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Development and application of high-efficiency filler with pinewood chip biochar in bioretention system

Jiake Li[a,*], Mengmeng Zhai[a], Zhouli Liu[a], Yajiao Li[b]

[a]*State Key Laboratory of Eco-Hydraulics in the Northwest Arid Region of China, Xi'an University of Technology, Xi'an 710048, China, email: sys@xaut.edu.cn (J. Li)*
[b]*School of Architecture and Civil Engineering, Xi'an University of Science and Technology, Xi'an 710054, China*

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ABSTRACT

The use of pinewood chip biochar to improve the traditional bioretention filler can effectively enhance the regulation of the bioretention system, and the prospect of applying biochar to bioretention facilities is very bright. In this paper, the bioretention system is studied from the development of improved filler, experimental analysis of the regulation effects of improved fillers, and the optimization of structural parameters of improved filler bioretention facilities. The results show that: the optimal preparation scheme of pinewood chip biochar was that rising to 600°C at a heating rate of 20°C/min and pyrolysis at 600°C for 3 h. The addition ratio of pinewood chip biochar improved filler was 5%. The pollutant removal efficiency of biochar improved filler (Bioretention soil media (BSM)+ 5% pinewood chip biochar, w/w) is generally greater than that of BSM and BSM+ 5% WTR (water treatment residues, w/w). Under the constraint conditions of 25 cm ≤ thickness of filler layer ≤ 120 cm and 80% ≤ water volume reduction rate ≤ 85%, with the maximum pollutant load reduction rate as the optimization objective, the bioretention system with BSM, BSM+ 5% WTR, and BSM+ 5% pinewood chip biochar can deal with the rainfall scenarios with a recurrence period of 3a and a discharge ratio of 20:1 and below. This study is of great significance to agricultural and forestry waste recycling and the parameters design of bioretention facilities.

Keywords: Bioretention; Pinewood chip biochar; Analysis hierarchy process; Hydrus-1D; Response surface method; Parameters optimization

1. Introduction

In recent years, the rapid urbanization process has brought many serious problems while driving economic development. Urban water problems are particularly prominent, which are mainly in terms of flooding, non-point source pollution, and destruction of the natural hydrological cycle [1]. Low impact development (LID) is a new stormwater management strategy for urban water environment protection and sustainable development that is widely recognized in the world. In the LID systems, the bioretention facilities have good effects on runoff pollution control, runoff volume regulation and flood discharge reduction [2,3]. As an efficient and economical technical measure necessary for LID systems, bioretention technology plays an important role [4,5]. The most representative bioretention studies include those of Davis and Heish of the University of Maryland, Hunt of the University of North Carolina, Dietz and Clausen of the University of Connecticut, and FAWB of Monash University in Australia [6–10]. In recent years, some progress has been made in the research on the effects of bioretention on the water quality and quantity control of urban rainwater runoff. However, there are still a few studies on filler improvement in bioretention systems [11,12].

Biochar is an excellent soil conditioner, which can improve the sustainability of soil fertility. The discovery has attracted the attention of researchers around the world,

* Corresponding author.

and many have begun to explore the potential value of biochar [13]. In recent years, a lot of studies have emerged that combine biochar as a filler modifier with bioretention systems. The modified bioretention facilities have improved water holding capacity and infiltration performance to varying degrees, as well as pollutant adsorption capacity and microbial activity and community diversity in the filler. It also can effectively reduce the load of pollutants such as total suspended solids, total nitrogen (TN), total phosphorus (TP), heavy metals and organic carbon in rainwater runoff [14,15]. Jin et al. [16] classified cork biochar into three types by particle size and modified the packing soils at 4% (w/w) addition ratio respectively, and found that all three modifications increased filler porosity. However, the saturated hydraulic conductivity of the filler will not increase with the increase of the porosity of the filler, and some will even decrease. Lim et al. [17] added the four types of biochar into the four fillers of coarse sand, fine sand, loam and clay at four addition ratios of 0%, 1%, 2% and 5% (w/w), respectively. The effects of biochar application on the saturated hydraulic conductivity of the filler are studied. The results showed that the saturated hydraulic conductivity of the improved filler decreased when biochar was added to coarse sand and fine sand. Xu et al. [15] added corn straw biochar to the soil column at the ratio of 2%, 4%, and 8% (w/w) respectively for improvement, and sequenced the 16S rRNA gene in the soil using PCR amplification. The results showed that the composition of microbial communities associated with the nitrogen cycle changed, suggesting that the microbial transformation of nitrogen may be affected by biochar. Xiong et al. [18] mixed 88% concrete sand with 12% soil (w/w) uniformly as the control group and then added rice husk biochar to it at 4% (w/w) to study the removal effect of biochar improved filler on simulated runoff pollutants. The results showed that the removal rate of the improved filler was above 90% for TN and NO_3–N, but the removal effect for TP was poor at 59.36%. HYDRUS is a physical model of the soil, currently available in HYDRUS-1D, HYDRUS-2D, and HYDRUS-3D versions. HYDRUS-1D is a one-dimensional vertical model that is widely used due to its simple operation and accuracy [19,20].

At present, there is a lack of relevant research on the preparation method of biochar in bioretention facilities. At the same time, there are few studies on parameters optimization combining the results of field monitoring and simulation to improve the operation effects of bioretention technology. Based on these considerations, this study aims: (i) to develop efficient biochar improved fillers by selecting suitable biomass raw materials. (ii) To analyze the rainfall regulation effects of bioretention systems before and after the improvement. (iii) To optimize the structure design parameters of bioretention systems via HYDRUS-1D model and Design-Expert software.

2. Materials and methods

2.1. Wood chip biochar preparation

Biochar is prepared using wood chips, and the raw material for which is the processing waste from a pine furniture factory in Xi'an, Shaanxi Province of China. The raw materials of wood chips were evenly tiled on the tray, placed in the oven, and dried at 60°C for 4 h. The dried wood chips were screened with a 2 mm sieve to obtain fine wood chips with uniform particle size, which were sealed in a self-sealing bag for use.

There are various preparation schemes of wood chips biochar. The common pyrolysis temperature is 400°C~700°C, and the pyrolysis time is 0.5~6 h [21–23]. Fifteen different preparation schemes were set, including five pyrolysis temperatures (400°C, 450°C, 500°C, 550°C, and 600°C) and three pyrolysis duration (2, 3, and 4 h). The design of the improved filler preparation scheme is shown in Table A1. A muffle furnace model KSL-1200X is used to prepare biochar. Before starting the muffle furnace each time to burn the biochar, the clean and dry crucible is weighed and counted as m_1. The right amount of wood chips is added, then weighed and counted as m_2. After the crucible is sealed with tin foil and placed in a muffle furnace, the muffle furnace can be started and the preparation program can be set up. After the muffle furnace automatically goes through all the procedures, the crucible is taken out with crucible pliers. The crucible is put to room temperature and weighed after removing the tin foil, which is counted as m_3. Finally, the fired biochar is poured into a self-sealed bag with a serial number for preservation. The yield of biochar is one of the important parameters of biochar. The calculation formula [Eq. (1)] for it is as follows:

$$\omega = \frac{m_3 - m_1}{m_2 - m_1} \times 100\% \tag{1}$$

2.2. Pinewood chip biochar bioretention efficient filler preferences

2.2.1. Analysis hierarchy process

Analysis hierarchy process (AHP) is a common method for determining the objective weights of a multi-objective decision system. It has been adopted and applied in many fields [24,25]. There are four steps in using AHP to analyze practical problems: (i) establishing the hierarchical structure model of the problem; (ii) constructing pairwise comparison judgment matrix, and obtaining its eigenvectors and maximum characteristic roots; (iii) checking the consistency of pairwise comparison judgment matrix; (iv) determining the weight of each element.

2.2.2. Optimal preparation scheme of pinewood chip biochar

The yield, specific surface area, cation exchange capacity, total nitrogen, total phosphorus, ash, and organic carbon contents of 15 prepared pinewood chips biochar were detected and analyzed. A multi-objective evaluation system was established for these seven indexes to select the best preparation scheme for pinewood chip biochar.

2.2.3. Optimal addition ratio of pinewood chip biochar

Fillers are very important for bioretention facilities. Adding biochar to traditional bioretention filler can not only increase the porosity of the fillers to improve their permeability and water retention performance, but also affect the structural characteristics of biochar and the adsorption ability of pollutants by fillers in bioretention facilities due to preparation conditions such as pyrolysis temperature.

