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Adsorption Characteristics of Several Bioretention-Modified Fillers for Phosphorus

Binhong Zhang [1], Jiake Li [1,*], Yajiao Li [2] and Huaien Li [1]

1 State Key Laboratory of Eco-hydraulics in Northwest Arid Region of China, Xi'an University of Technology, Xi'an 710048, China; 18391200387@163.com (B.Z.); sys@xaut.edu.cn (H.L.)
2 School of Architecture and Civil Engineering, Xi'an University of Science and Technology, Xi'an 710054, China; liyajiao@163.com
* Correspondence: xaut_ljk@163.com

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Abstract: To optimize the bioretention mixed fillers with better removal of phosphorus, this paper studies the adsorption characteristics of single filler and modified mixed filler through static adsorption experiments, and adopts the dynamical mini-column experiments to examine the adsorption capacities of the soil and modified mixed fillers. Results show that, in the static adsorption experiments, both water treatment residual (WTR) and fly ash exhibit good adsorption capacity when used as a single filler and modifier. Adsorption capacity increases with increasing WTR and fly ash dosage in the mixed filler. The modified mixed filler with WTR exerts a clear effect in the dynamic adsorption experiment, which is unsaturated when influent phosphorus concentration is 1 mg/L and inflow amount is equivalent to 15 years of precipitation. The adsorption capacity of WTR is 3.5–4.5 times that of other mixed fillers. Fly ash as a modifier shows a poor dynamic adsorption effect and thus must be continuously studied. In this study, WTR is recommended as a bioretention phosphorus removal additive. In engineering applications, the amount of WTR added can be controlled within 5–10% (by mass) according to influent phosphorus concentration.

Keywords: bioretention; single filler; modified mixed filler; adsorption; phosphorus removal

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1. Introduction

With the accelerating pace of urbanization, the structure and function of the city's underlying surface have gradually changed, and numerous water areas, forest lands, grasslands, and farmlands have been replaced by impervious cement, asphalt, and other impermeable materials. This phenomenon has led to a decrease in water permeability of the underlying surface of the city, followed by an increase in surface runoff, a reduction in confluence time, and an increase in flood peaks [1]. Meanwhile, surface runoff contains suspended solids, oxygen-consuming substances, nutrients, and toxic substances. Various pollutants, such as oils and fats enter rivers and lakes with runoff, resulting in contamination of the receiving water [2,3]. Among the various pollutants in rainfall runoff, nutrient salts (nitrogen and phosphorus) have attracted attention owing to their significant role in the eutrophication of water [4,5]. The Ministry of Water Resources evaluated 103 national lakes in 2011, and the comprehensive evaluation of the nutritional status of 471 reservoirs showed that the problem of eutrophication of lakes and reservoirs in China is extremely serious. The ratio of eutrophication in lakes and reservoirs is 100%, with urban storm water runoff being one of the main contributors [6,7]. Nitrogen and phosphorus are the two most important nutrients in ecosystems, and phosphorus is the main limiting element in eutrophication [8,9]. Therefore, the removal of phosphorus in urban rainfall runoff is an important research topic.

Bioretention is an efficient and economical rainwater treatment in the Low Impact Development (LID) management system. This treatment not only considerably affects runoff and peak reduction but also effectively and steadily removes the pollutants, such as suspended matter, heavy metal, oil, and oil and pathogenic bacteria in urban surface runoff [10–12]; however, the removal efficiency of nutrient elements such as phosphorus exhibits a certain fluctuation [13–15], in which the background value of phosphorus and the desorption of soluble phosphorus adsorbed at the later stages are the main causes of its destabilization. In the initial bioretention medium, natural soil with high permeability is selected, and sandy loam, loamy sand, and loam are considered as the best types of bioretention and used to date. The soil widely used at present is based on soil containing certain organic matter. As explicitly mentioned in certain design manuals and design methods for bioretention facilities, soil humus, such as hardwood, straw, or deciduous, should be added to mixed fillers to treat the soil [16,17]. In view of the deficiencies of traditional bioretention facilities for phosphorus purification, studies have shown that the addition of a certain amount of modifier can increase the phosphorus removal efficiency of the facility [18–20]. On the basis of the actual soil texture in Feng Xi New city in Xi'an New area, this study devised a bioretention soil media (BSM) and added the modifier to improve the adsorption capacity of phosphorus. The effect of the modified filler dosage on the adsorption effect was studied through the static adsorption experiment. The adsorption capacity of the bioretention fillers after modifier addition was studied using the state adsorption experiment, which provides a reference for the ratio of phosphorus retention material in the biological field of Feng Xi New city.

2. Materials and Methods

2.1. Media Characteristics

The BSM contained 30% soil, 65% sand, and 5% wood chips (by mass). The soil was obtained locally from Feng Xi New city. The river sand was purchased from a local construction company. Wood chips were sourced from a flower market in Xi'an. Soil, sand, and wood chips were air-dried after one week later and passed through a 2-mm sieve. The sieved soil, which contained 16.86% sand, 75.02% silt, and 8.30% clay was classified as the silt loam according to the United States Department of Agriculture's soil (USDA) texture classification. The mixture of soil and sand contained 49.05% of sand, 45.52% of powder, and 5.42% of clay without the wood chips and was classified as a sandy loam soil per USDA classification. In this study, zeolites, fly ash, water treatment residual (WTR), and medical stone were used as single modified fillers. WTR was obtained from a Xi'an's drinking water treatment plant and aluminum salt was used as coagulant. Because the initial WTR contained much moisture, before use, the WTR were air-dried for at least one week, manually crushed and passed through a 2 mm sieve, and stored in a closed container to retain its moisture content and adsorption capacity constant. Zeolite and fly ash were purchased from a company in Shaanxi.

