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Adsorption characteristics of amended bioretention fillers on heavy metals

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ABSTRACT

Static experiments of single fillers and mixed fillers were performed to study the adsorption and desorption characteristics of soil and amendments on heavy metals. Bioretention dynamic simulation experiments were conducted to study the effects of amended media on heavy metal removal in urban runoff. Efficient mixed improvement fillers were screened and developed. The results showed that the adsorption capacity of bioretention soil media (BSM) + 10% fly ash (by mass) for heavy metal Zn was higher than that of other fillers. Under the condition that the influent concentration of Zn was 0.5 mg/L, BSM, BSM + 10% medical stone, BSM + 10% water treatment residue, and BSM + 10% green zeolite were added to the minicolumn, and the effluent concentration of Zn increased with the water inflow. After the recurrence interval of the influent water volume reached 3 years, the effluent Zn concentration gradually approached 0.4 mg/L. The minicolumn packed with BSM + 10% fly ash showed a continuous long-term adsorption capacity. After 18 d of operation, the adsorption rate of minicolumn BSM + 10% fly ash was up to 83.06%, and the concentration of effluent Zn was less than 0.20 mg/L. These values meet the Class II surface water environmental quality standards of China. In engineering applications, mixed amended BSM can be added to control the degree of contamination of receiving water bodies by heavy metals.

Keywords: Bioretention; Runoff pollution; Isothermal adsorption; Heavy metal

1. Introduction

The advancement of urbanization process and the increase of impervious area in China, such as urban road, roofing, and others, have resulted in a large number of impervious areas blocking the path of rainfall infiltration, increased the amount and volume of runoff, shortened the time of runoff formation, and broken the existing hydrologic cycle of rain [1]. The floods caused by rain have seriously deteriorated the water quality. A large number of suspended particles, heavy metals, oxygen-consuming substances, and toxic substances accumulated on impervious surfaces and were carried into the receiving water body by rainwater runoff, which cause serious pollution to water bodies [2]. Heavy metals are difficult to be degraded by the environment. They are easy to accumulate in organisms and enter the human body through the food chain [3,4]. Their concentration at a certain extent can cause fatal injury to the human body. Many studies on runoff water quality at home and abroad have shown that heavy metals are important sources of pollution in the surface environment [5]. Therefore, effective reduction of heavy metal pollution in rainwater runoff is needed.

The bioretention technology is the current well-known international stormwater control technology that has wide adaptation, small occupation, and remarkable environmental ecological benefit. The removal mechanism of heavy

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metal in urban rainwater runoff is mainly through surface media interception, plant absorption, and physical adsorption of internal media [6,7]. The removal rate of bioretention technology for Cu, Pb, and Zn in storm runoff is higher than 90%, and most of the heavy metals are removed in the surface layer [8]. The removal rate of heavy metals is high with no plant cover layer [9]. Therefore, the composition and properties of the filler are the key factors in determining the removal effect of heavy metals.

This study analyzed the characteristics of soil and modified fillers in adsorption of heavy metals by selecting and developing improved bioretention soil media (BSM). Zinc, a common heavy metal in urban storm runoff, was selected as the main research pollutant. On the basis of BSM as a medium, fly ash was studied through experiment contrast with water treatment residue (WTR), green zeolite, medical stone, coconut chaff, peat soil, and vermiculite. The heavy metal adsorption capacity, desorption rate, and energy efficiency of the seven modifiers were explored through the experiment of biological retention simulation column with different design parameters. The highly efficient and improved filler was evaluated. Strengthening the bioretention facilities to control the heavy metal pollution in the affected water body could provide technical support for improving the heavy metal purification effect.

2. Materials and methods

2.1. Materials

BSM, fly ash, WTR, green zeolite, medical stone, coconut bran, turf soil, and vermiculite were selected as the study objects. The BSM consisted of 65% sand, 30% soil, and 5% wood chips (by mass). The soil was collected from the undisturbed soil in Xixian New Area of Shaanxi Province, the sand was collected from a construction market in Xi'an, and wood chips were collected from a flower market in Xi'an. The soil, sand, and wood chips were air dried once a week and passed through a 2-mm sieve. The soil was sieved and separated. It contained 16.86% sand, 75.02% powder, and 8.30% clay, which were classified in accordance with United States Department of Agriculture soil classification standards. The loam soil was then mixed and stored in proportion. The WTR was collected from the Qujiang Water Plant in Xi'an city. The plant was equipped with aluminum salt as a flocculant and sludge dewatering equipment. After the sample was retrieved, the air-dried filler was crushed, and the 2-mm sieve was stored in a sealed container for subsequent analysis. The remaining fillers were purchased from a company in Shaanxi (Xi'an Shixin Building Materials Market and Xi'an Yanjin Flower Market). The peat soil was air dried and crushed using 2-mm sieves. The sizes of the green zeolite and medical stone were selected to be from 3 mm to 6 mm and from 2 mm to 4 mm, respectively, all of which were kept in sealed containers to maintain stability.