Pinewood chip biochar was added to the bioretention media soil (BSM, 65% sand + 30% soil + 5% wood chip, w/w) as a new improved filler. It can enrich the microbial community diversity of the bioretention tank, improve its water retention and water holding capacity, and enhance the control of stormwater volume and water quality. Three addition ratios of 2%, 5% and 8% (w/w) are considered to take pinewood chip biochar as an improver to BSM, which is homogeneously mixed as a new improved filler, noted as BSM+ 2% pinewood chip biochar, BSM+ 5% pinewood chip biochar and BSM+ 8% pinewood chip biochar (w/w). The best addition ratio is selected from these three ratios through experiments and analysis. To evaluate the advantages and disadvantages of the improved filler, three aspects can be evaluated, that is, the hydrological characteristics of the filler, water purification capacity and cost. To evaluate the hydrological characteristics of the filler, the key physical parameters of the filler can be determined, including saturated hydraulic conductivity, saturated water content and field moisture capacity. The saturated hydraulic conductivity is determined by the osmotic bucket method, the field moisture capacity by the Wilkes method, and the saturated water content by the drying method. To evaluate the water purification capacity of the filler, the adsorption test of conventional pollutants, including chemical oxygen demand (COD), TN, NH_3–N, NO_3–N and TP, can be carried out by artificial water distribution for bioretention columns.

Artificially simulated rainwater is used as the influent water to carry out the bioretention column filtration and adsorption test. According to the effluent water quality, the removal effects of three kinds of improved fillers on conventional pollutants in rainwater runoff are evaluated and compared.

2.3. Small-scale experimental study on the regulation effects of bioretention facilities for pinewood chip biochar improved fillers

2.3.1. Design of the test device

A bioretention test unit was established at the Sponge City Technology Proving Ground of the Xi'an University of Technology, Shaanxi Province of China. The test facility consists of six bioretention columns, a water tank, connecting pipes, and a test platform. Four bioretention columns (1#~4#) were selected for the experimental study of artificial simulated rainfall. The bioretention columns are made of PVC material, each column is 120 cm high, with an external diameter of 40 cm and a wall thickness of 6 mm. The structure of the bioretention column consists of a 15 cm gravel support layer, a 70 cm artificial filler layer, a 5 cm bark cover layer, and a 15 cm aquifer layer from bottom to top. The overflow port of the bioretention column is located 15 cm down from the top and the outlet at the bottom. The gauze-wrapped guide tube is arranged at the bottom of the gravel support layer to collect the outlet water. To ensure that the collected water samples are representative and to reduce physical errors, six sampling holes are placed in the bioretention column filler layer. Three sampling points were evenly distributed 10–15 cm below the top of the filler layer and the other three sampling points were evenly distributed 10–15 cm above the bottom of the filler layer.

2.3.2. Design of the test scheme

To explore the regulation effects of bioretention facilities with pinewood chip biochar improved filler on surface runoff rainwater, an orthogonal experimental scheme of artificial simulated rainfall under different rainfall scenarios is established. The effects of different bioretention columns on the regulation of rainwater volume and water quality are analyzed. The design factors of the rainfall scenario include rainfall recurrence period, rainfall duration, rainfall type, and rainfall water quality.

2.3.2.1. Structural design of bioretention column

The gravel layer of the bioretention columns (1#, 2#, 3#, and 4#) is 2–5 cm in diameter. The artificial filler layers are planting soil, BSM, BSM+ 5% WTR (water treatment residues, w/w), and BSM+ 5% pinewood chip biochar (w/w), respectively. The overlays layer is matured bark. Boxwood is selected as a plant layer, and each bioretention column is planted with 3 plants.

2.3.2.2. Design of influent water volume scheme

Taking into account the actual rainfall situation in Xi'an, Shaanxi Province of China, this experiment is designed with four rainfall recurrence periods (0.5a, 1a, 2a, and 3a) and two rainfall duration (2 h, 6 h), respectively. According to the Technical Guide for Sponge City Construction-Construction of Low Impact Development Stormwater Systems (Trial), the ratio of the area of the bioretention facilities to the catchment area is generally 5% ~ 10%. The discharge ratio is chosen to be 20:1. The rainstorm intensity formula [Eqs. (2)–(4)] of Xi'an city is selected to calculate the simulated rainfall intensity [26].

$$i = \frac{16.715 \times \left(1 + 1.1658 \log P\right)}{\left(t + 16.813\right)^{0.9302}} \tag{2}$$

$$H = i \cdot t \tag{3}$$

$$V = \phi \cdot H \cdot F \cdot n \tag{4}$$

where i is the stormwater intensity, mm/min; P is the rainfall recurrence period, a; t is the rainfall duration, min; H is the rainfall volume, mm; V is the design volume, L; ϕ is the runoff coefficient, 0.9 for this study; F is the catchment area, m^2; and n is the number of bioretention columns.

The design calculation of influent water volume is shown in Table 1.

2.3.2.3. Design of rain type scheme

Pilgrim and Cordery rain type is selected to simulate the rainfall which the rainfall duration of 2 h and 6 h.

Table 1
Design calculation of influent water volume

Recurrence period	Rainfall duration	Rainfall intensity	Rainfall	Runoff coefficient	Discharge ratio	Discharge area	Design water volume V (L)	
P (a)	t (min)	i (mm/min)	H (mm)	ϕ	–	F (m²)	Single	6 sticks
0.5	120	0.1118	13.41	0.9	20:1	2.512	30.33	181.95
1	120	0.1722	20.67				46.72	280.33
2	120	0.2327	27.92				63.12	378.71
3	120	0.2680	32.16				72.71	436.26
0.5	360	0.0436	15.68				35.45	212.71
1	360	0.0671	24.16				54.62	327.73
2	360	0.0907	32.64				73.79	442.74
3	360	0.1044	37.60				85.00	510.02

The rainfall design for 2 h is divided into 24 sections, and that for 6 h is divided into 12 sections. The proportion of each section to the total rainfall is shown in Fig. 1.

2.3.2.4. Design of influent water quality scheme

Combined with the characteristics of actual rainfall, the water quality of each rainfall is divided into two stages in this experiment. The first stage is the initial rainfall with a high pollutant concentration, and the second stage in the middle and late rainfall with low pollutant concentration. Based on the research of scholars, the first 5 min of rainfall is chosen as the initial rainfall. The simulated rainfall water quality for the two stages is shown in Table A2.

2.3.2.5. Design of experimental scheme

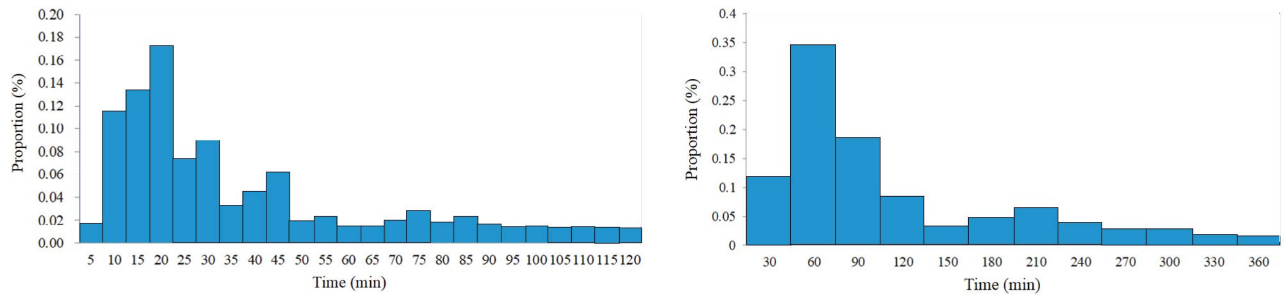
Four rainfall return periods, two rainfall duration and two influent concentrations were designed to establish an orthogonal test scheme, with a total of 8 times. According to the statistics of rainfall data in China's major cities in the past 30 y, more than 60% of rainfall intervals are less than 5 d. The pre-rain drying period of each rainfall in this study is set to be 4 d. Due to the influence of external factors such as weather, the specific experiment situation is shown in Table A3.

As you can see from Tables 1 and A3, in the 8 simulations, the maximum initial rainfall occurred at test 7. The rainfall return period is 3 a, and the rainfall duration is 6 h. According to the data in Table 1 and Fig. 1, the designed influent water volume of a single bioretention column is 85 L, the proportion of rainfall volume in the first 30 min to the total rainfall volume is 0.119. The initial rainfall influent volume for a single bioretention column can be calculated as 85 × 0.119/6 = 1.686 L. Due to the small amount of rainfall, this experiment used open-hole plastic buckets filled with initial rainfall. The initial rainfall is evenly poured into each bioretention column within 5 min by means of extruding flow. In the middle and late periods, the rainfall is discharged from the water tank.

