layer shown in Fig. 2a), 4 #, 5 # submerged area height (SAH) were 150 mm and 350 mm, and other devices do not have an internal water storage area (Table 2).

Experimental Design

Pilot-scale experiments were designed for a pre-experiment, and 9 orthogonal experiments, which included the design of rainfall intensity, contribution area, inflow concentration, and submerged zone heights

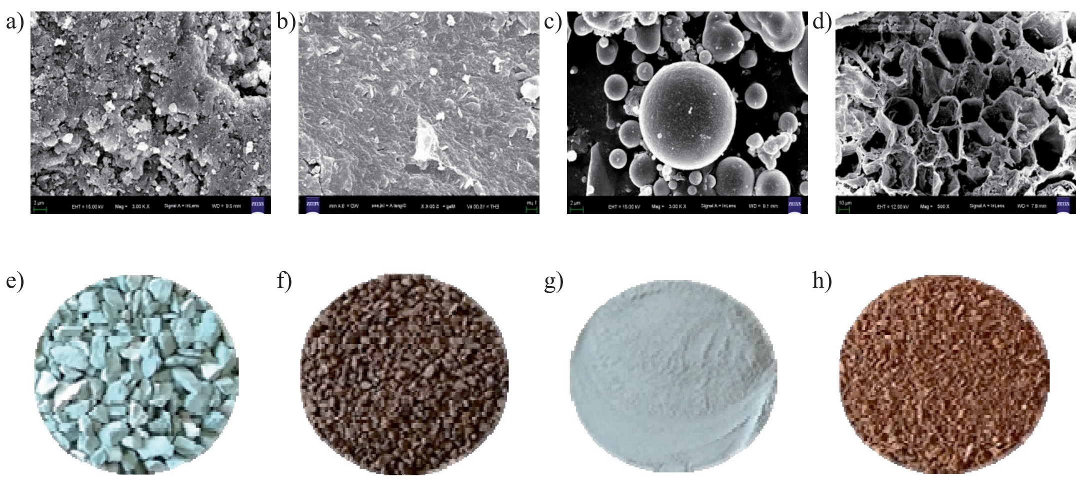

Fig. 1. Photos and SEM images of modifiers: a) Green zeolite, b) WTR, c) Flyash, d) Coconut bran, e) Green zeolite, f) WTR, g) Flyash, h) Coconut bran.