The pH, organic matter content, water-soluble phosphorus, total amount of metal element iron, aluminum, calcium, and magnesium in each component of the bioretention medium were measured before the experiment. The pH was measured using an HQ40D three-parameter tester (HACH, Loveland, CO, USA) (1/2.5 w/v), and the organic matter content was determined by potassium dichromate volumetric method (NY/T 85-1998). The total phosphorus (TP) was determined by potassium persulfate oxidation ultraviolet spectrophotometry (ascorbic acid and ammonium molybdate, 800 nm, detection limit of 0.6 mg/L). The water-soluble phosphorus was vacuum-filtered through a 0.22 μm membrane (XINYA, Shanghai, China) and then subjected to potassium persulfate oxidation UV spectrophotometry (DR5000, HACH, Loveland, CO, USA; ascorbic acid and ammonium molybdate, 800 nm, detection limit of 0.6 mg/L). Metal elements calcium, magnesium, and aluminum were determined by atomic absorption spectrophotometry (ZEEnit700, Analytik Jena, Jena, Thuringia, Germany), and aluminum was measured by inductively coupled plasma emission spectrometry (ICP-6800, Macy, Shanghai, China).

2.2. Static Isothermal Adsorption Experiment of Phosphorus with Single Fillers

Several 5.0 g portions of a single modifier were placed into 250 mL conical flasks and each added with 1, 2, 5, 10, 15, 20, 50, and 100 mg/L of KH_2PO_4 at 25 °C and 150 r/min. After shaking for 48 h, the Erlenmeyer flask was removed and let stand for 0.5 h. The supernatant was obtained to determine the phosphorus content, and the process was repeated thrice to reduce error. After the experiment was completed, the single filler after 100 mg/L KH_2PO_4 solution equilibrium adsorption experiment was naturally dried for one week, and 2 g was placed into a 250 mL conical flask. Then, 100 mL of distilled water was added and desorption was measured under the same conditions of isothermal adsorption experiment.

2.3. Static Isothermal Adsorption Experiment of Phosphorus with Modified Fillers

Zeolite, maifanite, fly ash, and WTR were added to the BSM at different mass ratios (5%, 10%, and 15%) for isothermal adsorption experiments. Owing to the small proportion of modifiers added in the experiment, the total amount of mixed fillers was appropriately enlarged, accurately 10 g portions of improved mixed fillers were placed into 250 mL conical flasks and added with 2, 5, 10, 20, 50, and 100 mg/L KH_2PO_4 solution. The mixture was shaken at 25 °C and 150 r/min for 24 h, and then the conical flask was taken out. After standing for 0.5 h, the supernatant was taken to determine the phosphorus content, and the process was repeated thrice to reduce errors.

2.4. Dynamic Adsorption and Desorption Experiment of Modified Fillers on Phosphorus

The dynamic adsorption experiment is conducive to simulating actual operating conditions and can effectively evaluate the adsorption capacity of the filler. In this experiment, six kinds of fillers were selected for dynamic adsorption experiments. This mini-column adsorption experiment, which was established at the Key Laboratory of Xi'an University and Technology, used a sealed upflow column with 22 cm height and 3.4 cm internal diameter. Six groups of mini-column experiment devices were filled with uniformly saturated modified fillers. The modified fillers were all of the same quality and weight of 180 g. The medium height was maintained at 16.3 to 19.2 cm. Different medium densities resulted in different medium heights. Six sets of improved filler adsorption experiments were conducted. Influent water was continuously injected into each column using a BT100-1L peristaltic pump (Longer, Baoding, Hebei, China), and the influent concentration and flow rate were calibrated before use to maintain influent concentration and flow rate within 5% of the required value. The mini-column number and fillers are shown in Table 1. The mini-column and field used in the experiment are shown in Figure 1.

(**a**) (**b**)

Figure 1. Mini-column dimensions (**a**) and running diagram (**b**).

Table 1. Type of media in mini-column.

Mini-Column	1	2	3	4	5	6
Filler types	Soil	BSM	BSM + 10% maifanite	BSM + 10% fly ash	BSM + 10% WTR	BSM + 10% zeolite

Note: WTR: water treatment residual; BSM: bioretention soil media.