2.4. Simulation of regulating effects and parameters optimization of bioretention facilities for pinewood chip biochar improved fillers

2.4.1. Parameter sensitivity analysis and calibration verification

The Hydrus-1D model is used to simulate the bioretention small-scale test. The modified Morris classification screening method [27] is used to analyze the sensitivity of the parameters. The main parameters of the model to be considered include four parts. The first part is the parameters related to external rainfall conditions. The second part is the structural parameters of the bioretention system. The third part is hydrological and hydraulic parameters.



(a) (b)

Fig. 1. Rainfall density distribution of (a) 2 h and (b) 6 h Pilgrim and Cordery rain type.

The fourth part is the solute transport parameters. Since all pollutant removal mechanisms are simplified into the same pure physical process in the model, TN is selected as the representative in the rainfall pollutant concentration parameter for sensitivity analysis. The bioretention column 4# with filler modification using pinewood chip biochar is selected as the representative object. Three typical tests (5, 6, and 7) in Table A3 are selected as the simulation scenarios for the sensitivity analysis of parameters. Scenario settings of the three tests are shown in Table A4.

Furthermore, test 3 and test 5 in Table A3 are selected to calibrate the models of bioretention columns (2#, 3# and 4#), while test 6 and test 8 in Table A3 are used to verify the models of bioretention columns (2#, 3# and 4#). Two representations of the determination coefficient R^2 and the Nash–Sutcliffe efficiency coefficient (NSE) are chosen to evaluate the applicability of the model. R^2 is used to evaluate the fit degree between measured values and simulated values. The closer R^2 is to 1, the closer linear relationship between measured values and simulated values is, and the more consistent the variation trend is. It is considered that there is a good correlation between simulated values of the model and measured values of the test when $R^2 > 0.6$ [28]. NSE is a standardized statistical value that distinguishes the relative quantity between residuals and variance of measured data. It is often used to evaluate the matching degree between measured values and simulated values. Its value ranges from minus infinity to 1. The closer its value is to 1, the closer simulated values are to measured values, and the more reliable the model simulation results are. It is generally accepted that when NSE > 0.5, the matching degree between measured values and simulated values is relatively high.

The specific calculation formula [Eqs. (5)–(6)] of R^2 and NSE are as follows:

$$R^2 = \left(\frac{\sum_{i=1}^{n} \left(x_i - x_{\text{avg}}\right)\left(Y_i - Y_{\text{avg}}\right)}{\sqrt{\sum_{i=1}^{n} \left(x_i - x_{\text{avg}}\right)^2 \sum_{i=1}^{n} \left(Y_i - Y_{\text{avg}}\right)^2}} \right)^2 \tag{5}$$

$$\text{NSE} = 1 - \frac{\sum_{i=1}^{n} \left(x_i - Y_i\right)^2}{\sum_{i=1}^{n} \left(x_i - x_{\text{avg}}\right)^2} \tag{6}$$

where R^2 is the determination coefficient; NSE is the Nash–Sutcliffe efficiency coefficient; x_i is the measured value at the ith time point; x_{avg} is the average of the measured values; Y_i is the simulated value at the ith time point; Y_{avg} is the average of the simulated values; n is the total number of samples.

2.4.2. Parameters optimization of bioretention facilities with pinewood chip biochar improved fillers

The response surface design method (RSM) in Design-Expert software is selected to optimize the structural parameters of the bioretention system. The design module offers four main types of design methods, namely Factor Design, Response Surface Design, Mixing Design and Integrated Design. The RSM is used to fit a mathematical model through more horizontal test scenarios, which ultimately results in a design with the best possible merit [29]. Firstly, the design module in RSM is used to design the test protocol, which takes into account both internal factors (filler type, thickness of filler layer and aquifer layer) and external factors (rainfall recurrence period and rainfall duration). There are 5 design factors, each design factor is taken at 3 levels, and a total of 46 scenarios. The filler types are BSM, BSM+ 5% WTR and BSM+ 5% pinewood chips biochar for the three bioretention columns 2#, 3# and 4#, respectively. As the model input parameters need to be digitized, the filler type is differentiated by the adsorption capacity factor of the filler. Where, the filler adsorption capacity factor = the adsorption capacity of the filler/the infiltration rate of the filler. Combined with the previous study of our group and related literature [30], the filler adsorption capacity factors of three bioretention columns 2#, 3# and 4# are 0.051, 0.196, and 0.367 d/m, respectively. The thicknesses of the filler layer are 60, 70 and 80 cm, and thicknesses of the aquifer layer are 10, 20 and 30 cm, respectively. The rainfall recurrence periods are 1a, 2a, and 3a, and the rainfall durations are 120, 240, and 360 min, respectively. The specific schemes are shown in Table A5. Each scenario is simulated using the calibrated HYDRUS-1D model and the corresponding response values are obtained.

Then, in the analysis module of RSM, the software will fit and analyze the variance of the mathematical relationship among the variables, and establish the best mathematical model among the variables. Finally, the optimization objective and constraint conditions are set in the optimization module of RSM, and the optimization results can be obtained after running.

3. Test results and discussion

3.1. Analysis of the physical and chemical properties of pinewood chip biochar

The biochar yields of the 15 preparation schemes are shown in Table A6.

The prepared biochars under 15 different schemes are numbered and detected. The detailed results are shown in Table A7.

When the pyrolysis temperature was between 400°C and 600°C, the yield decreased with the increase of pyrolysis temperature, but there was no obvious correlation between the yield and the pyrolysis duration. The yield of wood chip biochar under 15 preparation schemes was in the range of 29.46% to 36.05%. The specific surface area increased exponentially with the increase of preparation temperature. With the increase of preparation duration, the contents of total nitrogen and total phosphorus of wood chip biochar decreased gradually. The yields of pinewood chip biochar under the 15 preparation schemes ranged from 29.46% to 36.05%, and the fluctuation is small, which is negatively correlated with pyrolysis temperature.

3.2. Optimization of pinewood chip biochar bioretention efficient filler

3.2.1. Optimization results of preparation scheme

The hierarchical structure model of the optimal preparation scheme of pinewood chip biochar is shown in Fig. 2.

The yaahp software is used to construct the judgment matrix. The weights of these seven indicators are obtained as 0.088 (the yield), 0.335 (specific surface area), 0.088 (cation exchange capacity), 0.131 (total nitrogen), 0.131 (total phosphorus), 0.045 (ash), and 0.182 (organic carbon content). The scores of all indicators and the total scores of the 15 schemes are calculated and ranked separately. The scores are shown in Table A8. According to the evaluation results, scheme 10 is the best preparation scheme for wood chip biochar. This means that the temperature is raised to 600°C at a heating rate of 20°C/min, pyrolyzing at 600°C for 3 h, and then cooling to room temperature.

3.2.2. Preferred results for the optimum addition ratio of pinewood chip biochar

The hierarchical structure model of optimal addition ratio for pinewood chip biochar is established, as shown in Fig. 3. The experimental data of hydrological characteristics and water purification capacity of the three kinds of improved fillers are shown in Table A9.

In view of the high cost of biochar, the cost of three kinds of improved fillers is simplified to the mass of the pinewood chip biochar. The mass of pinewood chip biochar in the three bioretention columns could be calculated using the following equation [Eq. (7)]:

$$M_{\mathrm{Bi}} = x_i \cdot V \cdot \gamma_i \quad (7)$$

where i is the number of bioretention columns; M_{Bi} is the mass of biochar in column i; x_i is the proportion of biochar added to column i; V is the volume of the filler layer for the bioretention column; γ_i is the filler layer bulk density of column i.

Therefore, combined with the data in Table A9, the cost ratio of the three kinds of improved fillers can be calculated as 2.36: 5.275: 7.32. The data of the nine evaluation indexes, such as K_S, ϕ, θ_S, COD, TN, NH_3–N, NO_3–N, TP and Cost, are standardized. After data standardization is completed, yaahp software is used to establish the judgment matrix and calculate the weight of each index. By assigning the comprehensive weight of each index to the standardized data, the total score of each improved filler can be calculated, as shown in Table 2.

