Purification effects of amended bioretention columns on phosphorus in urban rainfall runoff

Jiake Li, Laiyan Li, Wen Dong and Huaien Li

ABSTRACT

In order to develop bioretention fillers with better phosphorus removal capacity, we built 12 bioretention columns with six kinds of modified fillers, and analyzed the operation effects of the columns under different conditions through field tests. Results show that adding water treatment residual has optimal removal rates for total phosphorus (TP) (median = 96.80%) and soluble reactive phosphorus (SRP) (median = 97.13%). The water reduction rates of the columns with improved fillers are 1.23–2.04 times that of the bioretention soil media column. The coconut chaff column has the best water storage capacity (median = 40.54%). Among the external factors affecting column operation, influent concentration of pollutants in urban surface runoff is the biggest influence factor on the removal efficiency of TP. However, there are no significant correlations between the removal efficiency of SRP and rainfall, influent concentration, and discharge ratio. The columns modified with medical stone, vermiculite, peat soil, medical stone + peat soil, green zeolite + peat soil all have good removal for phosphorus pollutant. After entering the columns, the contents of TP and SRP in most columns increased. The recommended fillers and the accumulation performance of phosphorus can help to improve purification effects in bioretention systems.

Key words | bioretention, column, modified filler, SRP, TP

INTRODUCTION

Nitrogen and phosphorus, the nutrients in rainwater runoff, have always been the most concerning pollutants in the aquatic ecological environments. Phosphorus comes mainly from green field fertilizers in urban stormwater runoff, atmospheric deposition, animal excrement, and detergents. Eutrophic water bodies are generally considered to be inferior water bodies and pose great harm. Identifying economic and convenient methods to control phosphorus pollution in urban runoff is the key point of rainwater management strategies.

Stormwater bioretention systems are increasingly used to address high levels of nutrients to protect surface water quality (Ryczewicz-Borecki et al. 2017). Phosphorus can be divided into particulate phosphorus ($\rho > 0.45 \mu m$) ($\rho$: the diameter of phosphorus-containing particles in water) and dissolved phosphorus ($\rho < 0.45 \mu m$) according to its physical form. Particulate phosphorus is mainly removed by total suspended solids in the runoff through filtration and precipitation of the filler. Soluble reactive phosphorus (SRP) is the main form of dissolved phosphorus, removed mainly through the adsorption of fillers and plant absorption (Liu 2016). Studies showed that nitrogen and dissolved phosphorus are very sensitive to the filler performance. If the filler does not have sufficient phosphorus adsorption and precipitation capacity, phosphorus will be re-dissolved to free orthophosphate from the filler, resulting in a significant reduction in the phosphorus removal from the system (Li et al. 2014). The traditional constructed rapid infiltration system fillers have better effects on the removal of organic matter and ammonia nitrogen in sewage, while the removal effects on total nitrogen and total phosphorus (TP) are not good (Liu 2016). Soleimanifar et al. (2016) used wood mulches coated with water treatment residual (WTR) to remove heavy metals and phosphorus from urban rainwater. The results showed that the WTR-coated wood mulches could absorb 97% lead (Pb), 76% zinc (Zn), 81% copper (Cu) and 97% phosphorus from the synthetic stormwater (Pb = 100 μg/L, Zn = 800 μg/L, Cu = 100 μg/L, P = 2.30 mg/L, and pH = 7.0) within 120 min. Oveissi & Fatehi (2015) reported that 53% of lignin, 49% of chemical
oxygen demand, and 89% of turbidity were removed from a pulping wastewater via treating with 55 mg/g fly ash for 3 h. Zhu (2017) added aluminum sludge and sawdust to the retention pond packing. They found that the filler in the bioretention pool was the main factor affecting the phosphorus removal from rainwater runoff, and adding the water plant sludge can increase the removal rate of phosphorus.