In understanding the superficial and morphological structures of the fillers, a scanning electron microscope (SEM) was used to analyze the surface physical structure of the modifiers. The pretreated sample was attached to the product seat with a conductive adhesive and sputtered with ion sputtering. The SEM images are shown as Fig. 1.

As shown in Fig. 1, the WTR, vermiculite, peat moss soil, and coconut bran are porous and have loose structure and adsorption points. The medical stone and green zeolite exhibited a surface sheet structure morphology. They were loosely fragmented and showed strong stability. The fly ash was spherical and exhibited a large specific surface area for adsorption and many binding sites. The risk of zinc release was low.

The physical properties and chemical composition of the filler considerably influence the adsorption and ion exchange of the filler. Thus, the physical and chemical properties of the modifier should be analyzed, and the individual components should be determined before the test. Organic matter was measured using the potassium dichromate volumetric method (NY/T 85-1988). The specific surface area was determined using the gas adsorption Brunauer Emmett Teller method (GB/T 19578-2004). The cation-exchange capacity was measured by inductively coupled plasma emission spectrometry, and the metal content was determined by atomic absorption spectrometry (LY/T 1250-1999). Table 1 shows the main physical chemical properties of BSM and modifiers.

2.2. Isothermal adsorption experiment of single improver

Heavy metal solutions of 1, 2, 5, 10, 15, 20, 50, and 100 mg/L were prepared. Then, 5 g of fly ash, WTR, green zeolite, medical stone, coconut bran, peat soil, and vermiculite were poured into a 250-mL conical flask, followed by adding 250 mL of $ZnSO_4$ solution and stirring into a suspension in a water bath shaker at a constant temperature of 25°C ± 0.5°C and vibration frequency of 120 ± 10 rpm for 24 h. Each sample was passed on a 0.45-μm filter, and the filtered sample was diluted with 5% HNO_3 and sealed in a freezer at 4°C. Flame atomic absorption spectrometry was used for heavy metal determination during the test. The amount of adsorption was determined using the difference between the initial and equilibrium concentrations of the solution. The experiment was repeated three times to reduce the error.

2.3. Adsorption and desorption experiment of single filler

2.3.1. Isothermal adsorption experiment

The BSM, fly ash, WTR, green zeolite, medical stone, coconut bran, peat soil, and vermiculite were air dried under natural conditions for 2 d. Then, 5 g of each improver was poured into a 250-mL triangle conical flask, added with 200 mL of $ZnSO_4$ solution with a concentration of 100 mg/L, and shaken at a frequency of 120 ± 10 rpm for 24 h in a water bath shaker at a constant temperature of 25°C ± 0.5°C. A small amount of the sample was passed on a 0.45-μm filter, and the filtered sample was diluted with 5% HNO_3, sealed, and stored in a refrigerator at 4°C. Flame atomic absorption spectrometry was used for heavy metal determination during the test. The amount of adsorption was determined using the difference between the initial and equilibrium concentrations of the solution. The experiment was repeated three times to reduce the error.

2.3.2. Isothermal desorption experiment

The BSM, fly ash, WTR, green zeolite, medical stone, coconut bran, peat soil, and vermiculite after equilibrium