3.3. Regulation effects of bioretention facilities with pinewood chip biochar improved fillers

3.3.1. Regulation effects of bioretention columns on artificially simulated rainfall volume

According to the specific performance of each bioretention column in all rainfall events, the regulation effects of bioretention columns on artificially simulated rainfall

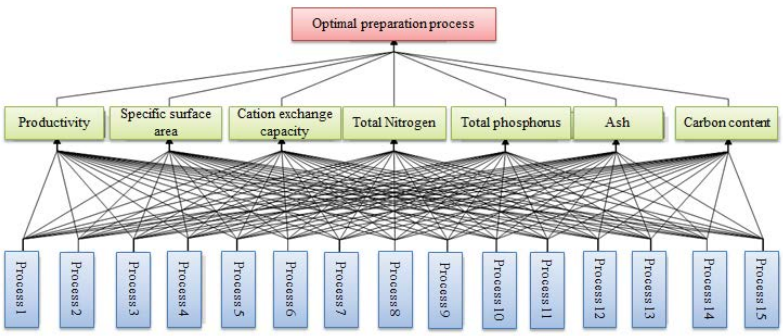


Fig. 2. Hierarchical structure model of optimal preparation scheme of wood chip biochar.

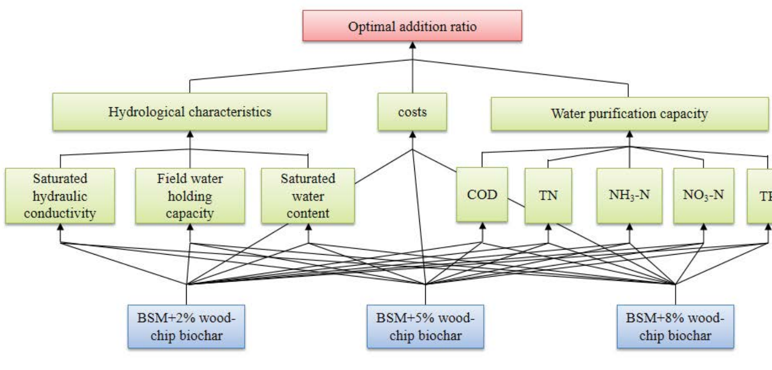


Fig. 3. Hierarchical structure diagram of the best addition ratio of wood chip biochar.

Table 2
Evaluation score and ranking of the three addition ratios of pinewood chip biochar

Fillers \ Indicators	Hydrological characteristics			Water quality purification					Costs	Overall rating	Sort
	K_S	φ	θ_S	COD	TN	NH_3–N	NO_3–N	TP	Cost		
BSM+2% biochar with pinewood chip	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.061	0.429	0.490	3
BSM+5% biochar with pinewood chip	0.082	0.007	0.060	0.101	0.053	0.024	0.027	0.018	0.177	0.549	1
BSM+8% biochar with pinewood chip	0.114	0.057	0.114	0.103	0.061	0.031	0.031	0.000	0.000	0.512	2

Based on scoring calculations, the optimal addition ratio of pinewood chip biochar is 5%.

Table 3
Fitting effect of water volume reduction rate and pollutant load reduction rate

Test phase	Number	Water volume reduction rate		Load reduction rate									
				COD		TN		TP		NH_3–N		NO_3–N	
		R^2	NSE	R^2	NSE	R^2	NSE	R^2	NSE	R^2	NSE	R^2	NSE
Calibration period	2#	0.92	0.85	0.83	0.81	0.74	0.71	0.73	0.68	0.82	0.76	0.69	0.65
	3#	0.89	0.87	0.82	0.77	0.73	0.66	0.84	0.79	0.85	0.77	0.78	0.71
	4#	0.94	0.83	0.84	0.81	0.78	0.68	0.75	0.70	0.79	0.76	0.64	0.64
Validation period	2#	0.86	0.87	0.81	0.79	0.68	0.69	0.69	0.61	0.81	0.72	0.73	0.65
	3#	0.87	0.82	0.79	0.80	0.71	0.64	0.86	0.84	0.83	0.79	0.72	0.63
	4#	0.91	0.85	0.81	0.78	0.67	0.63	0.66	0.64	0.85	0.78	0.67	0.62

volume are evaluated and analyzed. The key control indicators of water quantity include the influent volume, effluent volume, overflow volume, water volume reduction rate and effluent start time of four bioretention columns (1#, 2#, 3#, and 4#) in each rainfall event. The comparisons of the effluent start time for the bioretention columns are shown in Fig. 4a. The comparisons of the water volume reduction rates for the bioretention columns are shown in Fig. 4b.

The rainfall duration of the four tests (test 1, test 2, test 3, and test 6) is 2 h, and the rainfall duration of the other four tests is 6 h. Compared with the experiment with a rainfall duration of 2 h, the effluent start time of the bioretention column with a rainfall duration of 6 h is later. The average water volume reduction rates for the four bioretention columns (1#, 2#, 3#, and 4#) are 58.09%, 22.35%, 50.44% and 41.33%, respectively. Bioretention column 1# has the best water volume reduction effects, and the water volume reduction rate is relatively stable, mainly because the planting soil-filled by bioretention column 1# is fine and dense. Although the infiltration performance of the bioretention column 1# is not ideal, its water retention performance is very good, so that the water volume reduction effects can be guaranteed. The filler layer of bioretention column 2# is BSM, mostly sand, which has good infiltration performance, but poor water retention capacity, so the water volume reduction rate of bioretention column 2# is low. Compared with the bioretention column 2#, the water retention of bioretention columns (3# and 4#) increased significantly, but the infiltration rate doesn't decrease significantly. It allows the improved bioretention columns to perform well in terms of water volume reduction, peak rainfall reduction, and delaying peak time, as well as controlling the frequency of overflow. The water volume reduction rate of bioretention columns (3#, 4#) fluctuated

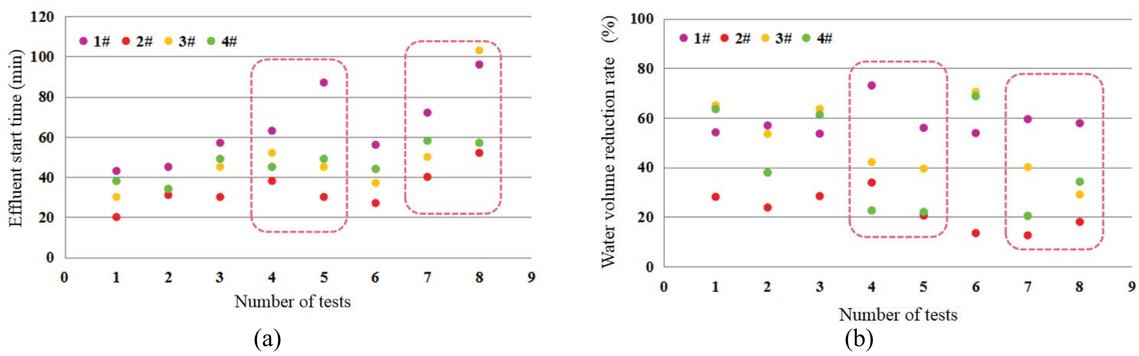


Fig. 4. (a) Comparisons of the effluent start time for the bioretention columns and (b) comparisons of the water volume reduction rates for the bioretention columns.

greatly, and the water volume reduction rate of the two bioretention columns decreased with the length of rainfall duration.

3.3.2. Regulation effects of bioretention column on water quality of artificial simulated rainfall

Artificially simulated rainfall can reflect its pollution level in terms of loads of five indicators: COD, TN, TP, NH_3–N, and NO_3–N. The effluent water quality of bioretention columns under eight kinds of different rainfall scenarios and the load reduction of the five pollutants are analyzed. As the overflow from bioretention column 1# is too frequent to be of much significance, only bioretention columns (2#, 3# and 4#) are studied for their effectiveness in regulating rainwater quality.

3.3.2.1. Analysis of effluent concentration of pollutant in bioretention column

The exceedance probability method is used to analyze the removal effects of pollutant concentration for bioretention columns. By sorting the data of all the effluent water quality for the three bioretention columns in the eight tests respectively, the exceedance probability can be calculated as shown in Fig. 5.

In general, the COD concentration removal effect of bioretention column 4# is significantly lower than that of 2# and 3#, and the probability of exceeding influent concentration is only 10.29%. Adding wood chip biochar greatly improved the removal effect of COD concentration of traditional bioretention filler. The effluent COD concentration of bioretention columns (2#, 3#) is very close, and the scatter-fitting trend lines of the two bioretention columns basically coincide. Therefore, after the traditional bioretention filler is improved by using WTR, the removal effect of the improved filler on the rainwater COD concentration is not obvious.

The bioretention column 2# is less effective in removing concentrations of NO_3–N and TN. The bioretention column 3# contains WTR, which greatly improves the removal of phosphorus from the system. The bioretention columns (2#, 3#, and 4#) all have good removal effects on NH_3–N. The fluctuation of effluent NH_3–N concentration of bioretention column 2# is the smallest, and the water quality control effect is the most stable.

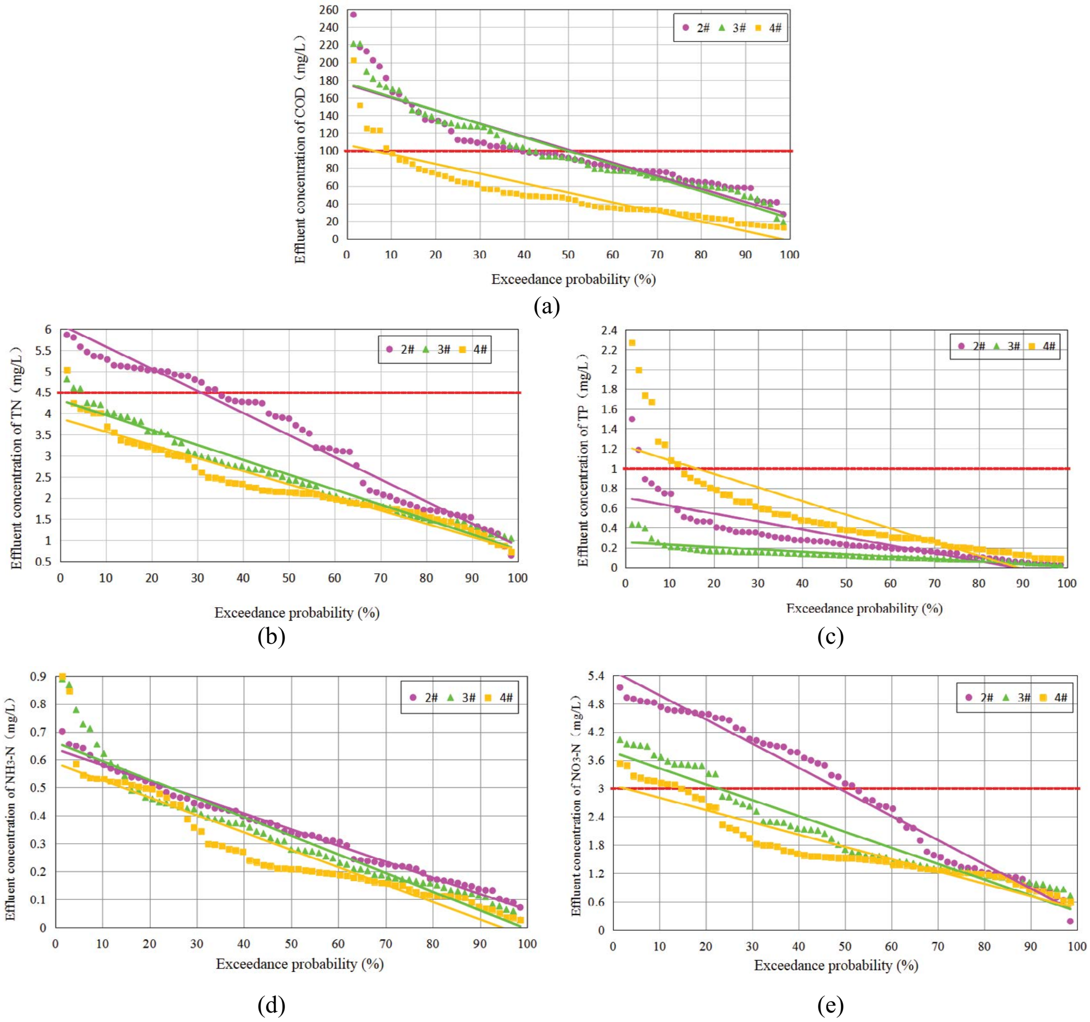


Fig. 5. Exceedance probability of (a) COD, (b) TN, (c) TP, (d) NH_3–N and (e) NO_3–N concentration in effluent.

3.3.2.2. Analysis of effluent load of pollutants in bioretention column

Combined with each pollutant concentration in each period and the entering and leaving water volume of the bioretention column, a load of pollutants and the load reduction rate of each pollutant of the bioretention column can be calculated. The load reduction of the pollutant for three bioretention columns at each test is statistically analyzed. The average load reduction rates of the five pollutant indexes for each bioretention column are obtained by taking the average value of the results of 8 tests, which are shown in Fig. 6.

As can be seen in Fig. 6, the load removal rates of the bioretention column 4# for COD, TN, TP, NH_3–N, and NO_3–N are 75.36%, 72.58%, 74.18%, 89.13% and 68.97% respectively, all above 68%. The use of pinewood chip biochar to improve the traditional bioretention fillers makes the bioretention facilities more stable and efficient in water quality control of conventional pollutants in rainwater. The load reduction rates of bioretention column 3# for TP, NH_3–N, TN, and NO_3–N are above 65%, but the load reduction rate for COD is only 58.56%. The load reduction level of each pollutant in rainwater for bioretention columns 2# is varied. The load reduction rate of NO_3–N for bioretention columns 2# ranging from –3.57% to 67.16%, with an average value of only 23.84%. The main reason for the negative NO_3–N load reduction of bioretention column 2# is that the bioretention column 2# has a poor effect on the removal of NO_3–N concentration in rainwater, and the water reduction rate of bioretention column 2# is low.

3.4. Simulation of regulating effects and parameter optimization of bioretention facilities with pinewood chip biochar improved fillers

3.4.1. Results of parameter sensitivity analysis and calibration verification

The following conclusions can be drawn from the sensitivity analysis of each parameter. For the model response values related to water volume, such as overflow start time, the total water volume of overflow and outflow. The parameters with higher sensitivity are rainfall volume, the height of aquifer layer, the thickness of filler layer, pore size distribution parameters of filler layer, the saturated water content of filler layer, saturated hydraulic conductivity of filler layer, and initial water content of filler layer. For the pollutant concentration removal rate, most parameters are at a high sensitivity level. For the pollutant load reduction rate, most of the parameters are at a low sensitivity level. The number of measured values of the parameters should be increased as much as possible to ensure the accuracy of the model, and the accuracy of the model should be gradually improved by adjusting model parameters.

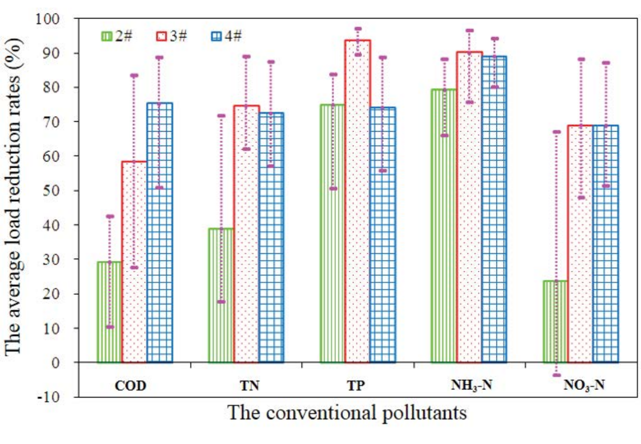


Fig. 6. The load reduction rate of bioretention column to conventional pollutants.

The calibration results of water volume and water quality-related parameters of the model are shown in Tables A10 and A11. The simulation fitting degree in the calibration period and validation period are evaluated using R^2 and NSE, as shown in Table 3.

From the results in Table 3, during the calibration period and verification period, the determination coefficients R^2 between simulated water volume reduction rate and load reduction rate and measured results are above 0.6. The Nash–Sutcliffe efficiency coefficient is above 0.5, and the degree of fitting and matching between simulated values and measured values is up to standard. Therefore, calibration and validation of the model are successful. The calibrated model can be used as a predictive model to simulate outflow in other scenarios. It can obtain response values of the model and predict the regulation effects of bioretention facilities under preset rainfall scenarios.

3.4.2. Variance test and regression analysis

Using the calibrated Hydrus-1D model, all scenarios are simulated in turn. The corresponding water volume reduction rate and pollutant load reduction rate, which is the model response value in design module, are calculated from the output simulation results. The specific results are shown in Table A12.

Through the analysis module of the RSM, variance test and model regression analysis of the mathematical relationship between the respective variables and the dependent variable are carried out. The multiple quadratic regression model expressed by the actual value between the load reduction rates of pollutants and each influencing factors is as follows [Eqs. (8)–(13)]:

$$\begin{aligned}\text{Water reduction rate} = {} & 134.15 + 15.75A + 0.15B - 9.97C \\ & + 2.4D + 148.74E + 0.01AB + 0.18AC + 0.22AD \\ & - 0.08AE - 0.11BE - 0.01CD - 0.04CE - 0.28DE \\ & - 8.29A^2 + 0.08C^2 - 0.03D^2 - 25.25E^2 \end{aligned} \tag{8}$$

$$\begin{aligned}\text{Load reduction rate of COD} = {} & -252.84 + 62.58A - 0.2B \\ & + 3.15C + 1.49D + 116.76E + 0.09AB - 0.32AC \\ & + 0.04AD + 3.34AE - 0.05BE - 0.33CE - 0.3DE \\ & - 16.5A^2 - 0.01C^2 - 0.02D^2 - 14.25E^2 \end{aligned} \tag{9}$$

$$\begin{aligned}\text{Load reduction rate of TN} = {} & -55.2 - 16.94A - 0.14B \\ & - 0.82C + 1.38D + 139.84E + 0.03AB - 0.13AC \\ & + 0.01AD + 0.23AE - 0.07BE - 0.04CE - 0.24DE \\ & + 3.76A^2 - 0.01D^2 - 23.08E^2 \end{aligned} \tag{10}$$

Table 4
Results of variance analysis

Object of analysis	F	Sig.	C.V. (%)	R^{2+}	R^2-Adj
Rate of water reduction (%)	54.64	<0.0001	8.09	0.9776	0.9597
COD load reduction rate (%)	15.78	<0.0001	10.62	0.9266	0.8679
TN load reduction rate (%)	51.05	<0.0001	6.08	0.9761	0.9570
TP load reduction rate (%)	19.10	<0.0001	3.28	0.9386	0.8894
NH_3–N load reduction rate (%)	19.23	<0.0001	2.40	0.9390	0.8902
NO_3–N load reduction rate (%)	71.58	<0.0001	6.80	0.9828	0.9691

Table 5
Optimization results with a recurrence period of 1a, 2a, 3a

Rainfall duration (h)	Filler type	Thickness of filler layer (cm)			Thickness of aquifer layer (cm)			Total height of the facility (cm)		
		1a	2a	3a	1a	2a	3a	1a	2a	3a
2	BSM	108	113	119	15	19	23	138	147	157
	BSM+ 5% WTR	94	101	107	18	21	24	127	137	146
	BSM+ 5% biochar with pinewood chip	89	96	101	19	23	26	123	134	142
6	BSM	101	107	114	17	23	26	133	145	155
	BSM+ 5% WTR	88	93	98	22	24	28	125	132	141
	BSM+ 5% biochar with pinewood chip	81	88	91	24	27	30	120	130	136

$$\text{Load reduction rate of TP} = 17.17 + 3.37A - 0.08B + 0.04C + 0.35D + 68.51E + 0.11AC + 2.83AE - 0.04BE + 0.02CE - 0.07DE - 5.47A^2 - 15.45E^2 \quad (11)$$

$$\text{Load reduction rate of } NH_3\text{–N} = -38.85 - 14.57A + 1.65C + 0.8D + 62.15E + 0.15AC + 0.07AD + 2.35250AE - 0.045208BE - 0.23950CE - 0.25075DE - 1.86750A^2 - 7.18E^2 \quad (12)$$

$$\text{Load reduction rate of } NO_3\text{–N} = -117.24 - 23.93A - 0.28B + 0.92C + 1.68D + 145.87E + 0.04AB - 0.12AC + 0.07AD + AE - 0.08BE + 0.07CE - 0.17DE + 3.88A^2 - 0.02D^2 - 25.53E^2 \quad (13)$$

where A: rainfall recurrence period; B: rainfall duration; C: thickness of filler layer; D: thickness of aquifer layer; E: filler type.

After the model is fitted, the probability of the normal distribution of the residuals is shown in Fig. A1. After completing the normal distribution test of the residuals, an analysis of variance is conducted on the relationship between the independent variables and each response value. The results are shown in Table 4.

As can be seen in Table 4, the F-values for each regression model are greater than 15 and the values of Sig. are less than 0.0001, indicating extremely high significance. The values of R^2 and R^2-Adj in the table are both greater than 0.86. In conclusion, the significance of the fitted equations is good. The established multiple quadratic regression model has high reliability, which can be used for the optimization analysis of the parameters of the bioretention system.

3.4.3. Analysis of parameter optimization results

The optimization results of the structural parameters for different filler types of bioretention systems are shown in Table 5.

According to the optimization results in Table 5, the recommended value for the thickness of filler layer is the largest and the value for the thickness of aquifer layer is the smallest for BSM. The recommended value for the thickness of the filler layer is the smallest and the thickness of the aquifer layer is the largest for BSM+ 5% pinewood chip biochar. The reason is that BSM has the best permeability and is not easy to form water on the surface of filler, but its ability to remove pollutants is limited. On the contrary, due to the addition of pinewood chip biochar improver in BSM+ 5% pinewood chip biochar, the infiltration performance of the filler is reduced, and the recommended value for the thickness of the aquifer layer is slightly higher. However, it greatly improves the ability of the filler to remove pollutants, which greatly reduces the need for the thickness of the filler layer. Under the constraint conditions of 25 cm ≤ thickness of filler layer ≤ 120 cm and 80% ≤ water volume reduction rate ≤ 85%, with the maximum pollutant load reduction rate as the optimization objective, the bioretention system with BSM, BSM+ 5% WTR, and BSM+ 5% pinewood chip biochar can deal with rainfall scenarios with a recurrence period of 3 a and a discharge ratio of 20:1 and below.

4. Conclusions

The application of biochar as a filler improver can effectively improve the regulation capacity of the bioretention system. The main findings of the study are as follows:

A method of using pinewood chip biochar as a filler modifier in a bioretention system is proposed, and the optimal preparation scheme and the optimal addition ratio of biochar are determined. The optimal preparation scheme of pinewood chip biochar is a muffle furnace with a heating rate of 20°C/min to 600°C, pyrolyzing at 600°C for 3 h, and then cooling to room temperature. The optimal addition ratio of wood chip biochar to improve the traditional bioretention filler is 5%.

A small-scale experimental device was built to analyze the rainfall regulation effect of the bioretention system before and after the improvement. The pollutant removal efficiency of bioretention facilities with biochar filler (BSM+ 5% pinewood chip biochar) is generally greater than those of the other two bioretention facilities (BSM and BSM+ 5% WTR). The reasons are that its large cation exchange capacity (CEC) and large specific surface area (BET), as well as the appropriate amount of carbon source for microorganisms to facilitate the removal of nitrate–nitrogen by nitrifying bacteria. The load reduction level of each pollutant for BSM is different.

Combined with the experimental data, the Hydrus-1D model and Design-Expert software were used to optimize the structural design parameters of the bioretention system. The recommended value for the thickness of the filler layer is the largest and the value for the thickness of the aquifer layer is the smallest for BSM. The recommended value for the thickness of the filler layer is the smallest and the thickness of the aquifer layer is the largest for BSM+ 5% pinewood chip biochar. Under the constraint conditions of 25 cm ≤ thickness of filler layer ≤ 120 cm and 80% ≤ water volume reduction rate ≤ 85%, with the maximum pollutant load reduction rate as the optimization objective, the bioretention system with BSM, BSM+ 5% WTR, and BSM+ 5% pinewood chip biochar can deal with rainfall scenarios with a recurrence period of 3a and a discharge ratio of 20:1 and below.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found in the file "Supplementary Information".