To enhance the effect of a bioretention system on phosphorus removal, we have improved the fillers of the bioretention facility. According to the surface runoff water volume and quality characteristics of Xi’an City, we designed an orthogonal test to study the optimal operating conditions of the bioretention column and established the relationship between purification effect and its influencing factors. On one hand, we monitored the effects of different modified fillers on runoff water quality (i.e. concentration removal and load reduction) and water volume (i.e. runoff volume reduction, peak flow reduction, and delay time). On the other hand, we examined the contaminant contents in the upper, middle and lower layers of columns before and after the test. Through the column test, we have developed efficient modified fillers with high water permeability to meet drainage requirements, strong water holding capacity, suitable for plant growth, and strong purification ability to satisfy the requirements for water quality improvement.

**MATERIALS AND METHODS**

**Media preparation**

In this test, the bioretention soil media (BSM) contained 50% soil, 65% sand, and 5% wood chips (by mass). Soil was collected from local topsoil by using a 2 mm sieve. To improve soil infiltration capacity, water retention capacity, and organic quality, sand and wood chips were separately added to get traditional BSM. 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 for 1 week and later passed through a 2 mm sieve. In addition, 12 columns were prepared containing WTR, fly ash, vermiculite, green zeolite, coconut chaff, and peat soil as functional materials as outlined in Table 1. All functional materials were purchased from a company in Shaanxi province. Natural sand was used. Two types of coarse sand with an average particle size of not less than 0.315 mm (type I) and not less than 0.630 mm (type II) were selected as the sand layer filler of the test. The bottom layer was filled with 15 cm pebbles. The middle consisting of mixed filler, such as sand and functional materials, was filled to 1.10 m high. After the completion of filling, we tried to release water for the first time, and then began to do the experiments after natural settlement of media.

**Device setting**

The test site is located at the water resource test site at the Xi’an University of Technology. Twelve columns have been built, and they share an inflow tank. The volume of the water tank is 1,000 L. The structure of the column is shown (Figure 1). The main body of each column is a polyvinyl chloride pipe, with the diameter of 40 cm, wall thickness of 6 mm, height of 1.2 m, and sectional area of 0.11 m². The packing layer is approximately 70 cm high, and consists of soil, sand, and organic matter. Specific fillers for the 12 columns are shown (Table 1). The plants planted in the columns are commonly used plants for road greening, including *Buxus microphylla* and *Ophiopogon japonicus* (Li et al. 2016a), and the cover is bark with a thickness of 5 cm. The gravel layer is composed of gravel with a particle size of 12–35 mm, with a maximum of not more than 50 mm and a thickness of 15 cm. In addition, an overflow port needs to be provided. Three sampling holes

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Filler structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column no.</td>
<td>1</td>
</tr>
<tr>
<td>Filler</td>
<td>Soil</td>
</tr>
<tr>
<td>Column no.</td>
<td>7</td>
</tr>
<tr>
<td>Filler</td>
<td>BSM + 10% fly ash</td>
</tr>
</tbody>
</table>

Note: All ratios are mass ratios.
were set at the height of 25, 50, and 75 cm of each column from bottom to top. Before and after the whole test, soil samples were taken from the three holes by using a spiral picker to detect the content of particulate and dissolved phosphorus in soil samples to analyze the accumulation of phosphorus. The test site is shown (Figure 2).

Experimental design

After plants had grown, we began to monitor 10 typical artificial runoffs designed to monitor the water volume and water quality of the entire rainfall process from 13 October 2017 to 1 December 2017, taking TP and SRP as the main analysis indicators. The water permeability of the device and the phosphorus purification rate are the technical indicators. The cost of packing is an economic indicator. During this period, we mainly explored the influences of external factors, such as rainfall intensity, rainfall duration, antecedent dry time, rainfall and pollutant concentration on the water purification effect. In order to provide a comprehensive analysis of the optimal packing ratios and other bioretention facility parameters (discharge ratio), the changes in packing characteristics were measured before and after each cycle of operation.