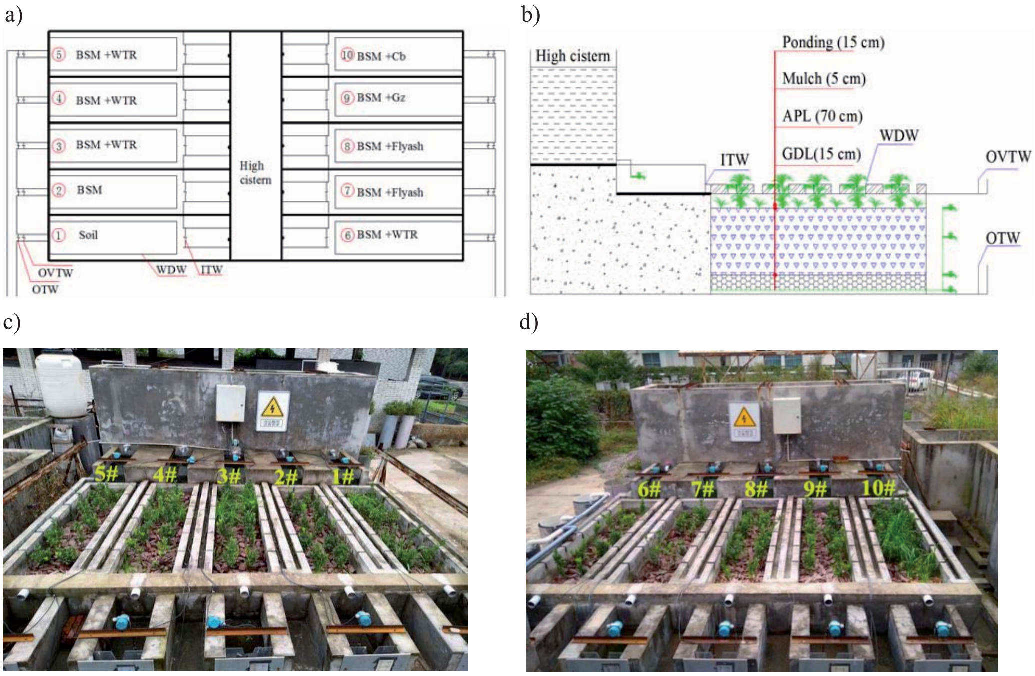

Fig. 2. Pilot plant structure and site photos: a) Floor plan, b) Sectional view, c) 1#~5#, d) 6#~10#.
Note: SZH is the submerged zone height; GDL is the gravel drainage layer. APL is artificial packing layer, ITW for inflow triangle weir, OTW for outflow triangle weir, OVTW for over triangle weir.

to determine the appropriate design parameters for the bioretention facilities. Water volume was calculated in three recurrence intervals, namely, 0.5, 2, and 3 years, and three catchment ratios (catchment area/bioretention surface area). Pollutant concentrations were determined by comparing the results of water quality assessment with urban road surface runoff in Xi′an, China. Tables 3 and 4 show the test schedule and inflow pollutant concentrations, respectively. In rainstorm design, the Pilgrim and Cordery (PC) method is insignificantly affected by rainfall duration and only increases or reduces the rain tail part when duration increases or decreases; consequently, the calculated peak flow is stable. The PC method was adopted in the rainstorm pattern calculation in the present study for the short-term rainfall data of 60 min from 1961 to 2014 in Xi′an [13]. A_1, A_2 and A_3 were 1 h rainfall volume under three recurrence intervals (0.5 yr, 2 yr and 3 yr). B_1, B_2 and B_3 correspond to catchment ratios of 10:1, 15:1 and 20:1, respectively,

Table 3. Test schedule for the pilot-scale bioretention systems.

Test number (Date)	Precipitation/mm, $A_{(Level\ 1,\ 2,\ 3)}$	CR, $B_{(Level\ 1,\ 2,\ 3)}$	IC/(mg/L), $C_{(Level\ 1,\ 2,\ 3)}$	ADT/d	Test conditions
0	11.47(A_1)	10(B_1)	high(C_1)	6d	$A_1B_1C_1$
1	11.47(A_1)	15(B_2)	medium(C_2)	6d	$A_1B_2C_2$
2	11.47(A_1)	20(B_3)	low(C_3)	6d	$A_1B_3C_3$
3	23.88(A_2)	10(B_1)	medium(C_2)	6d	$A_2B_1C_2$
4	23.88(A_2)	15(B_2)	low(C_3)	6d	$A_2B_2C_3$
5	23.88(A_2)	20(B_3)	high(C_1)	6d	$A_2B_3C_1$
6	27.51(A_3)	10(B_1)	low(C_3)	6d	$A_3B_1C_3$
7	27.51(A_3)	15(B_2)	high(C_1)	6d	$A_3B_2C_1$
8	27.51(A_3)	20(B_3)	medium(C_2)	6d	$A_3B_3C_2$
9	11.47(A_1)	10(B_1)	high(C_1)	6d	$A_1B_1C_1$

Note: Catchment ratio is the catchment area/bioretention surface area; CR is catchment ratio; IC is inflow concentration; ADT is antecedent dry time

Table 4. Concentrations of inflow pollutants (mg/L).

Pollutants	COD	Copper	Zinc	Cadmium	NO_3–N	NH_3–N	TP
High	600	1.0	1.5	0.5	12	6	2.5
Medium	300	0.5	1.0	0.3	6	3	1.5
Low	100	0.3	0.5	0.1	3	1.5	1.0

Note: The preparation reagents of COD, Cu, Zn, Cd, NO_3–N, NH_3–N and TP are glucose, copper chloride, zinc sulfate, and cadmium chloride, potassium nitrate, ammonium chloride and potassium dihydrogen phosphate, respectively.