The experiment influent water was prepared with reference to the concentration of rainfall runoff in Xi'an City. The influent water contained three kinds of pollutants, including soluble reactive phosphorus (SRP, 1 mg/L), NH_3-N (1.5 mg/L), and heavy metal Zn (0.5 mg/L) in pure water. KH_2PO_4, NH_4Cl, and $ZnSO_4$ were added separately for preparation. This experiment uses peristaltic pump to supply water continuously. Three different influent flow rates were used at the same concentration, and the flow rate proceeded from low to high. In the three return periods of 0.5, 2, and 3 a, design rainfall intensity at 60 min was used to design the inflow. The average annual rainfall of Xi'an in the past 50 years is 560 mm, and the total inflow of a single mini-column is equivalent to confluence for 10 years of rainfall with a ratio of 20:1. If not considerably saturated, the mixed filler can continue to operate during the 3a return period. The rainfall intensity was determined by the storm intensity Equation (1) [21] in Xi'an. Each mini-column inflow can be calculated using Equation (2). The calculation results are shown in Table 2:

$$q = \frac{2785.833 \times (1 + 1.1658 \lg P)}{(t + 16.813)^{0.9302}}, \tag{1}$$

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

where q is the design storm intensity, L/(s·hm^2); P is the return period, a; t is the rainfall duration, min; Q is a single mini-column inlet flow, mL/min; M is the mini-column media mass, 180 g; h is the actual height of the bioretention filler, 70 cm; and ρ is the actual BSM density, 1.116 g/cm^3.

Table 2. Calculation of water volume.

Return Period	0.5	2	3
Rainstorm intensity (L/(s·hm^2))	31.87	66.34	76.42
Influent flow (mL/min)	0.881	1.834	2.113
Running time (days)	6.78	3.26	2.83

During the mini-column experiment, inflow and outflow were sampled daily at specific time points, and the inflow and outflow process samples and the mixed sample were collected and measured simultaneously. If immediate measurement was not possible, the sample should be stored at a low temperature of 3.9 °C. For ensuring the stability of influent water quality, update water for every two days and determination of influent/effluent water quantity and quality were performed to accurately evaluate operating capacities and saturated adsorption capacities.

After completion of the modified filler dynamic adsorption experiment, the peristaltic pump was controlled to run in the reverse direction, residual water was drained, the influent water was replaced with distilled water, the rainfall intensity (2.11 mL/min) was returned during the 3a return period, and the operation continued for 4.24 days, which is equivalent to five years of rainfall. The effluent process samples and mixed samples were measured, and the total desorption amount was calculated.

3. Analysis and Evaluation Methods

Accuracy, integrity, and representativeness were ensured during the collection and analysis of all samples. The TP was determined by potassium persulfate oxidation ultraviolet spectrophotometry (ascorbic acid and ammonium molybdate, 800 nm, with a detection limit of 0.6 mg/L) method and

SRP using vacuum filtration 0.22 μm filter after UV spectrophotometry (ascorbic acid and ammonium molybdate, 800 nm, detection limit 0.6 mg/L) determination.

Static adsorption experiments consisted of a single modifier and a modified mixed filler. The adsorption results of a single filler were fitted to the experimental data by using the Langmuir and Freundlich adsorption models, and the adsorption capacity of a single modifier was evaluated by combining the physicochemical properties and composition. The adsorption performance of modified mixed fillers on phosphorus can be evaluated by the adsorption capacity per unit mass when saturated:

$$q_e = \frac{K_1 X_m c_e}{1 + K_1 c_e}, \tag{3}$$

$$q_e = K_f {c_e}^{1/n}, \tag{4}$$

where q_e is the amount of phosphorus adsorption per unit mass of matrix, mg/g; c_e is the equilibrium concentration of phosphorus adsorption, mg/L; K_1 represents the energy of adsorption bond strength, L/mg; X_m is the theoretical saturated adsorption capacity of Langmuir theory, mg/g; K_f reflects the adsorption capacity, and $1/n$ reflects the degree of adsorption of the filler.

From the start of the mini-column experiment, two influent and effluent water samples were obtained for each mini-column at a fixed daily time to ensure that the influent water quality measurement float range was within 5% of the required water quality, and the effluent water quality was analyzed subsequently. When the concentration of effluent water for two days was C_{out} = 0.9C_{in}, the adsorption of modified fillers were considered as saturated. The average adsorption capacity (unit mass filler adsorption capacity, mg/kg) can be used as a comparative evaluation between different modified filler indices. The result can be calculated according to Equations (5) and (6):

$$M_a = \sum C_{in} \cdot V_{in} - \sum C_{out} \cdot V_{out}, \tag{5}$$

$$m_a = \frac{M_a}{M_{media}}, \tag{6}$$

where M_a is the total amount of phosphorus adsorbed by the filler, mg; $C_{in/out}$ is the concentration of incoming and outgoing water in each period, mg/L; $Q_{in/out}$ is the volume of influent and effluent water at each stage, L; m_a is the unit mass filler adsorption capacity, mg/kg; and M_{media} is the quality of the mini-column filler, kg.

$$M_d = C_{out*} \cdot V_{out*}, \tag{7}$$

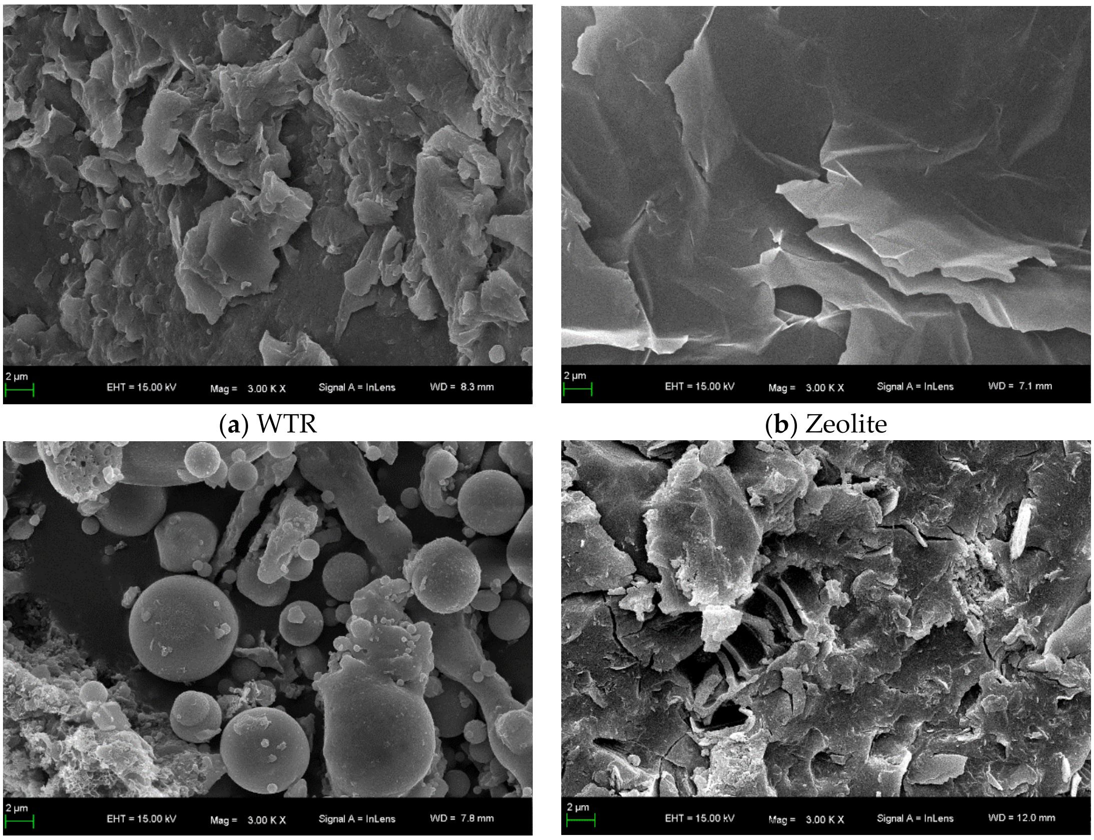
$$Y = \frac{M_a - M_d}{M_a}, \tag{8}$$

where M_d is the total amount of filler phosphorus desorption, mg; C_{out^*} is the concentration of desorption water, mg/L; V_{out^*} is the volume of desorption water, L; and Y is the desorption rate, %.

4. Results and Discussion

4.1. Media Characteristics

The physical and chemical properties of the modifier should be analyzed because they considerably influence the adsorption and ion exchange of the filler. In this study, the physical and chemical properties of the components and the modifiers in the traditional BSM were determined (Table 3) in addition to electron microscopy images of the four modifiers (Figure 2).



(**a**) WTR (**b**) Zeolite (**c**) Fly ash (**d**) Maifanite

Figure 2. SEM images of (**a**) WTR, (**b**) Zeolite, (**c**) Fly ash, and (**d**) Maifanite.

Table 3. Media characteristics.

Media	PS	pH	OM (%)	CEC (cmol/kg)	SP (mg/kg)	Total Elements (g/kg)			
						Ca	Mg	Fe	Al
Soil	<2 mm	8.44	0.0322	19.44	0.55	4.82	8.22	25.02	20.86
Sand	<2 mm	9.38	0.745	3.7	0.33	[a]	[a]	[a]	[a]
Wood chips	<2 mm	6.20	50	26.66	10.3	[a]	[a]	[a]	[a]
WTR	<2 mm	7.34	10.3	9.31	0.095	0.03	0.30	9.33	122.04
Zeolite	3–5 cm	8.15	6.98	27.50	0.23	1.92	5.63	11.49	67.72
Maifanite	2–4 cm	8.72	4.41	13.39	0.07	2.85	7.13	23.57	78.70
Fly ash	<0.1 mm	10.85	2.66	23.23	0.085	21.51	3.492	13.78	64.01
BSM	<2 mm	7.79	3.0	9.57	0.89	25.78	7.79	12.47	8.56

Note: PS: particle size; OM: organic matter; CEC: cation exchange capacity; SP: soluble phosphorus; WTR: water treatment residual; BSM: bioretention soil media. [a] Data not collected.

Single and mixed fillers should possess a certain clay content because fine particles are typically the most chemically active. The filler with high clay content exhibited good adsorption effect on phosphorus, but an excessive clay content affects the permeability of the entire system. The recommended clay content is less than 5% per US design guidelines and 10% to 25% per EPA regulations. Bioretention fillers must establish a balance between the permeability of the media and contaminant removal characteristics. The selected filler was found to be crucial for the removal of total phosphorus. The ability of the medium to adsorb phosphorus is related to the content of oxalate-extractable aluminum and iron content (Al_{ox} + Fe_{ox}) with high (Al_{ox} + Fe_{ox}) contents resulting in large amount of phosphorus adsorption [22]. Hunt and Jarrett [23] found that by increasing the CEC of the filler, the phosphorus content of the filler can be diminished, and a CEC exceeding 10 is suitable. In this study, the contents of iron and calcium in the fillers were small, and the difference was negligible. The WTR aluminum ion content was relatively high. Compared with the characteristics of these fillers, the specific surface area of WTR and zeolite is relatively large, and the CEC values of zeolite, fly ash, and BSM are high.

4.2. Static Adsorption Effect of Single Fillers

The isothermal adsorption curves of different single fillers for phosphorus are shown in Figure 3, which illustrates the different adsorption capacities of different modified fillers for phosphorus. Table 4 shows the isothermal adsorption equations and related parameters.

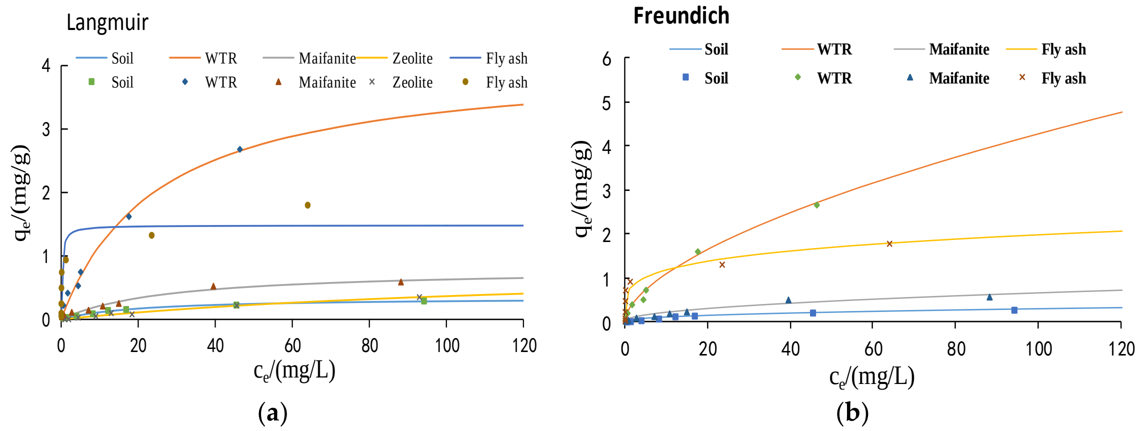


Figure 3. Adsorption characteristic curves of single filler. Curves are fitted (**a**) Langmuir isotherms and (**b**) Freundich isotherms.

Table 4. Isothermal adsorption equations and related parameters.

Single Filler	Langmuir			Freundlich		
	K_1 (L/mg)	X_m (mg/g)	R^2	K_f	$1/n$	R^2
Soil	0.048	0.345	0.986	0.038	0.451	0.968
Zeolite	0.0071	0.88	0.985	-	-	-
Fly ash	4.17	1.48	0.873	0.699	0.225	0.875
Maifanite	0.036	0.802	0.965	0.007	0.488	0.948
WTR	0.039	4.094	0.988	0.276	0.595	0.993

Note: WTR: water treatment residual.

As seen in Table 4, the correlation coefficients R^2 of Langmuir equations of single fillers other than fly ash all exceeded 0.90, well describing the adsorption characteristics of phosphorus for the above five single fillers. The saturated adsorption capacity of five kinds of single fillers for phosphorus is ranked as follows: WTR > fly ash > zeolite > maifanite > soil. Compared with other five kinds of fillers, Fly ash presented the largest energy intensity K_1, and the gap is apparent. The adsorption capacity of WTR is significantly higher than that of other fillers. The above table shows that the R^2 of the Freundlich adsorption equation is unstable and that the fitting of zeolite is difficult. The fitting of the Freundlich adsorption equation shows the order of adsorption capacity from large to small: fly ash > WTR > soil > maifanite.

Desorption experiments of materials after 100 mg/L phosphorus adsorption were conducted. The adsorption and desorption of different single fillers are shown in Table 5. According to the equilibrium adsorption amount after the addition of 100 mg/L KH_2PO_4 solution, the other fillers except fly ash can reach the theoretical saturated adsorption capacity possibly owing to insufficient contact time to not reach the saturated adsorption state. After adsorption equilibrium, the filler has the desorption phenomenon of phosphorus, but desorption degree is different. Phosphorus exhibits the highest maximum desorption amount. WTR shows the largest phosphorus desorption, followed by fly ash, and the desorption amount of other fillers is relatively low. The analysis rate shows WTR and fly ash exhibit superior effect compared with other single fillers.

Table 5. Experimental results of phosphorus adsorption by single fillers.

Single Filler	Total Adsorption Capacity (mg/g)	Desorption Capacity (mg/g)	Residual Adsorptive Capacity (mg/g)	Desorption Rate (%)
Soil	0.3	0.04	0.26	13.33
Fly ash	1.80	0.16	1.64	8.89
WTR	2.68	0.17	2.51	6.34
Maifanite	0.44	0.06	0.38	13.56
Zeolite	0.35	0.055	0.295	15.71

Note: WTR: water treatment residual.

4.3. Static Adsorption Effect of Modified Mixed Fillers

The modified zeolite, maifanite, fly ash, and WTR were added to the BSM at different mass ratios (5%, 10%, and 15%), and the effect of the modifier on the adsorption of mixed fillers were investigated. The experimental results are shown in Table 6.