Water distribution concentration refers to the pre-concentration, mid-term concentration and late concentration of the road runoff during the whole rainfall process in Xi’an (Wang 2016). Influent concentration is set at three levels, namely, 1 (high concentration), 2 (medium concentration), and 3 (low concentration) (Table 2).

The Sponge City Construction Technical Guide (MOHURD 2014) of China stipulates that the ratio of bioretention facilities to the catchment area should be generally 5% to 10%, and the bioretention scale should not be too large. Therefore, the setting of the discharge ratio is three levels, which are 10:1 and 15:1 and 20:1. The average
interval of rainfall is based on many years of rainfall data in Xi’an City and is set to 6 days. The experimental rain type is the 60-minute Pilgrim & Cordery-designed rainstorm type in Xi’an from 1961 to 2014 (Bi et al. 2015). Rainfall refers to the climate and rainfall characteristics of Xi’an over the years. Xi’an belongs to warm temperate and semi-humid monsoon climate regions. Annual rainfall in Xi’an City ranges from 522.4 mm to 719.5 mm. The rainfall is mainly concentrated from June to October. Daily rainfall during the year is mostly below 10 mm/day. The rainfall is set to three levels according to the return periods of 0.5, 2, and 3 years (Table 3), which is calculated using the storm intensity Formula (1) (Lu et al. 2010):

\[
i = \frac{16.715 \times (1 + 1.1658 \text{lg} P)}{(t + 16.813)^{0.9502}}
\]  

where \(i\) is the design storm intensity (mm/min); \(P\) is the return period (year); and \(t\) is the rainfall duration (min).

The design flow is given in Formula (2):

\[V = FH\]

where \(V\) is the rainfall volume within 60 minutes (L); \(F\) is the catchment area corresponding to different discharge ratios (ha); \(H\) is the rainfall height within 60 minutes (mm), \(H = 60i\).

The experimental design of the orthogonal tests is given in Table 4.

### Experimental method

The experiment used a high-seated water tank for artificial simulation of water distribution. The pure soil substrate was utilized as a control test, and duration of each test is set to 60 min. When the outlet produces runoff, it is necessary

### Table 2 | Manual dispensing water contamination and concentration

<table>
<thead>
<tr>
<th>Conc. level</th>
<th>COD (mg/L)</th>
<th>NO\textsubscript{2}-N (mg/L)</th>
<th>NH\textsubscript{3}-N (mg/L)</th>
<th>TP (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Cd (mg/L)</th>
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<tr>
<td>1</td>
<td>600</td>
<td>12.0</td>
<td>6.0</td>
<td>2.5</td>
<td>1.0</td>
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<td>0.5</td>
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<tr>
<td>2</td>
<td>500</td>
<td>6.0</td>
<td>5.0</td>
<td>1.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>3.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.3</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Reagent</td>
<td>Glucose</td>
<td>Potassium nitrate</td>
<td>Ammonium chloride</td>
<td>Potassium dihydrogen phosphate</td>
<td>Copper chloride</td>
<td>Zinc sulfate</td>
<td>Cadmium chloride</td>
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</table>

### Table 3 | Test water calculation table

<table>
<thead>
<tr>
<th>Rainfall duration (t) (min)</th>
<th>Return period (P) (yr)</th>
<th>Discharge ratio</th>
<th>Rainfall intensity (i) (mm/min)</th>
<th>Catchment area (F) (ha)</th>
<th>Rainfall height (H) (mm)</th>
<th>Design water (V) (L)</th>
</tr>
</thead>
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<td>60 min</td>
<td>0.5</td>
<td>10:1</td>
<td>0.191</td>
<td>1.1 \times 10^{-4}</td>
<td>11.46</td>
<td>12.606</td>
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<tr>
<td></td>
<td>2</td>
<td></td>
<td>0.398</td>
<td>23.88</td>
<td>26.268</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>0.459</td>
<td>27.54</td>
<td>30.294</td>
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<tr>
<td></td>
<td>0.5</td>
<td>15:1</td>
<td>0.191</td>
<td>1.65 \times 10^{-4}</td>
<td>11.46</td>
<td>18.909</td>
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<td>0.5</td>
<td>20:1</td>
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<tr>
<td></td>
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### Table 3 | Test water calculation table

<table>
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<th>Test number</th>
<th>Rainfall intensity (i) (mm/min)</th>
<th>Discharge ratio</th>
<th>Influent concentration (I) (mg/L)</th>
<th>Rainfall interval (d)</th>
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</thead>
<tbody>
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<td>0</td>
<td>0.191</td>
<td>10:1</td>
<td>1</td>
<td>6</td>
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<tr>
<td>1</td>
<td>0.398</td>
<td>15:1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>0.459</td>
<td>20:1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
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<td>0.191</td>
<td>10:1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>0.398</td>
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<td>3</td>
<td>6</td>
</tr>
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<td>5</td>
<td>0.459</td>
<td>20:1</td>
<td>1</td>
<td>6</td>
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<td>10:1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>0.398</td>
<td>15:1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>0.459</td>
<td>20:1</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>0.191</td>
<td>10:1</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>
to sample and record the start time immediately. The water samples were collected in 500 mL polyethylene water bottles and numbered according to the sampling order and position. During the sampling process, the sampling time is recorded by the stopwatch, and the sampling is performed once every 5 minutes. When the sampling time exceeds 5 minutes, the next sampling interval is 10 minutes. When the sampling time exceeds 10 minutes, the outflow is considered to stop.

The collected water samples should be brought back to the laboratory in time to be refrigerated at 4°C, and the water quality analysis should be carried out as soon as possible. The water sample should not be stored for more than 24 hours. Water quality analysis methods included the following: the TP was determined by potassium persulfate oxidation ultraviolet spectrophotometry; SRP was vacuum filtered through a 0.22 μm filter and determined by ultraviolet spectrophotometry.

**ANALYSIS METHODS**

We used Excel 2007 and SPSS 21.0 to process the data. The variance analysis module was utilized to analyze the influences of rainfall, influent concentrations, and discharge ratio on the effluent quality (p = 0.01, p = 0.05) and then multiple comparisons were made.

The indicators of water quality analysis are TP and SRP. The measured removal rate $R_i$ of each index was used, and the average removal rate $R_C$ (Li et al. 2016a) of individual indicators under different working conditions was evaluated as follows:

$$R_i = \frac{C_0 - C}{C_0} \times 100\%$$

$$R_C = \frac{\sum R_i}{m}$$

where $C_0$ is the influent pollutant concentration, mg/L; $C$ is the effluent pollutant concentration, mg/L; and $m$ is the number of test conditions, $m = 10$. The water reduction rate $R_W$ formula is

$$R_W = \left( R_{in} - R_{out} - R_{over} \right)/R_{in} \times 100\%$$

where $R_{in/out/over}$ is the inflow, outflow, and overflow volume, mL.

The pollutant accumulation formula is

$$L_{content} = L_{in} - L_{out}$$

where $L_{in/out/content}$ is the inflow, outflow, and accumulation amount, mg/kg.

**RESULTS AND ANALYSIS**

**Orthogonal test analysis of water quality**

Based on the experimental results of 10 runs, the $R_C$ change trend of the 12 columns is shown (Figure 3). The five lines from the bottom to the top of the box are the minimum value, the lower quartile, the median, the upper quartile, and the maximum value. The influent water formulated in this experiment was only SRP, so the particulate phosphorus in the effluent water quality may come from the background component of the filler. Due to no outflow in the #1 column during the experiment, there is no water quality data. The average $R_C$ between #4, #5, #8 and #9 columns was not much different, and the $R_C$ of the #4 column was the highest (medium = 96.80%). From the position of the interquartile box, the range of #4 column was slightly narrow (90.14–99.30%), and the position was the highest. Thus, the overall $R_C$ of the #4 column during the entire test was better than those of the #5, #8, and #9 columns. From the upper limit and the lower limit of box-plots of the four columns, the TP removal rate of #8 was stable. The $R_C$ of #7 was 93.57%, the worst compared to other columns, and the $R_C$ of pollutants was most unstable, in the range of 85.99–98.68%. According to Li et al. (2016b), fly ash has a very
good effect on phosphorus removal, but in our experiment it was not ideal. This may be due to the long time use of the column, and fly ash knot in the filler layer causes the polluted water not to infiltrate well. Under the condition of large water inflow, the adsorption capacity was limited.

As can be seen from Figure 4, the average removal rates of SRP for the #4, #6, and #8 columns were basically the same, which were 97.13%, 97.56%, and 97.26%, respectively. From the position of the interquartile box and the upper limit and the lower limit of box-plots, the $R_C$ of the #6 column is also relatively stable, followed by the #4 column. It indicates that the addition of the medical stone and the WTR is good for SRP removal.

Each test was performed with uniform water intake to the 12 columns. Although there was overflow during the test of the #1 column, other columns ran normally.

Compared with the overall $R_C$ of TP of 12 columns, the overall $R_C$ of SRP is obviously higher, because the upper layer of the column is mainly composed of silt loam and contains an amount of clay particles. The negatively charged phosphate is easily adsorbed by the positively charged clay particles; phosphate ions are easily chemically reacted with a large amount of Ca$^{2+}$, Fe$^{3+}$, and Al$^{3+}$ ions present in the soil to form various poorly soluble phosphates (Gao 2013). Therefore, the SRP can be well removed.

**Orthogonal test analysis of water quantity**

Bioretention systems are one of the most cost-effective and sustainable integrated management practices in the low impact development approach, using efficient rainwater contaminant filter media to control flow (Takaijudin et al. 2016). Inflow pattern affected the water volume and peak flow control effect. The worst media adsorption case may appear when the higher hydraulic load comes, and the accumulated pollutants from the system may rush out during rainfall peak flows. Only the overflows in #1, #2, and #3 columns were observed during the experiment, indicating that the soil had poor permeability. Figure 5 shows that during the entire test, the water reduction rates ($R_W$) of the columns with the improved fillers are 1.23–2.04 times that of #3 column (BSM). The #1 column only had overflow and no outflow, and the average moisture content was the highest (median = 51.20%). From the upper limit and the lower limit of box-plots, the range of $R_W$ of #1 column was relatively large, indicating that #1 column had good water storage capacity, but with poor permeability. The average $R_W$ of #10 column was 40.54%. From the position of the interquartile box and the upper limit and the lower limit of box-plots, the $R_W$ of #10 column varied from 24.14% to 59.57%, indicating that the water storage capacity was good and stable.

**The Pearson correlations of effluent concentrations of TP and SRP with rainfall, influent concentration, and discharge ratio respectively**

Table 5 shows that the influent concentration has a significant correlation with the effluent concentration of TP on the #3, #4, and #10 columns ($p < 0.05$), whereas the rainfall and discharge ratio had no correlation with effluent concentration of TP ($p > 0.05$). The effluent concentration of TP on the #12 column showed a significant correlation with discharge ratio ($p < 0.05$), but the rainfall and influent concentration had no influence on the effluent concentration of the #12 column ($p > 0.05$). The rainfall, influent concentration, and discharge ratio had no significant effect on the effluent concentrations of #2, #5, #6, #7, #8, #9, and #11 columns ($p > 0.05$). As mentioned above, it can be found that the influent concentration is an important
factor affecting the TP emission concentration in the effluent of the column.

As can be seen, the rainfall, influent concentration, and discharge ratio have no significant effect on the effluent concentration for SRP (Table 6).