C_1, C_2, and C_3 were high, medium and low design concentrations.

Sampling and Analysis Methods

The sampling was set as follows: i) inflow sampling at 0, 30, and 60 min after the start of the experiment; ii) overflow water sampling during overflow at 0, 15, 30, 45, and 60 min; and iii) effluent water sampling during outflow at 0, 15, 30, 45, and 60 min. The parameters for the water quality analysis were pH, electrical conductivity, dissolved oxygen (DO), copper (Cu), zinc (Zn), and cadmium (Cd). The first three parameters were used in the instrumental measurement with HACH HQ40d two-circuit input, multi-parameter numerical analysis. Water samples were filtered with a 0.45 µm filterable membrane. COD was examined using HACH DRB200 digestion and UV spectrophotometry. Flame atomic absorption spectrometry (analytik jena ZEEnit 700) was performed to determine heavy metal concentrations. The measuring accuracy is 0.1 ug·L^{-1}, and each sample result is an average value for four times measurement.

Water reduction rate ($R_{retention}$), peak flow cutting rate (R_p), pollutant removal rate (R_c), and load reduction rate (R_L) were determined using Eqs. (1-4), as follows:

$$R_{retention} = (V_{in} - V_{out} - V_{over}) / V_{in} \times 100\% \quad (1)$$

$$R_p = (Q_{p-in} - Q_{p-out}) / Q_{p-in} \times 100\% \quad (2)$$

$$R_c = (EMC_{in} - EMC_{out}) / EMC_{in} \times 100\% \quad (3)$$

$$R_L = (L_{in} - L_{out} - L_{over}) / L_{in} \times 100\% \quad (4)$$

…where $V_{in/out/over}$ is the inflow, outflow, and overflow volume, L; Q_{p-in} and Q_{p-out} is inflow and outflow peak flow; $EMC_{in/out}$ is the mean concentration in a single rainfall event for inflow or outflow, mg/L; and $L_{in/out/over}$ is the inflow, outflow, and overflow pollutant load for the per test, mg.

Results and Discussion

Improvement of Hydraulic Properties

A cost-effective filter media with high COD and heavy metal sorption capacity and adequate hydraulic conductivity are the key problems in bioretention basins. Inflow volumes calculated by three recurrence

Table 5. Water regulation effect of ten bioretention basins.

No.	*K* (m/d)	h (cm)	$R_{retention}$(%)min–max (median)	R_p (%)min–max (median)
1	0.89	>15	30.40%–51.42% (42.38%)	88.01%–96.85% (93.62%)
2	12.22	10	13.24%-34.32%(24.30%)	47.71%–66.05% (59.15%)
3	33.25	5	27.86%–52.15% (40.99%)	58.12%–74.59% (66.52%)
4	40.32	2	16.11%–39.78% (33.08%)	48.52%–71.43% (62.90%)
5	38.79	3	10.80%–54.80% (31.96%)	23.74%–80.22% (56.84%)
6	20.39	5	19.30%–57.35% (34.56%)	50.58%–78.15% (67.19%)
7	2.88	>15	13.75%–56.63% (30.14%)	78.09%–92.91% (86.52%)
8	4.95	7	16.32%–53.34% (27.40%)	33.18%–73.71% (66.75%)
9	33.12	2	10.22%–45.15% (19.89%)	32.67%–66.82% (52.82%)
10	55.75	0	13.22%–51.58% (30.91%)	41.03%–71.74% (57.55%)

Note: K is the stable infiltration rate, h is the maximal ponding depth intervals and three catchment ratios, respectively, were simulated in this paper; meanwhile, the tests required the complete process of rainfall from the start to the end, including the "grow-peak-fall." Waterflow was smaller in the early 20 min. Then, increases and decreases were also observed. Modifiers in the bioretention system were used to increase adsorption capacity, and sand could promote infiltration capacity [14]. Wood mulch is a common surface layer with multiple functions (e.g., moisture conservation and erosion prevention), and mulches can absorb certain metals to a degree [15-16]. Water regulation effects of 10 bioretention basins are shown in Table 5.