Table 6. Isothermal adsorption equation and parameters of modified mixed fillers for phosphorus.

Modified Mixed Filler	Langmuir			Modified Mixed Filler	Langmuir		
	K_1 (L/mg)	X_m (mg/g)	R^2		K_1 (L/mg)	X_m (mg/g)	R^2
BSM + 5% maifanite	0.024	0.463	0.922	BSM + 10% maifanite	0.021	0.479	0.976
BSM + 15% maifanite	0.020	0.507	0.964	BSM + 5% zeolite	0.02	0.50	0.977
BSM + 10% zeolite	0.021	0.492	0.975	BSM + 15% zeolite	0.024	0.511	0.90
BSM + 5% WTR	0.027	0.685	0.991	BSM + 10% WTR	0.034	0.847	0.999
BSM + 15% WTR	0.047	1.002	0.997	BSM + 5% fly ash	0.024	0.502	0.934
BSM + 10% fly ash	0.022	0.614	0.964	BSM + 15% fly ash	0.021	0.680	0.988

Note: BSM: bioretention soil media; WTR: water treatment residual.

In the experiment, the results of the mixed fillers adsorption with Freundlich equation were poorly accurate, and most of the mixed fillers cannot be fitted effectively. The adsorption capacity of mixed fillers was evaluated by the saturated adsorption capacity of the Langmuir equation. The adsorption results of BSM were fitted, and the adsorption theory was 0.455 mg/g. Table 6 shows that the theoretical saturated adsorption capacity of the three kinds of adding amount of maifanite and zeolite is slightly higher than that of BSM. The addition of a small amount of maifanite and zeolite exerts a minimal effect on the adsorption capacity of the mixed fillers. The adsorption capacity of the mixed filler clearly increased with the addition of fly ash and WTR, and the increase was directly proportional to the added amount.

4.4. Dynamic Adsorption Effect of Modified Mixed Fillers

This experiment defines that the modified filler can reach saturation when the concentration of $C_{out} = 0.9C_{in}$ for two consecutive days is saturated. The final experiment must determine the adsorption capacity of the medium when P reaches adsorption saturation. The mini-column runs slowly, and water may be stopped when the column is unsaturated. With concentration as the ordinate and the influent water volumes as the abscissa, the adsorption process of each mixed filler for phosphorus is shown in Figure 4.

