The removal of pollutants from runoff by different types of paving surface materials in permeable pavement systems
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Abstract
As the key factor permeable pavement systems, the permeable paving surface materials can provide a number of benefits, including filtration and settling of pollutants, reducing runoff volume and peak rate. However, until now, few reports focus on the comparison of different types of permeable paving surface materials on the runoff water quality, which limited the installation and application of permeable pavement systems in urban areas. In this study, six typical kinds of surface materials (porous asphalt, porous concrete, cement brick, ceramic brick, sand base brick and shale brick) were selected to investigate the removal of pollutants from urban runoff in permeable pavement systems. The results showed that the permeable paving surface materials influence the removal of pollutants greatly. In the column experiments, the shale brick has a good removal effect on nearly all pollutants. Porous asphalt has a certain effect on nearly all pollutions. Ceramic brick has significant removal capacity for COD and NH₄-N. The sand base brick and cement brick will continue to release COD pollutants into the runoff and rain water. This work could offer useful information and guideline for the design and installation of permeable pavement systems in the removal of pollutants from stormwater.

Keywords
Permeable pavement systems; surface materials; runoff; removal;

INTRODUCTION
With the development of society, the shift of rural to urban population increased greatly [1]. It is predicted that two-third of the world’s population will reside in urban center by 2050. With the increasing population of urban area, many natural features were replaced by the architecture of humanity and changed the recycle of aqueous solutions [2]. Furthermore, with the rapid urbanization, the increasing urban runoff pollution would deteriorate the urban water environment and decreasing the useable water resource in urban area [3, 4]. Green stormwater infrastructure, such as permeable pavement system (PPS), has been widely used in urban stormwater management to improve the water resource [5, 6]. Unlike impervious pavements, the PPS offer the possibility to recharge groundwater, recycle water use and reduce
hydraulic stress in receiving water bodies due to their high surface infiltration rates [7]. Furthermore, results showed that PPS could reduce the concentrations of several stormwater pollutants such as heavy metals, TSS, chemical oxygen demand (COD), ammonia nitrogen (NH$_4$-N), nitrate nitrogen (NO$_3$-N), total nitrogen (TN) and total phosphorus (TP) [8].

Many reports have investigated the removal efficiency of entire PPS [9, 10]. For example, the permeable asphalt pavement showed high removal capacity for heavy metals, oil, biochemical oxygen demand, chemical oxygen demand, ammonia and total phosphorus effectively [11]. As the key factor of PPS, the surface material is the top layer which contact directly with the runoff. The permeable paving surface materials (PPSM) can provide a number of benefits, including filtration and settling of pollutants, reducing runoff volume and peak rate [12, 13]. Until now, many researches focus on the permeable performance of PPS, while ignoring the removal efficiency of pollutants by PPSM [14]. In recently years, with the development of technologies, many new typed of surface materials were created and used in PPS, such as different permeable bricks [8]. However, few reports focus on the comparison of different types of PPSM on the runoff water quality, which limited the installation and application of permeable pavement systems in urban areas.

In this study, six typical kinds of surface materials (porous asphalt, porous concrete, cement brick, ceramic brick, sand base brick and shale brick) were chosen to investigate the removal of pollutants from runoff in batch and column experiment. Parameters of COD, NH$_4$-N, NO$_3$-N and TP in influent and effluent were measured. This work could offer useful information and guideline for the design and installation of permeable pavement systems in the removal of pollutants from urban runoff.

**MATERIALS AND METHODS**

**Materials**

According to the results showed in literature and research in our study. Six typical kinds of surface materials (porous asphalt, porous concrete, cement brick, ceramic brick, sand base brick and shale brick) were selected. The porous asphalt and porous concrete were prepared at the laboratory of Beijing University of Civil Engineering and Architecture. Other brick were bought from Ai Dao Ai He (Beijing) Technology Co., Ltd.

**Experimental setup**

Batch and column experiments were conducted in this study. Before the experiments, all six PPSM were smashed by hammer and sieve the size class from 2 mm to 5 mm. The PPSM were washed by tap water for 3 times and soaked into tap water for about 2 days in order to remove the inorganic, metal ions and organic matters which adhered on the surface of PPSM. Raw water was prepared based on the traditional surface runoff from other researchers (Table 1).