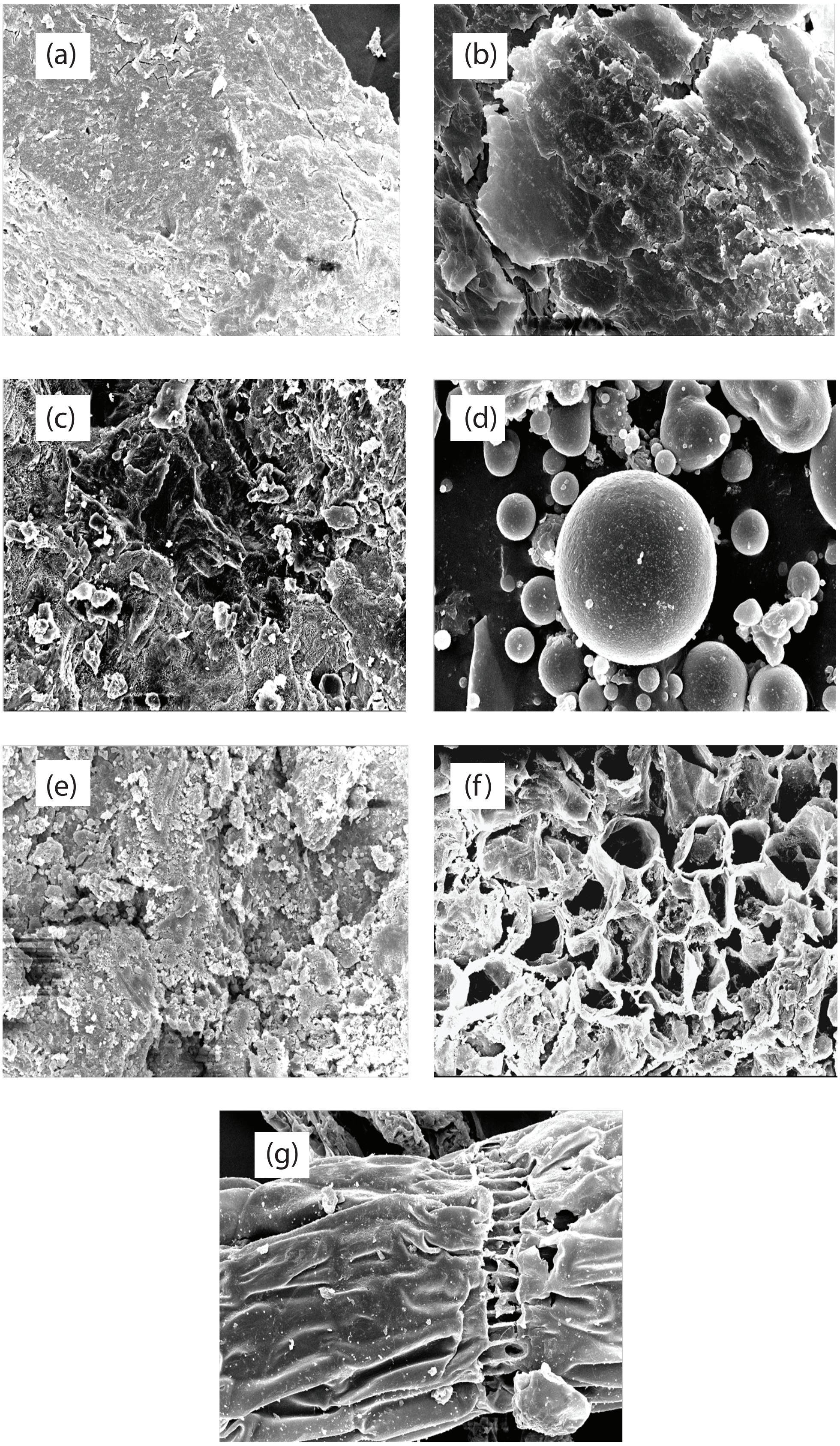

Fig. 1. Electron microscopy of improvers: (a) medical stone (Mag = 500×), (b) green zeolite (Mag = 500×), (c) WTR (Mag = 500×), (d) fly ash (Mag = 3.0 K×), (e) vermiculite (Mag = 500×), (f) peat soil (Mag = 500×) and (g) coconut bran (Mag = 500×).

adsorption experiment with 100 mg/L of $ZnSO_4$ were dried in the natural state. After 3 d, 3 g of each improver was weighed and poured into a 250-mL triangular Erlenmeyer flask, added with 200 mL of distilled water, and shaken at a frequency of 120 ± 10 rpm for 24 h in a water bath shaker at a constant temperature of 25°C ± 0.5°C. After passing through a 0.45-μm filter, the filtered sample was diluted with 5% HNO_3 and sealed in a freezer at 4°C. Flame atomic absorption spectrometry was used for heavy metal determination during the test. The amount of adsorption was determined using the difference between the initial and equilibrium concentrations of the solution. The experiment was repeated three times to reduce the error.

2.4. Isothermal adsorption experiment of mixed modified filler

Four types of modifiers, namely, fly ash, WTR, green zeolite, and medical stone, were mixed with traditional BSM at different mass ratios (5%, 10%, and 15%) and formulated as the mixed modified fillers. These improvers of 10 g each were accurately mixed in a 250-mL conical flask, added with 200 mL of $ZnSO_4$ solution, stirred into a suspension, and shaken at a frequency of 120 ± 10 rpm in a water bath shaker at a constant temperature of 25°C ± 0.5°C for 24 h. After passing through a 0.45-μm filter, the filtered sample was diluted with 5% HNO_3, sealed, and stored in a freezer at 4°C. Flame atomic absorption spectrometry was used for heavy metal determination during the test. The amount of adsorption was determined using the difference between the initial and equilibrium concentrations of the solution. The experiment was repeated three times to reduce the error.

2.5. Bioretention dynamic adsorption experiment

In this experiment, with no vegetation covering, the test apparatus was continuously operated to verify the purification mechanism of the mixed improved filler on the pollutants of stormwater runoff. The study setting ratio was 20:1, and filler height of actual bioretention facility was set to 70 cm. The artificially formulated Xi'an rainfall runoff was used as the inflow of mixed improved filler, and the water intake for 15 years was continuously operated to evaluate the adsorption capacity, operating capacity, and service life of the improved filler.

2.5.1. Test device

In this experiment, a sealed upright column of 22 cm height and 3.4 cm internal diameter was used to build a minicolumn test facility at the Key Laboratory of Xi'an University of Technology. Six groups of minicolumns were filled with uniformly mixed modified fillers. The quality of the fillers of 180 g each was consistent. The bioretention simulation

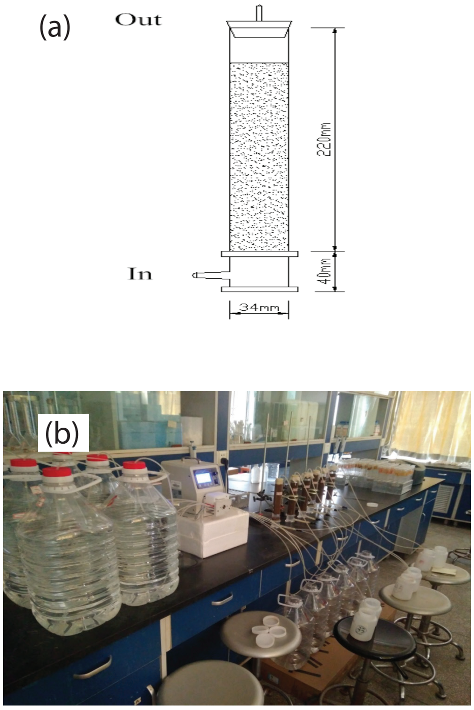

Fig. 2. Structure and operation process of bioretention simulation column: (a) analog column structure and (b) analog column operation diagram.

Table 1
Main physical and chemical properties of BSM and improvers

Filler	OM (%)	SUA (m^2/g)	CEC (cmol/kg)	PV (cm^3/g)	FD (g/mL)	Ca (mg/kg)	Mg	Fe	Al
Soil	0.0322	20.8365	19.44	0.0300	1.12	4,817	8,221	25,021	20,860
Sand	0.745	0.8037	11.76	0.0021	1.53				
Wood	45.4	0.4168	26.66	0.002	0.211				
BSM	2.755	4.9909	34.45	0.0096	1.116	25,778	7,790	12,466	8,563
Fly ash	2.66	1.3814	28.23	0.0066	1.008	21,509	3492	13,784	13,343
WTR	10.3	28.4333	9.31	0.0215	0.953	24.83	298	9,334	122,039
GZ	6.98	16.8707	27.50	0.0510	1.054	1,921	5,631	11,486	67,717
MS	4.14	1.2723	13.39	0.0033	1.297				
CB	73.7	0.8105	13.62	0.0026	0.092				
Peat soil	36.6	0.7400	14.44	0.0018	0.136				
VE	1.122	1.5942	17.38	0.0162	0.12				

OM, organic matter; SUA, specific surface area; CEC, cation-exchange capacity; PV, pore volume; FD, filling density; GZ, green zeolite; MS, medical stone; CB, coconut bran; VE, vermiculite.

column setup operation is shown in Fig. 2, and the packing composition of bioretention simulation column is as followed: soil, BSM, BSM + 10% medical stone, BSM + 10% fly ash, BSM + 10% WTR, and BSM + 10% green zeolite.

2.5.2. Test plan

2.5.2.1. Water quality design Three target pollutants were selected from Xixian New Area, Xi'an city, a resource-reduced and ecologically fragile city in Northwest China. The average concentration of road runoff was the influent concentration, and the influent concentration was kept constant. The water concentration and reagent selection is shown in Table 2.

2.5.2.2. Water design In this study, the design confluence ratio was 20:1, the single minicolumn confluence area was calculated to be 181.49 cm^2, and the average concentration of rainfall runoff in Xi'an was manually formulated as influent water. The filler height of actual bioretention facility was set to 70 cm. A continuous permeation with a peristaltic pump was used for testing. Three different influent flow rates were used at the same concentration, and the flow rate was followed from low to high. For the three recurrence intervals of 0.5a, 2a, and 3a, the rainfall intensity designed for the rainfall duration of 60 min was used to design the inflow, and the inflow of the same rainfall intensity was equal. The rainfall intensity was determined using the storm intensity equation (Eq. (1)) of Xi'an city. From the storm intensity and catchment area, the relevant inflow could be calculated by Eq. (2). The calculation results are shown in Table 3.

$$q = \frac{2785.833 \times (1 + 1.16581\text{g}\,P)}{(t + 16.813)^{0.9302}} \tag{1}$$

$$m = \frac{0.012 M \cdot q}{h \cdot \rho} \tag{2}$$

where q is the design storm intensity, L/(s·hm^2); P is the recurrence interval, a; t is the rainfall duration, min; m is the single minicolumn inflow, mL/min; M is the minicolumn filler mass, 180 g; F is the catchment area, 181.49 cm^2; h is the actual filler packing height, 70 cm; and ρ is the actual traditional BSM packing density, 1.116 g/cm^3.

2.6. Data analysis methods

2.6.1. Adsorption experiment

The Freundlich and Langmuir equations (Eqs. (3) and (4)) were used to fit the adsorption characteristics of Zn in static experimental media or fillers, respectively.

$$q_e = K_f C_e^n \tag{3}$$

$$q_e = \frac{K_l X_m C_e}{1 + K_l C_e} \tag{4}$$

where q_e is the heavy metal adsorption amount per mass matrix, mg/kg; C_e is the adsorption equilibrium concentration of heavy metal, mg/L; X_m is the Langmuir saturation adsorption amount, mg/kg; and K_f, K_l, and n are all constants.

Table 2
Water concentration and reagent selection

Pollutants	Zn	NH_3–N	TP
Average concentration (mg/L)	0.5	1.5	1
Water distribution reagent	$ZnSO_4$	NH_4Cl	KH_2PO_4

Table 3
Calculation of storm intensity and inflow flow

Recurrence interval	0.5	2	3
Storm intensity, L/(s·hm^2)	31.87	66.34	76.42
Inflow (filling density is 1.116 g/cm^3)	0.881	1.834	2.113

2.6.2. Bioretention minicolumn experiment

The medium adsorption capacity of bioretention simulating columns can be used as the comparison evaluation standard between different modified fillers (Eqs. (5) and (6)).

$$Q = \frac{T_{\text{in}} - T_{\text{out}}}{M_{\text{media}}} \tag{5}$$

$$T = \int_{t_0}^{t_1} C \cdot Q_0 \, \mathrm{d}t \tag{6}$$

where Q is the adsorption capacity per unit mass of filler, mg/kg; C is the concentration of water in and out, mg/L; Q_0 is the flow of water in and out, L/min; and M_{media} is the mass of modified filler in the column, Kg.

3. Results and discussion

3.1. Isotherm adsorption characteristics of heavy metal Zn by single modifier

Fly ash, WTR, green zeolite, medical stone, coconut bran, peat soil, and vermiculite adsorbed different concentrations of heavy metal Zn solution. The removal rate of heavy metal Zn after adsorption equilibrium is shown in Table 4, and the relationship between the equilibrium adsorption capacity of heavy metal Zn and the equilibrium concentration of heavy metal Zn in solution are shown in Fig. 3.

Table 5 shows that the seven single modifiers exhibited isothermal adsorption of heavy metal Zn at different concentrations. When the concentration of heavy metal Zn in the solution was 5–50 mg/L, the removal rate of heavy metal Zn by the improver was more than 70%. As heavy metal Zn concentration increased, the removal rate of heavy metal Zn by the seven improvers decreased. When the concentration of heavy metal Zn was 10 mg/L, fly ash has the highest removal rate of heavy metal Zn, which is 13% higher than that of medical stone with the lowest removal rate. As the concentration of heavy metal Zn in the solution increased, the fly ash showed a strong removal capability, whereas the removal effect of other modifiers gradually weakened. As shown in Fig. 3, the maximum equilibrium adsorption capacities of the seven modifiers under experimental conditions from large to small were as follows: fly ash > WTR > vermiculite > green zeolite > medical stone > coconut bran > peat soil. Notably, fly ash presented the best adsorption effect for heavy metal Zn. At the same equilibrium concentration, the adsorptive capacity of Zn for the heavy metals was relatively close for vermiculite and green zeolite. Medical stone and coconut bran showed nearly the same adsorption capacity for heavy metal Zn. In practice, the most suitable modifier can be selected in combination with the specific conditions. Results of fitting the isothermal adsorption equation of the modifier are shown in Table 5.

Table 6 shows that the R^2 values of the Langmuir and Freundlich models were all above 0.9, of which the Freundlich model exhibited an R^2 of approximately 0.99, which shows that the adsorption characteristics of the heavy metal Zn by the seven modifiers can be well fitted. Studies have shown that the Langmuir and Freundlich models can well fit the adsorption characteristics of the selected filler, which is basically consistent with this study [10,11]. At the same time, the model precision is positively correlated with the model fitting parameter R^2. As shown in Table 6, the R^2 of the Freundlich model was high, indicating that it is suitable for the fitting of the seven modifiers to the adsorption characteristics of heavy metal Zn. In the Freundlich model, K_f is related to the adsorption capacity of the modifier. A greater K_f value indicates a stronger adsorption capacity of the surface modifier, and the $1/n$ value indicates the degree of adsorption difficulty. When the numerical value is low, the adsorption capacity is strong [12]. Adsorption is easy when $1/n$ is from 0.5 to 1, and adsorption is difficult when $1/n > 2$ [13]. From the table, the fly ash was found to present the highest K_f value and the strongest adsorption capacity, followed by the green zeolite, WTR, medical stone, and vermiculite. By contrast, the coconut bran and peat soil showed weak adsorption capacity. This finding is equivalent to the isothermal adsorption curve. The experimental results are nearly identical. The $1/n$ values of the seven modifiers were all in the range of 0.5 to 1, indicating that the modifiers easily adsorb heavy metal Zn.

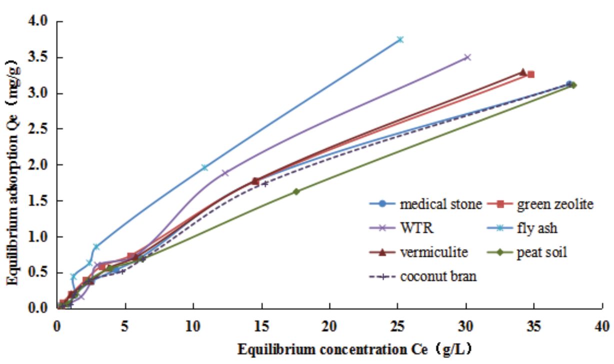

Fig. 3. Isothermal adsorption curve of modifier on heavy metal Zn.

Table 4
The removal rate of heavy metal Zn after adsorption balance

Zn concentration (mg/L)	The removal rate heavy metal Zn after adsorption balance (%)						
	MS	GZ	WTR	Fly ash	VE	Peat soil	CB
1	65.30	66.80	65.04	66.12	65.86	61.33	61.33
2	55.43	77.33	58.66	62.24	68.06	58.65	50.32
5	73.91	78.73	64.03	73.72	78.63	72.54	74.54
10	74.44	78.65	74.61	87.63	75.14	76.63	76.63
15	70.96	77.93	80.09	83.97	74.50	73.70	68.15
20	69.56	72.97	71.56	85.42	70.95	68.50	68.50
50	70.76	70.81	75.27	78.29	69.51	64.84	69.51
100	62.38	65.22	69.86	74.79	65.79	62.09	62.42

GZ, green zeolite; MS, medical stone; CB, coconut bran; VE, vermiculite.

Table 5
Isothermal adsorption equation of improver fitting results

Filler	Langmuir			Freundlich		
	X_m (g/kg)	K_1	R^2	K_f	$1/n$	R^2
MS	7.3234	0.0199	0.9353	0.1895	0.7781	0.9867
GZ	8.085	0.0193	0.9248	0.2183	0.7641	0.9975
WTR	11.728	0.0142	0.9303	0.1913	0.8581	0.9855
Fly ash	9.129	0.0271	0.9888	0.2991	0.7843	0.9887
VE	10.71178	0.0129	0.9486	0.1758	0.8305	0.9987
Peat soil	10.020	0.0117	0.9545	0.1571	0.8200	0.9972
CB	8.31799	0.0161	0.9345	0.1715	0.8051	0.9889

GZ, green zeolite; MS, medical stone; CB, coconut bran; VE, vermiculite.

Table 6
Parameters of Freundlich and Langmuir adsorption isotherms for mixed filler

Filler	Langmuir			Freundlich		
	X_m	K_1 (L/kg)	R^2	K_f	$1/n$	R^2
Soil	5.850	0.040	0.933	0.228	0.860	0.925
BSM	2.395	0.118	0.910	0.279	0.612	0.873
BSM + 5% MS	2.800	0.045	0.929	0.147	0.720	0.901
BSM + 10% MS	3.927	0.028	0.939	0.119	0.814	0.923
BSM + 15% MS	2.867	0.045	0.906	0.147	0.729	0.878
BSM + 5% GZ	3.692	0.035	0.872	0.145	0.787	0.858
BSM + 10% GZ	4.890	0.024	0.886	0.128	0.846	0.877
BSM + 15% GZ	3.913	0.031	0.907	0.134	0.807	0.892
BSM + 5% WTR	2.968	0.045	0.951	0.150	0.737	0.923
BSM + 10% WTR	4.196	0.027	0.867	0.122	0.827	0.853
BSM + 15% WTR	3.202	0.034	0.941	0.128	0.762	0.920
BSM + 5% fly ash	2.763	0.054	0.919	0.171	0.699	0.891
BSM + 10% fly ash	2.788	0.130	0.890	0.320	0.665	0.857
BSM + 15% fly ash	2.555	0.104	0.949	0.264	0.642	0.912

GZ, green zeolite; MS, medical stone.

3.2. Isothermal adsorption and desorption characteristics of heavy metal Zn by filler

Isothermal adsorption and desorption tests were further conducted through the investigation of the sorption properties of BSM, fly ash, WTR, green zeolite, medical stone, coconut bran, peat soil, and vermiculite. Fig. 4 shows the results.

Fig. 4 shows that the adsorbed equilibrated fillers all exhibited desorption of heavy metal Zn; however, the degree of desorption was different. The isothermal desorption rates of heavy metal Zn in medical stone, green zeolite, WTR, fly ash, vermiculite, peat soil, coconut bran, and BSM were 53.32%, 43.23%, 46.99%, 17.95%, 68.70%, 71.82%, 71.37%, and 44.12%, respectively. Among the improvers, fly ash showed the highest equilibrium adsorption capacity, followed by the green zeolite, BSM, WTR, and medical stone. By contrast, the adsorption effect of vermiculite, peat soil, and coconut bran was weak. Fly ash also presented the strongest adsorption capacity for heavy metal Zn (maximum K_f value of 0.2991), the highest equilibrium adsorption capacity, and the lowest desorption rate, indicating that the adsorption effect of fly ash is the most stable (minimum desorption rate of 17.95%). Although the equilibrium adsorption capacity of BSM reached more than 50 mg/kg, the amount of desorption was high and the comprehensive adsorption effect was worse than that of fly ash. In summary, the eight fillers exhibited favorable heavy metal Zn adsorption, and the $1/n$ value was between 0.5 and 1.0. The heavy metal Zn adsorbed by fly ash showed extremely strong stability. BSM, WTR, medical stone, and green zeolite also exerted satisfactory adsorption effect.