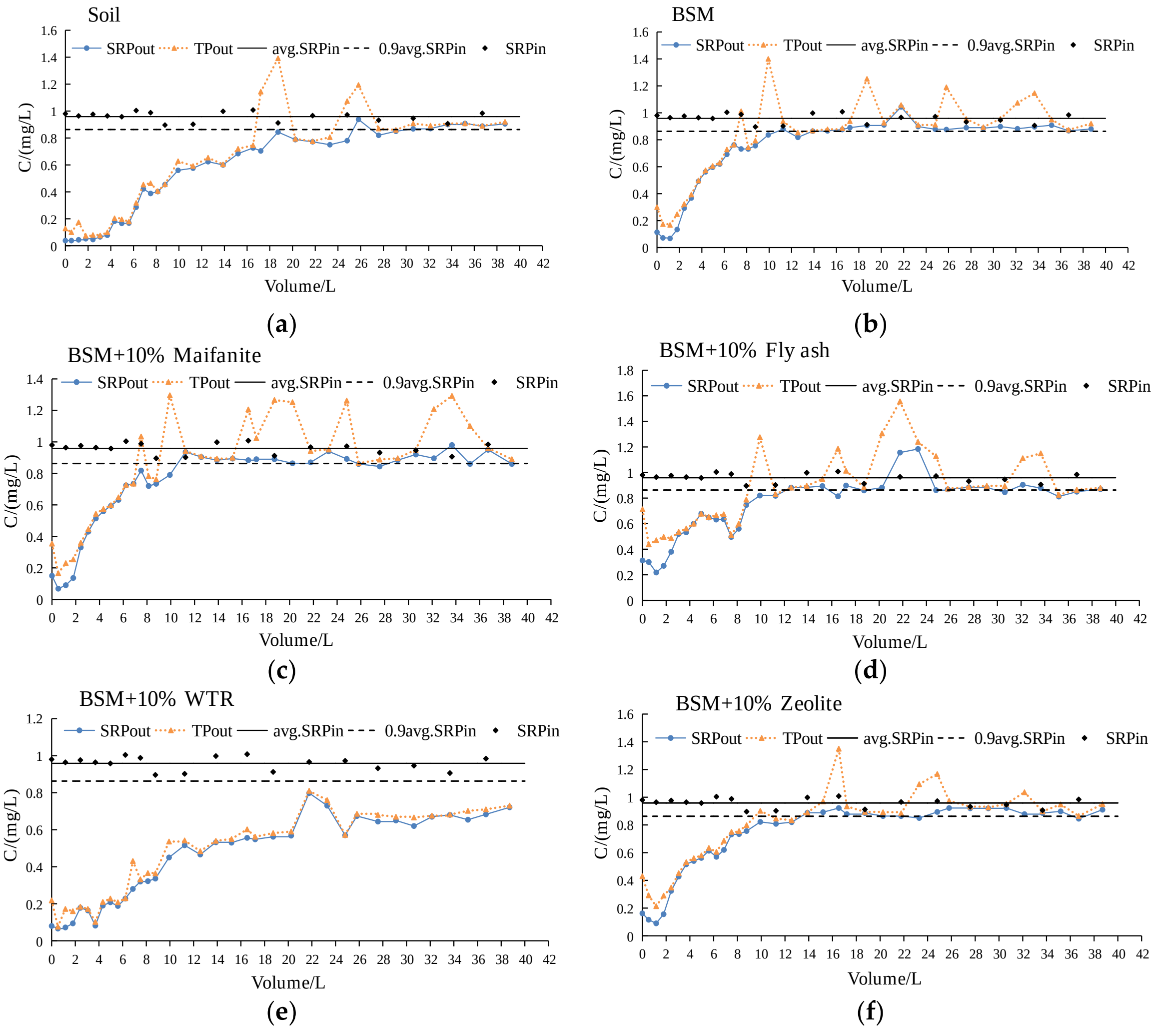


Figure 4. Dynamic adsorption curves of (**a**) soil, (**b**) BSM, (**c**) BSM+10% maifanite, (**d**) BSM+10% fly ash, (**e**) BSM+10%WTR and (**f**) BSM+10%zeolite for phosphorus.

The total water volume of mini-column operation is equivalent to 15 years of rainfall at the confluence ratio of 20:1. As shown in Figure 4, when the water intake of the mini-column is equivalent to 10 years of water intake, the effluent concentration of the mixed filler continuously increased only when the mixture with WTR as modifier, and the mixed filler was not saturated. At the beginning of the mini-column operation, TP and SPR briefly leached. The minor leaching phenomenon occurred in the mini-column influent 2 L, and the adsorption capacity of the filler exceeded the leaching amount. The mixed filler contained a certain amount of phosphorus because of leaching. The determination of the soluble phosphorus of six kinds of fillers shows that the maximum initial phosphorus contents in BSM was the largest (0.89 mg/kg), and the soil was the smallest (0.55 mg/kg). The difference of other improved fillers is approximately 0.81 mg/kg, and the content of soluble phosphorus in the filler mainly originates from wood chips (10.3 mg/kg). After the initial leaching, the effluent concentration of the mini-column showed a significant upward trend. The saturation rate of soil and WTR-modified filler was comparatively slow, whereas the saturation rate of the other mixed fillers was close to the saturated point and reached a certain water concentration. During the operation of the mini-column, the effluent concentration of TP and SRP increased briefly when the inflow was switched possibly owing to the release of particles and increase in influent concentration. Owing to the irregular release of particulate matter during the operation of mini-columns, SRP was used as a standard for evaluating the adsorption capacity of fillers.

The adsorption capacity of several modified fillers on SPR (Table 7) was calculated using Equation (6). The saturated adsorption capacity of the filler was lower than that in the static adsorption experiment. Figure 4 and Table 7 show that the modified filler of the added zeolite and maifanite did not change considerably with the traditional BSM unit adsorption, which is similar to the static isothermal adsorption results of mixed filler. The unit adsorption capacity of the modified mixture added 10% WTR reached 94.29 mg/kg, which is approximately 3.5–4.5 times that of BSM and other mixed fillers. The research result of Wang Jianjun et al. [24] shows that adsorption capacity of the modified filler with 4% WTR is about four times of the traditional filler, it is recommended to add 4–5% by mass of WTR to improve the effect of phosphorus removal in the bioretention facility. O'Nell et al. [17] also recommend adding at least 4–5% by mass of WTR to BSM to achieve phosphorus removal. The dynamic adsorption capacity of the 10% fly ash-modified mixture was not clearly enhanced and as the adsorption capacity is inferior to that of BSM. This result is not consistent with those of single-filler and the mixed-fillers static adsorption experiments and may be related to the competitive adsorption formed by numerous kinds of pollutants in dynamic adsorption. Cheng Ting et al. [25] studied the competitive adsorption of PO_4^{3-}, F^-,and Cr^{6+} by zeolites synthesized from fly ash, the order of competitive removal rates of the three ions was $F^- < PO_4^{3-} < Cr^{6+}$, and the adsorption rate of Cr^{6+} was considerably higher than those of the other two ions. The poor adsorption effect of fly ash-added mixed filler may also be the mixing of fly ash and BSM for dynamic adsorption, and the surface-active point was partially covered in the experiment. The unit adsorption capacity of soil reached 59.44 mg/kg when the soil adsorption was saturated, and this capacity was second only to that of WTR-modified filler. Clay in the soil shows good adsorption to phosphorus.

Table 7. Saturation point and accumulation of SRP.

Mini-Column	Total Influent (L)	Influent SPR Load (mg)	Effluent SPR Load (mg)	Adsorption Capacity (mg)	Adsorption Amount Unit (mg/kg)
1	30.71	29.44	18.74	10.70	59.44
2	13.05	12.51	7.55	4.96	27.54
3	13.05	12.51	7.84	4.67	25.95
4	13.05	12.51	8.53	3.98	22.09
5	38.71	37.11	20.14	16.97	94.29
6	13.05	12.51	7.22	5.29	29.38

Note: SRP: soluble reactive phosphorus.