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Appendix A. Supplementary information

Table A1
Design of the improved filler preparation schemes

Process number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Pyrolysis temperature (°C)	400	450	500	550	600	400	450	500	550	600	400	450	500	550	600
Pyrolysis duration (h)	2	2	2	2	2	3	3	3	3	3	4	4	4	4	4
Heating rate (°C/min)	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20

Table A2
Water quality of artificial synthetic rainfall

Water quality indicators / Rainfall periods	COD	NO_3–N	NH_3–N	TP
	(mg/L)			
Initial period	600	12	6	2.5
Mid to late	100	3	1.5	1

Table A3
Test scheme of artificial synthetic rainfall

Number of trials	Date	Rainfall recurrence period	Rainfall duration	Dry period before rain	Influent concentration	
		a	h	d	Initial period (first 5min)	Mid to late
Pre-test	2019/9/30	–	–	–	–	–
Test1	2019/10/7	3	2	6	High	Low
Test2	2019/10/12	0.5	2	4	High	Low
Test3	2019/10/17	1	2	4	High	Low
Test4	2019/10/22	0.5	6	4	High	Low
Test5	2019/10/27	2	6	4	High	Low
Test6	2019/11/1	2	2	4	High	Low
Test7	2019/11/7	3	6	5	High	Low
Test8	2019/11/12	1	6	4	High	Low

Table A4
Scenario settings of parameter sensitivity analysis

Tests	Rainfall recurrence period (P/a)	Rainfall duration (t/min)	Discharge ratio	Runoff coefficient
Test5	2	360	20:1	0.9
Test6	2	120	20:1	0.9
Test7	3	360	20:1	0.9

Table A5
Design of optimization scheme

Test number	Rainfall recurrence period	Duration of rainfall	Thickness of filler layer	Aquifer height	Filler types
	P/a	t/min	H_t/cm	H_x/cm	
1	1	240	60	20	BSM+ 5% WTR
2	1	240	70	20	BSM+ 5% pinewood chips biochar
3	2	360	70	20	BSM
4	2	240	80	20	BSM+ 5% pinewood chips biochar
5	3	240	70	20	BSM
6	1	240	70	30	BSM+ 5% WTR
7	2	120	60	20	BSM+ 5% WTR
8	1	120	70	20	BSM+ 5% WTR
9	1	360	70	20	BSM+ 5% WTR
10	2	360	80	20	BSM+ 5% WTR
11	3	240	80	20	BSM+ 5% WTR
12	2	360	60	20	BSM+ 5% WTR
13	2	240	60	10	BSM+ 5% WTR
14	2	240	80	30	BSM+ 5% WTR
15	2	240	70	20	BSM+ 5% WTR
16	2	240	70	20	BSM+ 5% WTR
17	2	240	80	10	BSM+ 5% WTR
18	1	240	80	20	BSM+ 5% WTR
19	2	240	70	30	BSM+ 5% pinewood chips biochar
20	2	120	70	20	BSM
21	3	360	70	20	BSM+ 5% WTR
22	2	240	70	30	BSM
23	2	240	60	20	BSM
24	3	240	70	20	BSM+ 5% pinewood chips biochar
25	2	360	70	20	BSM+ 5% pinewood chips biochar
26	2	120	70	30	BSM+ 5% WTR
27	2	240	70	20	BSM+ 5% WTR
28	2	360	70	30	BSM+ 5% WTR
29	2	240	70	20	BSM+ 5% WTR
30	2	240	60	20	BSM+ 5% pinewood chips biochar
31	3	120	70	20	BSM+ 5% WTR
32	1	240	70	20	BSM
33	1	240	70	10	BSM+ 5% WTR
34	2	120	80	20	BSM+ 5% WTR
35	2	360	70	10	BSM+ 5% WTR
36	3	240	70	10	BSM+ 5% WTR
37	2	240	80	20	BSM
38	2	120	70	20	BSM+ 5% pinewood chips biochar
39	2	240	70	10	BSM
40	2	120	70	10	BSM+ 5% WTR
41	2	240	70	20	BSM+ 5% WTR
42	2	240	70	10	BSM+ 5% pinewood chips biochar
43	3	240	70	30	BSM+ 5% WTR
44	3	240	60	20	BSM+ 5% WTR
45	2	240	70	20	BSM+ 5% WTR
46	2	240	60	30	BSM+ 5% WTR

Table A6
The biochar yields of the 15 preparation schemes

Program number	Pyrolysis temperature (°C)	Pyrolysis duration (h)	Heating rate[a] (°C/min)	Yield rates[b] (%)
1	400	2		34.53–35.05 (34.79)
2	450	2		33.97–34.34 (34.16)
3	500	2		31.33–31.59 (31.48)
4	550	2		31.62–31.96 (31.77)
5	600	2		29.46–29.68 (29.59)
6	400	3		35.74–36.05 (35.86)
7	450	3		32.37–32.55 (32.46)
8	500	3	20	31.43–31.50 (31.46)
9	550	3		30.27–30.33 (30.30)
10	600	3		30.77–30.98 (30.88)
11	400	4		34.92–35.46 (35.20)
12	450	4		32.52–32.79 (32.67)
13	500	4		31.55–31.92 (31.76)
14	550	4		30.33–30.41 (30.38)
15	600	4		29.58–29.92 (29.76)

[a]In this study, slow thermal cracking is used for biochar preparation and the muffle heating rate is set at a constant value of 20°C/min;
[b]Yield rates contain the range of yields and their averages under the corresponding scenarios.

Table A7
Results of pinewood chip biochar detection

Indicators / Number	Specific surface area	Cation exchange capacity	Total nitrogen	Total phosphorus	Ash	Organic carbon
	m^2/g	cmol/kg	%	mg/kg	%	%
1	2.243	118.41	0.364	1570	10.805	7.1
2	3.159	119.67	0.328	1550	15.21	6.14
3	4.447	117.64	0.24	1880	12.4	6.67
4	58.505	110.145	0.2735	1640	16.13	7.685
5	133.559	107.3	0.3275	1390	12.975	6.61
6	3.041	111.715	0.290	1160	14.615	8.265
7	18.127	117.32	0.213	1180	11.465	7.32
8	5.421	121.06	0.292	1710	10.845	7.275
9	80.982	117.375	0.232	664	12.915	6.29
10	113.638	103.735	0.249	1080	16.525	8.42
11	2.339	107.835	0.222	594	10.01	5.815
12	2.059	117.095	0.186	777	11.225	7.495
13	11.107	107.705	0.2225	662	13.535	7.660
14	15.516	110.485	0.357	880.5	12.915	4.785
15	54.336	111.91	0.138	905.5	14.04	5.880

Table A8
Evaluation score and ranking of 15 preparation schemes of pinewood chip biochar

Weights number	Yield rates	Specific surface area	Cation exchange	Total nitrogen	Total phosphorus	Ash	Organic carbon content	Total points	Sort
	(0.088)	(0.335)	(0.088)	(0.131)	(0.131)	(0.045)	(0.182)		
1	0.150	0.000	0.153	0.000	0.030	0.030	0.021	0.335	12
2	0.132	0.003	0.166	0.020	0.032	0.007	0.013	0.280	14
3	0.055	0.006	0.145	0.068	0.000	0.021	0.017	0.298	13
4	0.063	0.138	0.067	0.050	0.023	0.002	0.027	0.432	9
5	0.000	0.321	0.037	0.020	0.047	0.018	0.017	0.539	3
6	0.181	0.002	0.083	0.041	0.070	0.010	0.032	0.435	8
7	0.083	0.039	0.142	0.083	0.068	0.026	0.024	0.471	6
8	0.054	0.008	0.181	0.040	0.016	0.029	0.023	0.346	11
9	0.021	0.193	0.142	0.073	0.118	0.019	0.014	0.581	2
10	0.037	0.273	0.000	0.063	0.078	0.000	0.034	0.632	1
11	0.162	0.001	0.043	0.078	0.125	0.034	0.010	0.410	10
12	0.089	0.000	0.140	0.098	0.107	0.027	0.025	0.499	4
13	0.063	0.022	0.041	0.078	0.118	0.015	0.027	0.444	7
14	0.023	0.033	0.071	0.004	0.097	0.019	0.000	0.211	15
15	0.005	0.128	0.085	0.125	0.094	0.013	0.010	0.479	5

Table A9
Hydrological characteristics and water purification capacity of three improved fillers

Parameters[a] \ Filler type		BSM[b]	BSM+ 2% biochar with pinewood chips	BSM+ 5% biochar with pinewood chips	BSM+ 8% biochar with pinewood chips
Saturated hydraulic conductivity	γ	1.14	1.19 (1.17)[c]	1.04 (1.07)	0.92 (0.91)
	H	–	4.9 (4.8)	5.1 (5.0)	4.8 (4.8)
	K_S	–	1.717 (1.769)	1.292 (1.270	1.128 (1.078)
	Average	1.476	1.743	1.281	1.103
Field water holding capacity	ϕ	–	18.75 (18.59)	19.54 (19.61)	26.16 (26.08)
	Average	18.02	18.67	19.575	26.12
Saturated water content	θ_S	–	23.80 (23.47)	31.02 (30.95)	37.57 (37.66)
	Average	22.45	23.635	30.985	37.615
Water quality purification[d]	COD	–	60.13	84.35	84.70
	TN	–	52.79	79.47	83.31
	NO_3–N	–	76.40	85.67	88.46
	NH_3–N	–	36.25	76.05	82.64
	TP	–	73.81	54.89	46.89

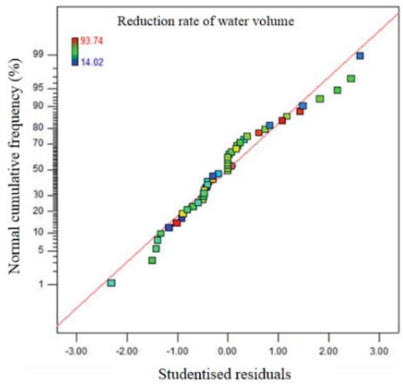
[a]γ is the volume weight, g/cm^3; H is the stable head height above the fill, cm; ϕ is the field water holding capacity, %;
θ_S is the saturated water content, %;
[b]Hydrological parameters of the BSM were derived from previous studies by this group;
[c]Data for experimental groups are shown outside parentheses and data for parallel samples are shown in parentheses;
[d]Water quality purification contains concentration removal rates for 5 conventional water quality indicators, %.