The implementation of bioretention facilities enables us to attenuate peak runoff, reduce combined sewer overflow to receiving water, and contribute to groundwater recharge [17]. In this study, the infiltration capacity of plant soil was relatively minimum, and the steady infiltration rate of modified filler was 3.25~62.78 times that of plant soil. The peak flow reduction rates of 1 # and 7 # bioretention basins were significantly high, ranging from 78.09% to 92.91% (median = 86.52%) and 88.01% to 96.85% (median = 93.62%), respectively, and others are about 60%. The water retention capacity of modified media was slightly lower than that of plant soil, which was 0.84~1.73 times than that of traditional BSM. It is also possible that a side wall flow or partial preferential flow might have occurred to a certain extent, which led to a high infiltration rate. The 10 bioretention systems smoothed the hydrograph by reducing peak flow and volume for all 10 events monitored in detail. Overflow occurred in 8 events, $A_2B_2C_3$, $A_2B_3C_1$, $A_3B_1C_3$, $A_3B_2C_1$ and $A_3B_3C_2$ for 1# bioretention basin, $A_2B_3C_1$, $A_3B_2C_1$, and $A_3B_3C_2$ for 7# bioretention basin, indicating that the increased permeability did not fully compensate water regulation capacity for 7# bioretention basin. So we suggest that during the 2-yr recurrence intervals, the contribution area should be controlled below 15:1 for planted soil, and that should be controlled below 20:1 for BSM + 10% fly ash. In the 3-yr recurrence intervals, for all the modified media no overflow occurs at the 20:1 contribution area.

Heavy Metal and COD Concentration Removal Effects

The filter media in biofiltration systems play an important role in removing potentially harmful pollutants from urban stormwater runoff. The tests compared the COD and heavy metal removal potential (Cu, Zn, Cd) of 10 poilt bioretention systems that had different media or structure combinations. In addition, inflow patterns for the tests affected the water volume and peak flow control effect, and the worst media adsorption case may have appeared when the high hydraulic load comes, and the accumulated pollutants from the system may rush out during rainfall peak flows. Fig. 3 illustrated the concentration removal of pollutants, and five lines in the box from bottom to top were the minimum, under quartile, median, upper quartile, and maximum data.

Laboratory and field test results showed that bioretention basins had high purification efficiency for

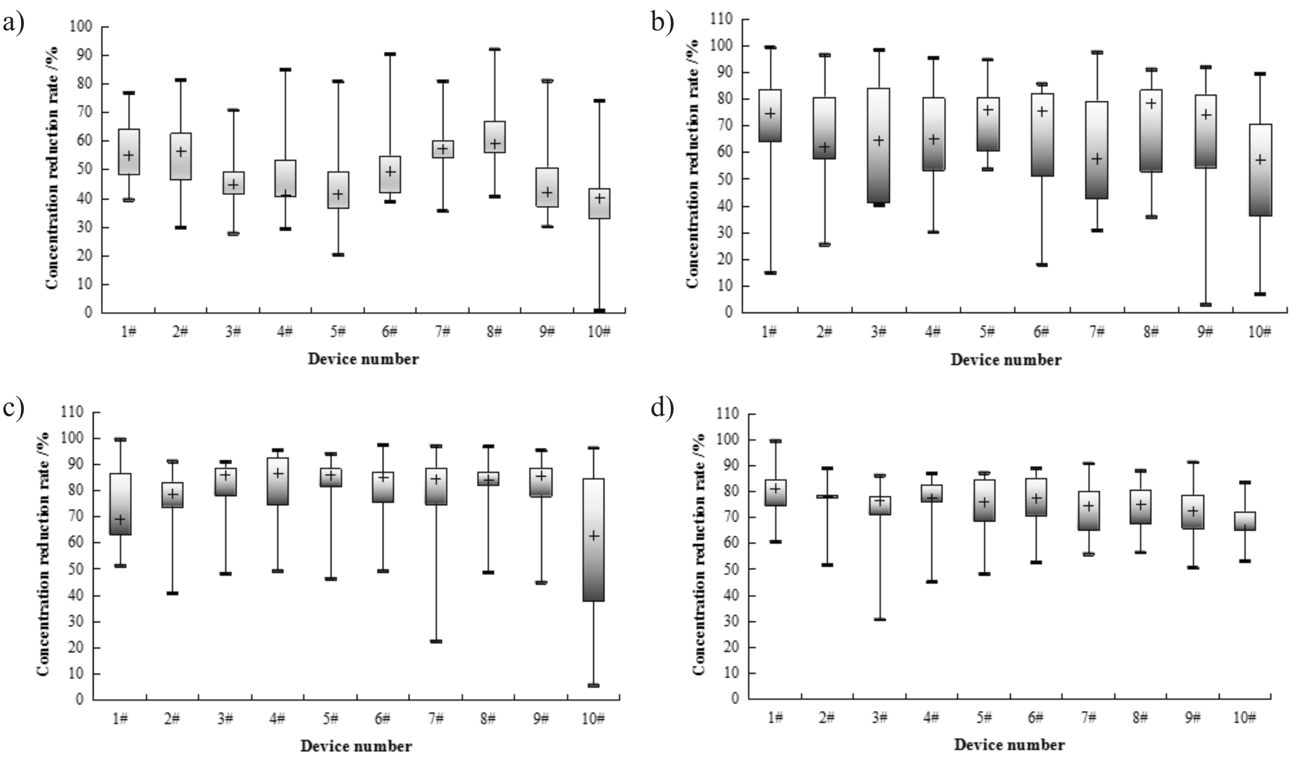

Fig. 3. Heavy metal removal in different media combinations: a) COD, b) Cu, c) Zn, d) Cd.

Table 6. Outflow concentrations under different conditions.

No.	$C_{outflow}$-COD	$C_{outflow}$-Cu	$C_{outflow}$-Zn	$C_{outflow}$-Cd
1#	33.63~338.12 (146.01)	0.007~0.368 (0.173)	0.001~0.698 (0.207)	0.002~0.127 (0.056)
2#	40.32~244.16 (123.63)	0.032~0.486 (0.213)	0.030~0.575 (0.200)	0.042~0.103 (0.070)
3#	52.31~327.50 (160.06)	0.015~0.446 (0.203)	0.031~0.502 (0.166)	0.046~0.123 (0.082)
4#	40.17~364.24 (157.29)	0.044~0.590 (0.218)	0.023~0.723 (0.232)	0.045~0.112 (0.071)
5#	48.94~378.40 (162.57)	0.050~0.493 (0.180)	0.018~0.522 (0.183)	0.043~0.112 (0.074)
6#	43.58~342.64 (144.49)	0.070~0.615 (0.238)	0.011~0.538 (0.199)	0.038~0.106 (0.068)
7#	38.56~256.02 (120.25)	0.023~0.531 (0.235)	0.013~0.750 (0.255)	0.042~0.121 (0.077)
8#	27.09~276.90 (113.06)	0.029~0.591 (0.229)	0.014~0.501 (0.182)	0.044~0.118 (0.075)
9#	39.45~376.88 (160.44)	0.026~0.632 (0.253)	0.012~0.645 (0.238)	0.039~0.129 (0.080)
10#	49.76~416.34 (181.99)	0.035~0.822 (0.369)	0.016~0.993 (0.336)	0.042~0.164 (0.099)