To obtain the maximum phosphorus adsorption efficiency and the lowest desorption amount, the desorption rate of phosphorus in the filler should be considered during filler selection. Numerous fillers have a strong phosphorus adsorption capacity but exhibit a high desorption rate and can easily cause secondary pollution [26]. To examine the final removal of phosphorus from the above six fillers, we carried out a dynamic desorption experiment. The experimental results are shown in Figures 5 and 6.

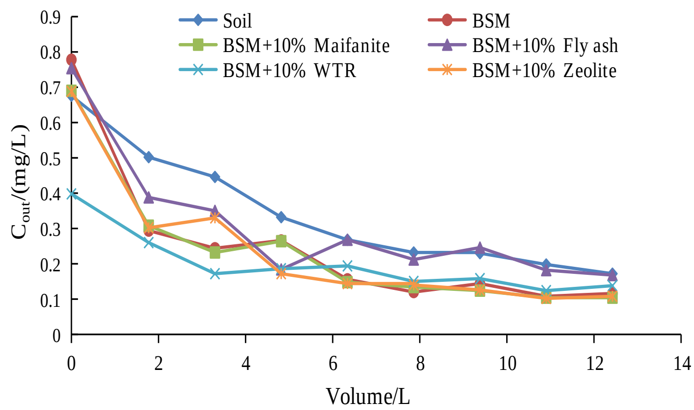


Figure 5. Dynamic desorption curve of phosphorus in modified fillers.

Figure 5 shows the lowest adsorption of improved fillers by adding WTR at the beginning of desorption because WTR contains a large amount of aluminum salts, which is not saturated during operation with the equivalent of 15 years of rainfall. When desorption is carried out, the phosphorus released from other components in physical adsorption can be adsorbed. Phosphorus characterized by reversible adsorption in the rest of the fillers precipitates in a large amount with desorption experiments, and the soil desorption curve is relatively highest, indicating that the physical adsorption was highest compared with other fillers. Figure 6 shows the comparison of the effect of adsorption/desorption and desorption ratio of each filler. The amount of desorption of modified fillers containing WTR, Maifanshi, and Zeolite exhibits minimal difference with the BSM, all being close to 1.3 mg, while the desorption amount of soil is 2.14 mg, and the modified filler with fly ash is 1.87 mg. The desorption rates of soil, BSM, BSM + 10% maifanite, BSM + 10% fly ash, BSM + 10% WTR, BSM + 10% zeolite were 20.03%, 26.42%, 26.85%, 47.15%, 7.62%, and 24.53%, respectively. Mixed filler with WTR showed the highest equilibrium adsorption capacity, followed by soil.

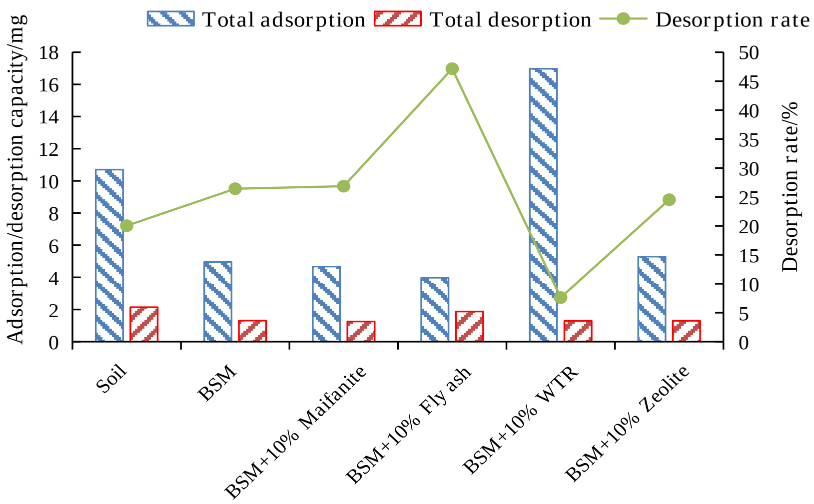


Figure 6. Experimental results of the dynamic desorption of phosphorus in modified fillers.

5. Conclusions

(a) During isothermal adsorption, the high Al content conferred WTR with an adsorption capacity of 4.094 g/kg. Fly ash showed the second highest capacity, and the capacities of other fillers were not considerably different. Fly ash was found to be saturated adsorption process is faster, which is related to its smaller particle size.

(b) In the static isothermal adsorption experiment of mixed fillers, the adsorption capacities of WTR and fly ash as additives were higher than that of the modifier, and the adsorption capacity increased with the increase in added amount.

(c) In the early period of operation, a large amount of particulate matter and soluble phosphorus are released, which mainly originated from wood chips. Therefore, bioretention facilities should select wood chips with stable and fully-fermented properties so as to avoid secondary pollution caused by decay during operation. In the experiment, the addition of 5% of the wood chips increased the organic matter content of the mixed filler, thereby weakening the leaching effect.

(d) According to the dynamic adsorption experiment in the mini-column, the adsorption capacity of the improved mixed filler added with 10% WTR reached a maximum of 94.29 mg/kg in 15 years of influent, which was about 3.5 times that of BSM, WTR is recommended as a bioretention modifier, and the amount of WTR added can be controlled within 5–10% (by mass) according to influent phosphorus concentration.

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