3.3. Isotherm adsorption characteristics of heavy metal Zn by mixed modified filler

After exploring the single fillers, the bioretention mixed fillers were further studied. The improved fly ash, WTR, medical stone, and green zeolite, which had excellent results in the isothermal adsorption and desorption experiments, were preferred. The isothermal adsorption test was conducted in different proportions (5%, 10%, and 15%) of the BSM. Table 6 shows the results of fitting the isothermal adsorption equation of the mixed modified filler.

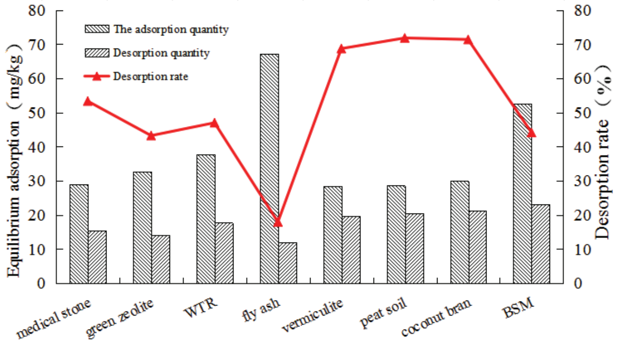

Fig. 4. Test results of isothermal adsorption and desorption of fillers.

Table 6 shows that the R^2 values of the Langmuir and Freundlich models were all above 0.85, indicating that the adsorption characteristics of the heavy metal Zn by the mixed modified fillers can be well fitted. In the Langmuir equation, K_1 denotes the adsorption binding constant and X_m denotes the theoretical saturated adsorption amount. A large X_m value indicates a large amount of saturated adsorption of the heavy metal Zn by the mixed modified filler. In terms of the combined adsorption constant and the theoretical saturated adsorption amount, the adsorption effect of BSM added with 10% medical stone, green zeolite, or WTR was better under the condition of nearly the same K_f. In the Freundlich equation, K_f should be enlarged to improve the constant of the adsorption capacity of heavy metal Zn for the mixed modified fillers [14]. The X_m of fly ash with different proportions of BSM was only slightly different. When adding

10% fly ash, the K_f value was the largest and the adsorption effect was improved. Researchers have shown that the ratio of modifiers is between 5% and 20% with excellent results [15,16]. Based on the theoretical saturation adsorption capacity and adsorption binding constant obtained by combining Langmuir model and Freundlich model as well as the experimental results of researchers, selected BSM was added with 10% improver.

3.4. Bioretention dynamic adsorption experiment

In this experiment, with no vegetation covering, a continuous running test was conducted to explore the purification mechanism of the mixed improved packing on the contaminants of stormwater runoff. The continuous running water intake for 15 years was used to evaluate the adsorption capacity and service life of the mixed improved packing. The modified improved filler was produced using preferred modifier fly ash, WTR, medical stone, and green zeolite with 10% BSM. Through manual water distribution and adding 0.01 M of KCl as the background electrolyte, Lange BT100-1L peristaltic pump was used to inject each column with a ratio of 20:1 at three different flow rates continuously (recurrence intervals of 0.5a, 2a, and 3a), running underwater for approximately 18 d, and the amount of influent water corresponded to 15 years of total rainfall on the confluent area. Fig. 5 shows the total adsorption amount of heavy metal Zn, and Table 7 shows the load and the adsorption rate of the bioretention minicolumn.

Fig. 5 and Table 7 show that under the same experimental conditions and after 15 years of continuous operation, the adsorption capacity of BSM + 10% fly ash was as high as 15.781 mg, that of soil was 13.368 mg, and that of BSM was 10.348 mg. BSM + 10% medical stone, BSM + 10% WTR, and BSM + 10% green zeolite exhibited poor adsorption. Fig. 6 shows the adsorption curve of heavy metal Zn.

Fig. 6 shows that the adsorption curves of heavy metal Zn in soil, BSM, and four mixed modified fillers presented an upward trend. As time progressed, the adsorption capacity of heavy metal Zn gradually weakened for 15 years. In the year of influent loading, all the fillers did not reach the saturation state of adsorption, except that soil and BSM + 10% fly ash were still in a gradually increasing state during the adsorption of heavy metal Zn, and the effluent Zn concentration gradually approached 0.4 mg/L. In the first stage, Q = 0.881 mL/min (recurrence interval of 0.5a), the concentration of heavy metal Zn in the initial effluent was slightly high. A small amount of pollutant was leachable from the filler, followed by soil and BSM + 10% fly ash at a steady upward trend. BSM also maintained a relatively stable upward trend. Although BSM + 10% medical stone, BSM + 10% WTR, and BSM + 10% green zeolite showed an upward trend, they were volatile and stable and showed poor stability. In the second stage, Q = 1.834 mL/min (recurrence interval of 2a), the concentration of effluent contaminants in the initial volumetric flow had jumped, especially for BSM + 10% medical stone, BSM + 10% WTR, and BSM+10% green zeolite. By contrast BSM, soil, and BSM + 10% fly ash had a small jump, and then they showed an upward trend. The performance of each filler type was not considerably different from that in the first phase. In the third stage, Q = 2.113 mL/min (recurrence interval of 3a), the other fillers had smaller jumps after the volume adjustment, except for the obvious jump in soil. Thereafter, the effluent Zn concentration of BSM, BSM + 10% medical stone, BSM + 10%

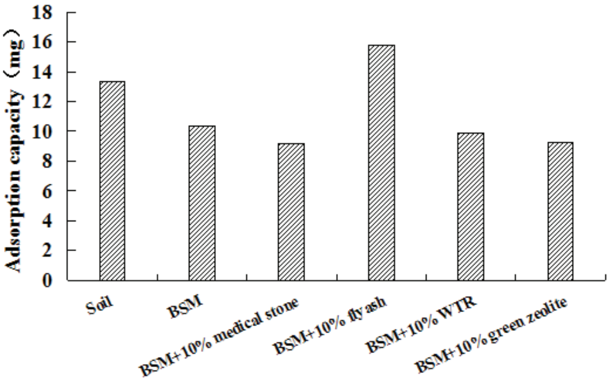

Fig. 5. Total adsorption of heavy metal Zn.

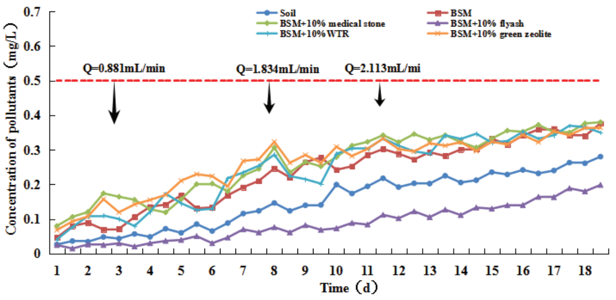

Fig. 6. Adsorption process curve of heavy metal Zn.

Table 7
Load and adsorption rate of bioretention simulation column inlet and outlet water

Zn (mg)	Bioretention simulation column					
	Soil	BSM	BSM + 10% MS	BSM + 10% fly ash	BSM + 10% WTR	BSM + 10% GZ
Incoming water load	19.0	19.0	19.0	19.0	19.0	19.0
Total water load	5.632	8.652	9.808	3.219	9.124	9.754
Adsorption capacity	13.368	10.348	9.192	15.781	9.876	9.246
Adsorption rate (%)	70.36	54.46	48.38	83.06	51.98	48.66

GZ, green zeolite; MS, medical stone.

WTR, and BSM + 10% green zeolite gradually approached 0.4 mg/L, whereas soil and BSM + 10% fly ash still maintained a stable upward trend. In summary, BSM + 10% fly ash exhibited the best adsorption capacity for continuous operation of heavy metal Zn. This finding is consistent with the results of previous isotherm adsorption experiments. Soil, BSM, BSM + 10% medical stone, BSM + 10% WTR, and BSM + 10% green zeolite exhibited poor adsorption capacity for continuous operation.

4. Conclusions

(1) At the same isothermal adsorption conditions and the concentration of heavy metal Zn in the solution of 5–50 mg/L, the removal rate of heavy metal Zn by the improver was more than 70%. As the concentration of heavy metal Zn in solution increased, fly ash showed a strong removal capability, whereas the effect of other modifiers gradually decreased. The Freundlich model was suitable for the modifiers to describe the adsorption process of Zn. The $1/n$ values of the seven modifiers were all between 0.5 and 1, indicating that the modifiers easily adsorb Zn.

(2) The results of combined adsorption and desorption tests showed that the fly ash had the strongest adsorption capacity for Zn and the lowest desorption rate among the seven modifiers and BSM, and its adsorption effect was relatively stable. BSM, WTR, medical stone, and green zeolite also exerted satisfactory adsorption effects. Fly ash, WTR, medical stone, and green zeolite were added at different ratios (5%, 10%, and 15%) to BSM for isotherm adsorption experiments. The results from the Langmuir and Freundlich models were compared with those of previous research, selected BSM was added with 10% improver.

(3) At the condition of the influent Zn concentration of 0.5 mg/L, the concentration of Zn in the effluent of the bioretention minicolumn packed with BSM, BSM + 10% medical stone, BSM + 10% WTR, and BSM + 10% green zeolite increased with the increase in the influent amount. After the water reached a recurrence interval of 3a, the Zn concentration of outflow gradually approached 0.4 mg/L. The minicolumn packed with BSM + 10% fly ash showed a continuous long-term adsorption capacity. After 18 d of operation, the simulated column adsorption rate was as high as 83.06%, and the concentration of effluent Zn was less than 0.20 mg/L. These values meet the Class II surface water environmental quality standards. When the influent reached 15 years of water, all types of mixed filler showed satisfactory adsorption effect, especially fly ash. The operating period could be extended, and further exploration could be conducted on this topic.

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