<table>
<thead>
<tr>
<th>Table 1 Raw water quality</th>
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<td>Items</td>
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<tr>
<td>Items</td>
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<tr>
<td>NH₄-N</td>
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<td>COD</td>
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<td>TN</td>
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<td>NO₃-N</td>
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The batch experiments were conducted by added PPSM to aqueous solutions with the dosage of 2 g/L. The mixed solution was shaken with a speed of 170 rpm. The samples were collected at different time intervals and filtrated through a 0.22 μm polytetrafluoroethylene membrane filter and the concentrations of pollutants were measured according to the Table 2.

Table 2 Laboratory methods used in analysis of samples

<table>
<thead>
<tr>
<th>Items</th>
<th>Method</th>
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<tr>
<td>Ammonia</td>
<td>Nessler’s reagent spectrophotometry (HJ 535-2009)</td>
</tr>
<tr>
<td>COD</td>
<td>Fast digestion-spectrophotometric method (HJ/T 399-2007)</td>
</tr>
<tr>
<td>TN</td>
<td>Alkaline potassium persulfate digestion UVs pectrophotometric method (HJ 636-2012)</td>
</tr>
<tr>
<td>NO₃-N</td>
<td>Standard examination methods for drinking water - Nonmetal parameters (GB/T 5750.5-2006)</td>
</tr>
</tbody>
</table>

The six types of PPSM were loaded into same experimental columns (4 cm inner diameter and 20 cm inner height). Each column’s filler consists of 2 cm glass bead (laying on top and bottom with 1 cm), 18 cm permeable paving materials, and 4 pieces of gauze (the upper and lower parts of the two layer glass beads are respectively laid). Before the columns experiment began, the columns were washed with tap water for 3 days (the flow rate is 29.86 ml/min), in order to removal the organic matter. During the experiment, the influent flow rate is 29.86 ml/min, which is to simulate the seepage velocity of the actual permeable pavement. The column experiment was shown in Fig. 1.
RESULTS AND DISCUSSIONS

As showed in Fig. 2, with the experimental duration increased, the NH$_4$-N concentration in the effluent showed great differences. Compared with initial concentration of NH$_4$-N (5.0 mg/L), the six kinds PPSM can be roughly divided into two categories, the concentration of effluent could be first rose then being stable or rose continuously. For sand base brick, shale brick, cement brick and porous concrete, the NH$_4$-N concentration increased with the experimental duration increased and...
become stable at 9 h. The final effluent concentration of the four materials were 5.71 mg/L, 6.07 mg/L, 6.34 mg/L, 6.95 mg/L, respectively. The results indicated that under the condition of wear and tear, the NH₄-N will release from PPSM to aqueous solution and increase the concentration of NH₄-N in runoff. For porous asphalt and ceramic brick, the NH₄-N concentration increased with the experimental duration increased, and the final concentration were 6.44 mg/L and 6.18 mg/L respectively in this experiment. The ceramic brick is re-adhered and manufactured by the discarded tiles, as a result of a long period of time, the waste ceramic and the binder are continuously dissolved in water, resulting in the increase of pollutant concentration. The surface of porous asphalt is coated with a mixture of organic compounds, and the organic matter in the process of continuous precipitation is dissolved in water, resulting in the increase of NH₄-N concentration.

NO₃-N is not toxic, but it will be converted into nitrite, thereby endangering human health. As shown in Fig. 2, six PPSM will purify part of NO₃-N with the increase of experimental duration, but the effect is not the same. The six kinds of materials can be roughly divided into three categories, compared with initial concentration of NO₃-N, the NO₃-N concentration in the effluent could be rose, decreased and nearly unchanged. For ceramic brick and porous asphalt, the concentration of NO₃-N increased with the experimental duration and the final concentration are about 13.0 mg/L and 13.3 mg/L, which may be caused by more organic matter dissolved into the runoff. The ceramic brick is mainly made of waste ceramic residue and organic binder, and porous asphalt surface is coated with a layer of hydrocarbon organic matter. In the course of the experiment, the two kinds of materials may continue to release nitrogen containing organic matter into the water, resulting increasing of NO₃-N concentration. For shale brick, sand base brick and cement brick, the concentration of NO₃-N increased with the experimental duration and the final concentration are about 2.9 mg/L, 4.2 mg/L and 5.1 mg/L, which may be these materials have different amounts of adsorption sites for NO₃-N. Shale brick contains a lot of Fe₂O₃, which can effectively absorb a certain amount of NO₃-N. Due to the similar structure of sand base brick and cement brick, the porosity is larger, so it has more adsorption sites for NO₃-N. And there is a layer of red sand containing Fe₂O₃ on the surface of the sand brick, which can effectively adsorb NO₃-N. For porous concrete, compared the actual effluent with the final effluent, there is no obviously difference about the concentration of NO₃-N.