Table A10
Calibration results of hydrologic and hydraulic parameters of bioretention column

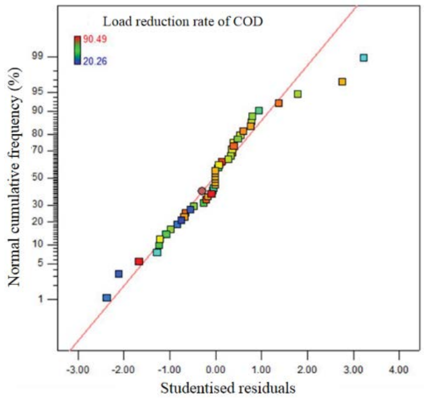
Filler types	q_r (cm^3/cm^3)	q_s (cm^3/cm^3)	α (cm^{-1})	n	K_S (cm/min)	l
BSM	0.038	0.327	0.011	1.58	1.351	0.5
BSM+ 5% WTR	0.054	0.395	0.011	1.81	1.325	0.5
BSM+ 5% biochar with pinewood chip	0.061	0.426	0.013	1.76	1.049	0.5

Table A11
Calibration results of solute transport parameters of bioretention column

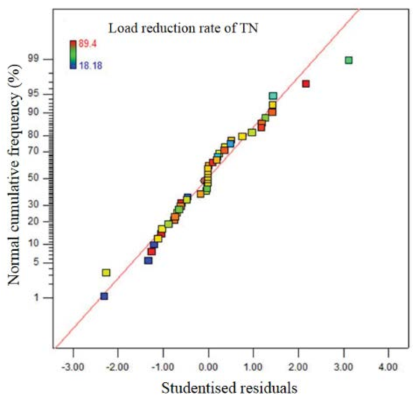
Filler types	Saturated adsorption coefficient of filler K_d (cm^3/g)					Empirical coefficient of filler adsorption β				
	COD	TN	TP	NH_3–N	NO_3–N	COD	TN	TP	NH_3–N	NO_3–N
BSM	1.06	0.24	0.76	0.092	0.084	1.77	0.79	1.54	0.72	0.61
BSM+ 5% WTR	1.14	0.61	2.45	0.117	0.139	1.68	0.97	1.90	0.96	0.78
BSM+ 5% biochar with pinewood chip	2.28	0.78	0.31	0.183	0.165	0.85	0.91	0.87	0.93	0.84



(**a**)



(**b**)



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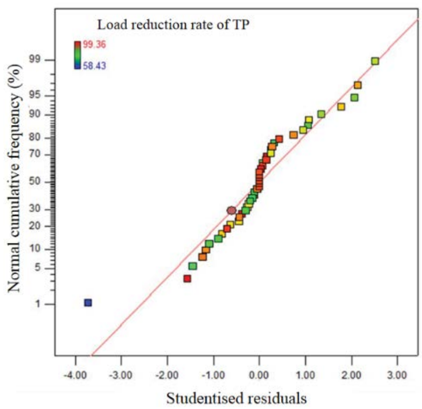
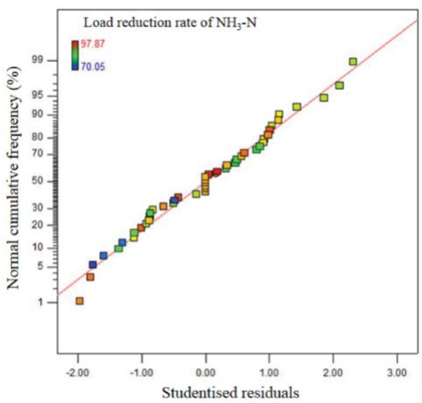
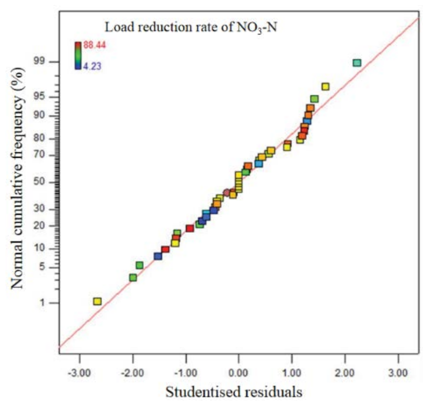


(**d**)



(**e**)



(**f**)

Fig. A1. Normal probability distribution of residuals of (a) water volume, (b) COD, (c) TN, (d) TP, (e) NH_3–N and (f) NO_3–N.

Table A12
Simulation results of the optimization scheme

Test number	Water reduction rate (%)	Load reduction rate (%)				
		COD	TN	TP	NH_3–N	NO_3–N
1	37.63	40.07	72.75	93.84	91.96	65.3
2	48.07	78.12	83.42	83.87	92.26	80.04
3	24.56	44.77	26.54	84.22	88.57	16.63
4	76.48	90.49	89.11	91.25	94.14	85.73
5	19.57	20.26	29.44	58.43	70.05	12.49
6	47.47	52.11	80.93	94.27	93.72	75.65
7	62.74	79.37	82.11	96.45	91.06	77.42
8	63.72	74.31	89.4	93.76	95.62	88.44
9	32.97	28.89	71.06	94.88	91.53	62.31
10	72.81	79.52	73.84	99.25	94.17	68.08
11	88.64	71.27	79.73	90.45	91.24	75.68
12	34.35	65.29	57.38	90.41	84.46	43.61
13	52.47	69.54	67.7	90.58	85.37	52.17
14	93.74	84.68	81.05	99.36	97.87	80.38
15	64.06	78.24	74.72	96.59	93.02	69.54
16	64.06	78.24	74.72	96.59	93.02	69.54
17	90.18	82.17	79.63	98.71	95.56	77.92
18	77.68	64.86	87.55	94.61	95.24	83.62
19	47.19	86.36	75.62	83.8	91.09	72.71
20	15.84	26.41	19.78	74.81	73.13	10.42
21	42.01	65.43	74.26	92.68	89.75	67.71
22	29.28	43.43	32.19	81.38	84.42	18.24
23	14.02	25.54	18.18	74.37	71.75	4.23
24	43.89	72.76	69.23	74.54	86.77	66.14
25	24.51	82.12	62.25	79.07	88.43	56.08
26	71.86	84.07	85.56	97.14	94.93	81.25
27	64.06	78.24	74.72	96.59	93.02	69.54
28	44.62	73.23	65.59	98.33	92.4	53.39
29	64.06	78.24	74.72	96.59	93.02	69.54
30	39.78	79.64	68.47	78.13	86.24	65.81
31	66.62	66.93	78.32	89.87	89.48	74.04
32	23.43	38.97	44.53	79.06	84.95	30.37
33	45.44	48.82	78.19	94.03	93.08	72.72
34	92.22	84.59	86.84	97.23	96.31	81.78
35	38.34	68.96	60.27	94.63	87.74	46.68
36	50.38	63.49	73.62	87.56	85.67	66.75
37	52.12	49.68	40.43	86.57	89.23	21.31
38	69.85	89.73	88.82	89.21	94.69	87.03
39	14.54	28.61	18.26	75.79	73.17	7.32
40	65.48	80.82	82.98	96.73	92.35	78.41
41	64.06	78.24	74.72	96.59	93.02	69.54
42	43.63	83.72	71.33	80.82	89.87	68.46
43	61.3	68.28	76.84	88.16	89.13	72.3
44	41.51	59.13	70.31	85.12	82.04	62.27
45	64.06	78.24	74.72	96.59	93.02	69.54
46	60.74	72.46	71.28	91.44	87.68	57.46