As can be seen from Tables 5 and 6, the effluent pollutant concentration in #3, #4 and #10 columns is negatively correlated with the influent concentration. The effluent concentration of the three columns decreases significantly with the increase of the influent concentration. Therefore, the filler combinations of BSM, BSM + 10% WTR, and BSM + 5% coconut chaff excel in TP removal.

### Change of pollutants before and after the experiment

Before and after the test, 500 g soil samples were taken from the bulk sampler at the height of 25, 50, and 75 cm of each column, and were sent for inspection on the same day. The soil test results are shown (Figure 6).

Figure 6(a) shows clearly that the TP content in each column after the test was higher than that before the test. The TP content after the test of #1 and #2 columns was significantly higher than the background value. Because there was only SRP in the influent water, so it can be seen that the filler has a good adsorption effect on SRP. Figure 6(b) shows that the cumulative amounts of TP in #2, #3, #6, #8, #9, #11, and #12 columns were approximately 22–600 times higher than their bottom value in the upper, middle, or lower soil layers. It indicates that these types of combined fillers have a very good adsorption effect on TP.

From Figure 6(c) and 6(d), the contents of SRP in the filler after the test were not much different from the background value of SRP before the test for #6–#12 columns. The SRP contents in the soil of #1–#5 columns before and after the experiment changed significantly. The SRP cumulative amount in #4 column was higher than its background value after the test. But the SRP contents of the #1, #3, and #5 columns were lower than the background value of the SRP after the experiment. No outflow was present in #1 column, so all the SRP entering #1 column was retained. Microorganisms play an important role in the degradation of pollutants (Li et al. 2016c). Planted bioretention systems remove significantly more pollutants than unplanted systems (Dagenais et al. 2018). Hence, microorganisms and plants in the soil contribute greatly to the removal of phosphorus. The SRP content in #4 column increased most significantly, and the SRP content in the upper layer soil doubled before the test. Therefore, adding WTR can effectively increase the amount of phosphorus adsorbed by the filler.

### CONCLUSIONS

Through comprehensive analysis of experimental results, the filler combinations of BSM + 10%WTR, BSM + 10% green zeolite, BSM + 10% medical stone and BSM + 5% peat soil have good removal effect on TP. Among them, the column of BSM + 10% WTR is best (median = 96.80%), and the removal efficiency is relatively stable. The columns of BSM + 10% WTR, BSM + 10% medical
Figure 6 | Change in TP content and SRP content in the column.
stone and BSM + 5% vermiculite have the same effect on SRP removal, which is 97.15%, 97.56% and 97.26%, respectively. Therefore, it is considered that the addition of WTR can effectively improve the efficiency of phosphorus removal in bioretention facilities.

The water reduction rates of the improved columns are 1.23–2.04 times that of #3 column (BSM). Planting soils have the best water storage capacity, but they have poor infiltration capacity and are only suitable for dry areas with less rainfall. The average reduction rate of coconut chaff column was highest than other columns, so adding coconut chaff can effectively improve the water storage capacity of the column.

According to the results of Pearson correlation analysis, we can conclude that the influent concentration of pollutants in urban surface runoff is the greatest impact factor on the removal efficiency of TP in the bioretention system. However, no significant correlation was observed between the effect of bioretention on SRP removal and rainfall, influent concentration, and discharge ratio.

The columns with the combination of soil and sand, BSM, BSM + medical stone, BSM + vermiculite, BSM + peat soil, BSM + medical stone + peat soil, and BSM + green zeolite + peat soil all have good retention effect. After the phosphorus contaminants enter the column, except for the #1 and #5 columns, the contents of TP and SRP in the columns increased compared with those before the test, and the content of TP increased by about 22–600 times compared with those before the test. It shows that particulate phosphorus has a tendency to convert to dissolved phosphorus.

There are still some aspects of this study that need further research, such as the durability of modified filler, the risk of secondary contamination due to contaminant leaching in fillers, the problem of filler blockage, and the loss of filler function.

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