TP is one of the most important indexes in the detection of surface water, too much phosphorus discharged into the water will lead to the abnormal growth and reproduction of aquatic organisms and plants. As it shown in Fig 2, each material has a certain effect on the removal of TP. Compared to the raw water (1.52 mg/L), with the increase of experimental duration, the removal effect is gradually improved. The TP is normally removed by the adsorption and filtration of different kinds of surface materials. For porous asphalt, the treatment effect is relatively poor in the surface material, the TP concentration of final effluent was 0.84 mg/L when the experimental time is 48 h. It is probably due to the surface of the porous asphalt is coated with a layer of modified asphalt, which blocks the adsorption site of TP itself. For ceramic
brick, it has a better effect on TP removal than porous asphalt, the final concentration of TP in effluent is 0.56 mg/L. It may be because the ceramic surface contains more adsorption sites for TP than porous asphalt. For sand base and shale brick, although their final concentrations of TP were similar, the trend of purification is a lot different. The sand base brick has a trend of continuous decline in TP, and the final effluent concentration is 0.24 mg/L. Sand base brick is made from sand and concrete composite, the efficiency of TP removal is mainly due to the adsorption effect of sand and the lime is released continuously in the concrete to form phosphate precipitation. The shale brick for the removal of trend of TP first decreased rapidly, and gradually stabilized after, and its final effluent concentration of TP is 0.28 mg/L. The purification mechanism of shale brick is the adsorption of Fe$_2$O$_3$ on TP, the shale brick contains more Fe$_2$O$_3$, it can effectively absorb the water in the TP [15]. For cement brick and porous concrete, the two kinds of materials have a similar trend to the purification of TP, and the difference of TP concentration in the final effluent is also very small, 0.03 mg/L and 0.08 mg/L respectively. In addition to the two materials can effectively adsorb TP, due to its own characteristics lead to the increase of pH value of water samples, so that the formation of phosphate in water precipitation, resulting in a significant purification effect.

The concentration of COD is also an important index for detecting the environmental quality of surface water, too high will cause the degradation of the dissolved oxygen content of the water, resulting in water black odor. The COD concentration change of different kinds of surface layer materials are shown in Fig. 2. The PPSM influences the changes of COD greatly. The six kinds of surface materials can be divided into two categories, compared with initial COD concentration (419.0 mg/L), the COD in the final effluent could be increased and decreased. For the increasing materials (except shale brick), the concentration of COD increased with the experimental duration increased. The final effluent of each material is increased to 633.1 mg/L in ceramic brick, 627.0 mg/L in sand brick, 560.1 mg/L in cement brick, 593.5 mg/L in porous asphalt and 609.4 mg/L in porous concrete. Due to the release of organic matter coated in its surface materials, the concentration of COD increases continuously for nearly all materials. Only the shale brick can effectively treat COD in runoff. This is probably because shale brick containing more iron in the structure. Some studies have shown that the content of iron will directly affect the purification of COD pollutants in water.
The concentration of pollutants in column experiments is shown in Fig 3, after the prepared runoff passes through the experimental column composed of different layers of materials, and the pollutants concentration in the water are different. For TN, the porous asphalt, shale brick and ceramic brick has better purification effect, the removal rate is about 30%. The reason is that the three kinds of surface materials have a better adsorb ability in NH$_4$-N in column experiment, the concentration of NH$_4$-N in effluent are 1.3 mg/L, 1.5 mg/L and 1.7 mg/L, respectively, so as to achieve the purpose of purifying TN. The cement brick purification effect is a bit poor to NH$_4$-N, but also significantly better than sand base brick and porous concrete, about 2.1 mg/L NH$_4$-N in the effluent. Sand base brick and porous concrete has the lowest treatment ability, the concentration of NH$_4$-N in effluent are 3.9 mg/L and 3.2 mg/L. The effect of 6 surface materials on the purification of NO$_3$-N is poor, and the difference was not great in the column experiment.