Note: Values represent min~max(mean), mg/L

heavy metals in stormwater runoff [18-19]. However, the different available stormwater best management practices and proprietary devices were reported to be capable of reductions of between 20% and almost 100% for both suspended solids and a range of metals [20]. The median removal efficiency of COD, Cu, Zn and Cd from 3 # to 10 # modified media bioretention basins were 41.36%~59.07%, 57.67%~78.48%, 76.03%~88.28% and 72.36% ~77.45%, respectively. The removal rate of heavy metals in 10 # (BSM mixing coconut) was the lowest, and the removal rates of copper, zinc and cadmium were 7.04~89.35% (57.38%), 5.71~96.15% (62.69%), and 7.04~89.35% (65.29%). Chang et al. [21] showed that there was a clear and positive correlation between the total concentration of Zn, Cu, Cd, and the content of suspended particulate matter (TSS). There were no total suspended solids in the synthetic rainwater prepared in this experiment. Therefore, it did not consider the bioretention system heavy metals removal by intercepting particulate matter in stormwater runoff. The pore spaces were unevenly sized and may be connected in the column to form preferential flow pathways, and the loose structure allowed for rapid movement of water through the column, decreasing contact with the coconut material and lowering metal removal performance.

Removal mechanisms can be divided into physical, chemical and biological processes. The physical process includes filtration and retention; the chemical process include adsorption and sedimentation; and the biological process includes plant absorption and uptake, microbial removal and other biological processes. Among them, interception filtration, adsorption and precipitation play a leading role in the removal of heavy metals. The order of metal removal percentages was found as Pb>Cu>Zn, and Zn is mainly retained via adsorption, while Pb and Cu are retained via both adsorption and filtration [22-23]. Wang et al. chose compound bioretention media composed of fine sand, zeolite, sand, quartz sand and lignin mixed in a certain proportion as the research object [24]. The results showed that heavy metal concentration, medium height and rainfall duration in rainwater runoff had little effect on the removal of heavy metals in composite bioretention media. Moreover, the dissolution process of different heavy metals in the same kind of composite medium was similar. The average values of DO, conductivity, and pH were 7.6 $mg\cdot L^{-1}$, 283.7 $\mu s\cdot cm^{-1}$, and 7.4 in these tests. Inflow concentration of other pollutants was shown in Table 3. The outflow pollutant concentration for 45 synthetic rainfall tests data were analyzed with Class II~V in environmental quality standards for surface water of China (GB3838-2002) taken as a benchmark (Table 6). Under the operating conditions, the effluent concentrations of Cu and Zn were less than 1.0 $mg\cdot L^{-1}$ (Class II). Despite high removal efficiency, median concentrations of COD and Cd exiting, the outflow concentration is above Class V in surface water environmental quality standards in China, which is affected by inflow conditions (rainfall recurrence, confluence, inflow concentration) and system limitations. The standard deviation of COD, Cu, Zn and Cd outflow concentration were 66.59~116.99 $mg\cdot L^{-1}$, 0.13~0.31 $mg\cdot L^{-1}$, 0.17~0.35 $mg\cdot L^{-1}$ and 0.02~0.04 $mg\cdot L^{-1}$, respectively, under different operating conditions. Affected by the operating conditions, the concentration of outflow pollutants in the bioretention basins were more discrete.

Pollutant Load Treatments and Hydrologic/Hydraulic Design Parameters

The treatment performance of bioretention basins relies heavily on various external factors, such as rainfall depth, duration, ADT, contribution area, etc. [25]. In this experiment ADT was 6d, and the rainfall lasted 60 min. The main factors that influenced the

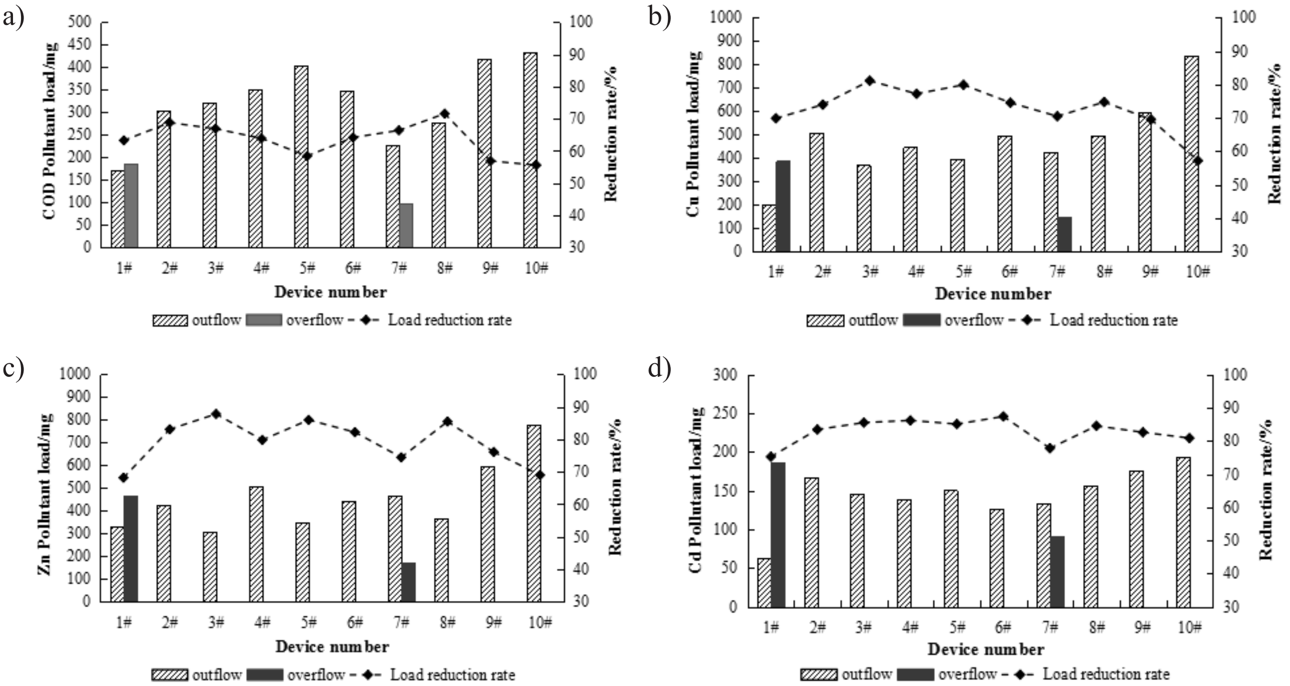

Fig. 4. Inflow/outflow loads and load reduction rates: a) COD, b) Cu, c) Zn, d) Cd.

design were rainfall recurrence interval, contribution area, and inflow concentration. In this study, the load reduction rate of bioretention systems under different design conditions fluctuated greatly. Overall, COD load reduction rate decreased with the increase of recurrence interval and discharge ratio, which increased with the increase of inflow concentration. The load reduction rate of heavy metal Cd increased with the increase of the recurrence interval, discharge ratio, and inflow concentration. However, the reduction rate of Zn and Cu in heavy metals was without certain regularity.

A series of bioretention tests showed that the type of media and the structure of bioretention facilities, and other internal factors, have a great effect on the purification of heavy metals [26-27]. The median loading reduction rate of COD was the highest for 6# and 8#, the layered filler structure with WTR and fly ash as modifier, which were 70.98% and 75.88%, respectively. 3#, 4#, 5# and 6# (mixed or layered filler structure, adding 10% WTR as modifier) and 8# (layered filler structure with fly ash as modifier), the heavy metal load reduction rate is higher than other media, and the median load reduction rate is mostly above 80%. The poor performance of coconut coir may be attributed to its porous and heterogeneous nature. One of the concerns related to heavy metal removal in bioretention systems is the limited capacity of the systems to store these metals [28]. The data from 10 simulated rainfall events of 1#~10# bioretention systems were taken into Formula (5). The bioretention system pollutant load reduction during the test periods were obtained.

$$R_{L(total)} = \left(\sum_{i=1}^{10} L_{i(\inf low)} - \sum_{i=1}^{10} L_{i(outflow)}\right) / \sum_{i=1}^{10} L_{i(\inf low)} \times 100\% \tag{5}$$

Research showed that dry periods reduced heavy metal uptake due to a multitude of factors, including mobilization, leaching of accumulated metals and flushing of metal-organic matter complexes upon wetting [29-30]. A one-month dry period between dosing experiments did not affect metal removal, and TOC concentrations from all materials increased after the dry period [31]. In this experiment, the interval between all rainfall events is 6 days, and the difference of running effect is only affected by its own structure and external conditions. The total inflow loads of COD, Cu, Zn and Cd in the 10 simulated rainfall events were 973.410 g, 1.954 g and 2.502 g, 1.009 g, respectively. The times to reach the adsorption capacities for Cu, Zn and Cd were calculated under the following assumptions: media depth of 50 cm, media composed of 30% compost and 70% sand (by volume), with a bulk density of 1.2 $g \cdot cm^{-3}$. The calculated inflow total load of Cu, Zn, and Cd were 6.72 g, 83.52 g and 1.8 g. Estimated times to reach metal adsorption capacities were 21 yr, 36 yr and 90 yr for Cu, Zn and Cd, respectively [32]. The estimated system lifetimes need to depend on site-specific characteristics, including the media composition, rainfall patterns, inflow pollutant loading, and the extent of organic matter decomposition. The effluent loads were 171.25~432.08 g, 0.20~0.84 g, 0.33~0.78 g, 0.64~0.19g in this paper. All simulation rainfall results are as follows: 1# (plant soil) outflow load is the smallest, and 10# (BSM mixing coconut bran) outflow load is the largest. Overflow load of 1# bioretention system were greater than the outflow load, and COD, Cu, Zn overflow load accounted for the percentage of inflow load were: 19.12%, 19.80%, 18.57% and 18.44%. 7# (BSM mixing fly ash) bioretention overflow load is less than the outflow load, and the percentage of overflow loads of COD, Cu, Zn and Cd to the inflow load are, respectively, 10.11%, 7.73%, 6.85% and 9.03%. There were different degrees of overflow pollution risk, and the load reduction rate is lower due to the overflow events in the 1# and 7# bioretention basins. The heavy metal load reduction in 3# (BSM mixing WTR, without submerged area), 5# (BSM mixing WTR, 350 mm submerged area) and 8# (BSM + fly ash layering) bioretention basins were higher than others, and the Cu load reduction rate was greater than 75%, and Zn and Cd were greater than 85%.

Conclusions

The media in the bioretention system were designed to have high permeability and high metal removal potential. The steady infiltration rate of modified filler is 3.25~62.78 times that of plant soil, and the median value of water retention capacity of modified media is 0.84~1.73 times that of traditional BSM. The ten bioretention systems smoothed the hydrograph by reducing peak flow and volume for all 10 events monitored in detail. Overflow occurred in 8 events of 1# and 7#, indicating that the increased permeability did not fully compensate water regulation capacity for 7# bioretention basins. The loose structure allowed rapid movement of water through the column, decreasing the time which the runoff contact with the media, especially for coconut material, lowering metal removal performance. The effluent concentrations of Cu and Zn were less than 1.0 $mg \cdot L^{-1}$ (Class II) under the operating conditions, and the outflow concentrations of COD and Cd were above Class V (40 $mg \cdot L^{-1}$ for COD, and 0.01 $mg \cdot L^{-1}$ for Cd) in surface water environmental quality standards in China. COD and heavy metal Cd presents certain regularity with the recurrence interval, discharge ratio, and inflow concentration change. However, the load reduction rate of Zn and Cu under different design conditions fluctuated greatly. The COD loading reduction rate of 6# and 8# was the highest among all the media, which the layered filler structure with WTR and fly ash as modifier. 3#, 4#, 5# and 6# (mixed or layered filler structure, adding 10% WTR as modifier) and 8# (layered filler structure with fly ash as modifier), the heavy metal load reduction rate is higher than other media.

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Conflict of Interest

The authors declare no conflict of interest.

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