For COD, four kinds of surface materials (ceramic brick, shale brick, porous concrete and porous asphalt) can effectively treat COD pollutants, which is the best effect of porous asphalt, followed by porous concrete, shale brick, ceramic tile for the worst. When the concentration of COD in raw water is 419.0 mg/L, the concentration of COD in porous asphalt’s effluent is about 139.6 mg/L, the porous concrete, shale brick and ceramic brick are 253.6 mg/L, 313.7 mg/L and 355.6 mg/L, respectively. But cement bricks and sand base bricks still release COD pollutants, their effluent COD concentrations are 456.9 mg/L and 474.6 mg/L. This is similar to the results of a static batch test.

For TP, six kinds of surface materials can remove a certain amount of TP in column experiment. The best effect for treat TP is cement brick, followed by sand base brick, porous concrete, brick and porous asphalt, and the worst for ceramic brick. When the concentration of TP in raw water is 1.52 mg/L, the concentration of TP in cement brick’s effluent is about...
0.28 mg/L, the sand base brick, porous concrete, shale brick, porous asphalt and ceramic brick are 0.46 mg/L, 0.48 mg/L, 0.65 mg/L, 0.81 mg/L and 0.99 mg/L, respectively. The TP is normally removed by the adsorption and filtration of the surface materials, as well as the precipitin reactions of phosphate and calcium ions in surface materials.

The change of NH$_4$-N values with different PV values in different materials is showed in Fig. 3. With the PV values increased, all the materials showed the similar trend that the concentration of NH$_4$-N decreased greatly first then followed by a relatively increased. Compared with the initial concentration (5.0 mg/L), the concentration of NH$_4$-N decreased to 1.6 mg/L, 1.7 mg/L, 2.1 mg/L, 3.2 mg/L, 3.9 mg/L for shale brick, ceramic brick, cement brick, porous concrete and sand base brick, respectively when the value of PV is 1.00. With the values of PV increased further, the removal efficiency of NH$_4$-N gradually decreased. When the value of PV reached 29.57, the NH$_4$-N concentration in five samples were between 4.31 mg/L to 4.88 mg/L. The high removal efficiency of NH$_4$-N is mainly attributed to the ion exchange which is closely related to the content of monovalent and divalent cations. The result is same as Lucas Niehuns et al. and Wei et al. [11, 16]. The decreases of NH$_4$-N can be attributed to the interception and adsorption of porous asphalt. The high removal efficiency of porous asphalt on NH$_4$-N may be due to the organic matter on the surface of asphalt material provides more adsorption sites for NH$_4$-N.

As shown in Fig. 2, six kinds of surface materials will purify part of NO$_3$-N with the PV values increased, but the effect is not the same. For shale brick, its treatment effect is the best among the materials, the concentration of NO$_3$-N is 3.9 mg/L when PV is 29.57. NO$_3$-N removal efficiency gradually increased with the PV increasing. The mechanism of NO$_3$-N removal was mainly caused by interception and adsorption. Previous research showed that the content of iron oxide in the materials would influence the nitrate nitrogen removal [17]. And there is no statistical differences of NO$_3$-N between ceramic brick’s inlet and effluent were observed, because ceramic material itself contains very little iron.

As shown in Fig. 3, with the PV values increased, the concentration of COD in the effluent showed great differences. The six PPSM can be also roughly divided into three categories, compared with initial concentration of COD (419.0 mg/L), the COD in the effluent could be increased, decreased and decreasing-rising. For shale brick and ceramic brick, the concentration COD continued to decline, the final concentrations were 49.2 mg/L and 170.4 mg/L. The high removal efficiency may be attributed to the abundant microporous structure in the materials. In addition, the effect treatment of shale brick is better than ceramic brick, which may be caused by iron oxide in the materials [18]. For porous asphalt and porous concrete, the COD concentration showed a decreasing-rising trend. For the porous asphalt, the COD concentration is 139.6 mg/L when the PV is 1.00. With PV value increase further, the concentration of COD increased gradually, and finally reached 269.6mg/L, which is similar with the result of Wei et.al [11]. The porous concrete exhibit similar characteristics to asphalt, only difference is that the treatment effect is relatively poor than asphalt, the COD concentration is 253.6 mg/L when the PV is 1.00 and final effluent is 377.6 mg/L. The decreases of COD can be attributed to the interception and adsorption of porous asphalt. For cement and sand base brick, the COD concentration increased with the PV values increased until 683.9 mg/L and 542.9 mg/L, which may be caused by more organic binder in the process of production.
References: