Removing nitrogen and phosphorus simultaneously in stormwater runoff using permeable asphalt pavement system with a zeolite-regulated reservoir

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ABSTRACT

Stormwater runoff is identified as a major source of pollution in water bodies, and to limit the impact of these pollutants on groundwater quality, permeable asphalt pavement systems (PAPS) have been built worldwide. But so far, few have considered zeolite or regulated zeolite as a post-treatment in reservoirs in PAPS. This study aimed at investigating the efficiencies of modified zeolites in removing NH₄⁺-N and TP from stormwater runoff and providing a novel insight into the research on the reuse of stormwater runoff by PAPS. The effect of PAPS with a zeolite-regulated reservoir on removing nutrient in stormwater was explored by artificial rainfall experiments and temporary storage experiments. Results showed that the removal rate of NH₄⁺-N and TP in PAPS with a regulated-zeolite reservoir increased by 23.7% and 37.2%, respectively, during simulated rainfall events when compared to those without a regulated-zeolite reservoir. TP was mainly removed by the form of phosphorus precipitation such as Zr(H₂PO₄)₂. Ion exchange and adsorption during the temporary storage period were considered as the main approaches for removal of NH₄⁺-N and TP. This study can help develop an optimal strategy for the operation of PAPS in treating stormwater runoff from urban roads.

Key words | nitrogen and phosphorus removal, permeable asphalt pavement system, regulated zeolite, reservoir, stormwater runoff

INTRODUCTION

In recent years, a series of problems like deterioration of urban water environment, frequent occurrence of flood disasters, and severe runoff pollution has become increasingly prominent. Notably, urban non-point source pollution has been gradually identified as one of the most important reasons for degradation of urban water quality (Line et al. 2012; Page et al. 2016). The road, a critical element of urban catchments, is closely linked to drainage facilities and also a key source of urban non-point source pollution. The source-based, decentralized, and small-scale low impact development (LID) rainwater control system is a novel management system featuring excellent performance in solving drainage problems induced by urbanization (Zhao et al. 2018). The permeable asphalt pavement system (PAPS) is a typical infiltration facility with strong adsorption capacity and purification capacity for rainwater runoff, which can further maximize the efficacy of LID technology in rainwater control. The permeable pavement system has been applied as an essential element of water control system in many countries for years, such as the sustainable urban drainage system of the UK (Construction Industry Research and Information...
Association 2006) and the water-sensitive urban design of Australia (Wong 2006).

PAPS is a special type of permeable pavement with hot-mix asphalt mixture as the top wear layer. The most distinct feature of the permeable pavement system from a typical hot-mix asphalt mixture is that the ratio of fine aggregate content is significantly decreased in the mix material (Dietz 2007; Brodie 2012). The base layer is made of permeable concrete, large particle-sized permeable asphalt mixture (LSPM), and graded gravel. The reservoir is mainly made of large porous materials like graded gravel, which makes it a good temporary reservoir for rainwater to penetrate, pass through the top permeable surface layer, and slowly infiltrate into subgrade soil (Zhao & Zhao 2014). The reservoir has multiple functions, including reducing stormwater, replenishing groundwater, regulating atmospheric humidity, alleviating urban heat island effect, etc. (Jiang et al. 2015; Sounthararajah et al. 2017).

Surface runoff typically contains various pollutants that can reduce the qualities of urban water resources, including total suspended solids (TSS), nutrients such as phosphorus (TP) and nitrogen (TN), hydrocarbons, and heavy metals (Kayhanian et al. 2012). Generally, stormwater runoff contains substantial pollutants that cannot be completely absorbed by PAPS, such as nutrients like nitrogen and phosphorus (Bentarzi et al. 2016). Such nutrients will flow into groundwater and cause severe pollution, which impedes water restoration and destroys the regional ecological environment (Chen et al. 2015). Thus, it is of great importance for environmental protection to improve the quality of water that infiltrates into soil, especially water on urban roads with a certain traffic flow (Zhao et al. 2017). Biological, chemical, and physical methods are common methods for removing nitrogen and phosphorus in polluted water, among which, the physical method is the most common one, especially the physical adsorption method (Lin et al. 2015). The adsorption method features many advantages, including low cost, high accessibility to adsorption materials, high efficiency, simple process, stable effects, and easy operation (Ganrot et al. 2007). Zeolite, as a microporous material, displays unique physicochemical properties, such as the presence of strong acidic centers, large specific surface area, and a precisely defined system of micropores and channels, and can be an ideal material for the reservoir layer in roads. Natural zeolites are characterized by good performance in cation exchange and ammonium removal, whereas it is almost incapable of removing phosphate because of the electro-negativity (Kuroki et al. 2014; Guaya et al. 2015). Metal oxide could provide large numbers of coordination sites and exhibits good sensitivity toward phosphate even at trace levels. Thus, it is necessary to modify the properties of natural zeolites in order to equip it with phosphate removal capacity in addition to its ammonium removal capacity.

Numerous studies have shown that compared to natural zeolites, the adsorption capacity of inorganic salt-regulated and acid activated zeolites was greatly improved, which enabled regulated zeolites to increase pore structure and remove nitrogen and phosphorus from water bodies simultaneously (Zamparas et al. 2013; Deng et al. 2016). There are several methods for improving the purification efficiency of surface runoff by PAPS, such as altering mix ratios, void ratios, or infiltration rates of surface asphalt mixture (Jiang et al. 2015). Some studies have considered regulated zeolite as a treatment device in reservoirs in PAPS (Zhao & Zhao 2014; Sounthararajah et al. 2017; Zhao et al. 2017, 2018) at the laboratory scale and in field conditions (Liu et al. 2012). These studies highlighted applicability and efficiency during rain events, but limited studies have explored the simultaneous removal of nitrogen and phosphorus in stormwater runoff through PAPS with regulated zeolite in the reservoir layer. Yet, some authors have shown that physico-chemical changes in the reservoir can be dramatic and can control the release of heavy metals to the groundwater (Zhao et al. 2018).

There are no good methods to remove nitrogen and phosphorus simultaneously with PAPS in the existing studies. The aim was to investigate and characterize the effect of a PAPS with a zeolite-regulated reservoir in removing pollutants. In this study, sodium chloride ion exchange and zirconium oxychloride deposition baking and a two-step method were applied to modify zeolites for generating denitrified and deposphorized zirconium–sodium-regulated zeolites (Zr/Na/Z). The process of surface modification of zeolites was analyzed using a scanning electron microscope (SEM)–energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). The capacity of regulated zeolites to adsorb NH$_4^+$-N and TP at
different pH and initial concentrations was also investigated. With the natural zeolite reservoir as control, this study investigated the effects of PAPS with a zeolite-regulated reservoir on removal of NH$_4^+$-N and TP simultaneously in stormwater runoff under artificial rainfall events of 120 min duration and a 48 h temporary storage period. The findings provide a novel research insight into stormwater runoff purification by PAPS in the process of ultra-rapid urbanization in China.

**MATERIALS AND METHODS**

**Materials**

**Modification of zeolites**

Natural zeolite, obtained from Henan Zeolite Company, China, was mainly composed of SiO$_2$ (68.87%), Al$_2$O$_3$ (10.62%), Fe$_2$O$_3$ (0.78%), CaO (0.67%), Na$_2$O (0.42%), and K$_2$O (0.12%). The zeolite was first sieved through 200 and 300 mesh screens and soaked in 1.0 mol/L HCl for 24 h, then washed to a neutral pH by deionized water and dried at 100°C (denoted as acid activated zeolite), and labeled as N/Z. Twenty grams of zeolite were placed in a beaker containing 200 mL of 1.0 mol/L NaOH, ionic change conducted for 24 h, then washed with deionized water, calcined at 300°C for 2 h to obtain sodium-regulated zeolite, and labeled as Z/Na. Ten grams of Z/Na were put into a beaker containing 60 mL of 0.706 g ZrOCl$_2$·8H$_2$O solution, magnetically stirred for 2 h, dripped 1.0 mol/L NaOH solution, the pH value adjusted to 7.0, then stirred continuously for 24 h, calcined at 300°C for 2 h after separation and washed, to obtain zirconium–sodium-regulated zeolite, which was labeled as Z/Na/Zr.

**Structure of PAPS**

Two model PAPS were constructed in this study. Each contained three main courses (Table 1) that included a 10 cm-thick surface of porous asphalt, a 10 cm-thick choker course of LSPM which sits above a 40 cm-thick base reservoir of zeolite or modified zeolite. Geotextiles, for permeability and separation purposes, were set underneath the reservoir layer. All of the system courses were designed in accordance with the technical specifications for permeable asphalt pavement (CJJ/T 190–2012) (Zamparas et al. 2013) and other related standards in China.

**Preparation of synthetic rainwater**

Synthetic water was prepared based on the research findings on the quality of road water in Nanjing, Jiangsu, China and several other influencing factors. Several previous studies have reported on runoff rainwater collected from different functional areas of urban regions (Zhao & Zhao 2014; Jiang et al. 2015; Sounthararajah et al. 2017). In the early stage of artificial rainfall events, runoff rainwater was mixed with a large amount of road surface sediments, suggesting that the concentrations of pollutants in stormwater runoff were highest at the beginning. Then, the concentrations of pollutants gradually decreased along with the duration of rainfall. Notably, there was a significant initial effect. The chemicals for synthetic stormwater and influent components are shown in Table 2.

**Experimental device**

An artificial simulated rainfall device was designed for simulating natural rainfall indoors in this study. The system included four main parts: rainfall nozzle, water

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**Table 1 | Characteristics of structure layers in permeable pavement system**

| Pavement structure | Type of material | Gradation | Void ratio (%) | Molding method |
|--------------------|-----------------|-----------|---------------|---------------|
| Surface course     | Permeable asphalt mixture | PAC-16    | 21.4          | Vibration compaction |
| Basic unit         | LSPM            | LSPM-25   | 24.7          | Vibration compaction |
| Reservoir base     | Zeolite         | Particle size: 4-8 mm | 36.8         | Loosely packed |
| Filter layer       | Non-woven geotextile | /         | /             | Tile horizontal |
storage tank, control system, and pavement structure model (Figure 1). The test chamber was made of polyvinyl chloride sheet with a height of 55 cm and an inner diameter of 102 mm. The water outlet was arranged at the bottom of the test chamber and connected to the drain pipe at a lower site for collecting the samples of filtered runoff water. The simulated rainfall nozzle, supported by the steel frame, was directly installed above the pavement structure model box. Each rain-bird series nozzle was set at a flow rate of 0.01 m$^3$/h and a control range of 340 mm (approximately 0.09 m$^2$) under a working pressure of 0.1 MPa. The rainfall uniformity of the simulated rainfall system was maintained at 0.923. The intensity of actual rainfall could be adjusted and controlled by the control valve. Rainfall was measured using the flow meter as shown in Figure 1.

### Methods

#### Static adsorption

Simulated water samples for adsorption tests were prepared by a mixture of NH$_4^+$Cl, KH$_2$PO$_4$ and deionized water. Adsorption experiments were performed using a water bath in a 200 mL conical flask with a cover. NH$_4^+$-N or TP solution (100 mL) of different concentrations and a certain amount of zeolites were added into the conical flask. Then, the conical flask was submerged in a water bath shaker with a constant temperature and shaken at 25 $^\circ$C for 24 h (150 r/min).

#### Artificial rainfall schedule

In order to carry out simulated rainfall events with a rainfall intensity similar to natural rainfall, the rainfall intensity in the Chicago rainfall model (Bentarzi et al. 2016) was

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**Table 2** | Concentrations for synthetic stormwater runoff used in this study

| Component | Concentration (mg/L) Range | Concentration in artificial stormwater (mg/L) | Source |
|-----------|---------------------------|--------------------------------------------|--------|
| COD       | 42.2–679.8                | 132.3 ± 4.7                                | Glucose|
| NH$_4^+$-N| 1.7–11.3                  | 5.1 ± 0.4                                  | NH$_4$Cl|
| NO$_3^-$-N| 0.6–4.3                   | 3.4 ± 0.3                                  | KNO$_3$|
| NO$_2^-$-N| 0.2–3.9                   | 1.8 ± 0.3                                  | NaNO$_2$|
| TP        | 0.2–2.6                   | 1.2 ± 0.2                                  | KH$_2$PO$_4$|
| pH        | 6.2–8.1                   | 7                                           | NaOH/HCl|

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**Figure 1** | The artificial simulated rainfall system.
adjusted to an interval of 5 min. The whole process of the artificial rainfall experiment was divided into 24 periods. The time-span rainfall of the rainfall generator was calculated based on the rainfall intensity and typical rainfall scenario with a rainfall duration of 120 min and the parameters of test devices. The synthetic scenario is shown in Figure 2.

Experimental process

Before the artificially simulated rainfall tests, synthetic rainwater was taken out from the water tank using a polyethylene plastic bottle and set as raw water. Then, the conductivity and values of the raw water were measured and recorded. When the outlet of the discharging pipe was found to be suspended with water droplets for the first time, the initial filtered runoff water sample was collected for water quality analysis. By comparison with the original water sample, the removal effects of permeable asphalt roads before and after modification on pollutants in the initial pavement runoff were determined. The filtered runoff water samples were collected at 0 min, 30 min, 45 min, 60 min, 90 min, and 120 min, respectively, after outflow. A total of 13 water samples (including the raw water sample) were collected.

Adsorption kinetics for modified zeolite

The adsorption data were applied to three different kinetic models: pseudo-first order, pseudo-second order, and intraparticle diffusion models. In both the pseudo-first order and pseudo-second order models, the adsorption steps, including external diffusion, internal diffusion, and adsorption, are lumped together. Nonlinear forms of the pseudo-first order and pseudo-second order equations (Chi & Ramarao 2014) are given in Equations (1) and (2), as well as intraparticle diffusion in Equation (3):

\[ q_t = q_e (1 - e^{-k_1 t}) \]  
\[ q_t = \frac{k_2 q_e t}{1 + k_2 q_e t} \]  
\[ q_t = k_p t^{1/2} + c \]

where \( q_e \) and \( q_t \) are the amount of dye adsorbed (mg/g) on the adsorbents at equilibrium and at time \( t \), respectively, \( k_1 \) is the rate constant of adsorption (1/h), \( k_2 \) is the rate constant of pseudo-second order adsorption (g/mg h), \( k_p \) is the rate constant for intraparticle diffusion (1/h), and \( c \) is the intercept.

Chemical compositions and surface characterization

The chemical compositions of all materials were analyzed with X-ray fluorescence (XRF) by the Advanced Analysis and Testing Center. The materials before and after the leaching and adsorption tests were characterized by SEM and XRD to evaluate the changes in morphology, crystal structure, and the chemical compositions of the surface. For all analytical tests, the materials were dried in an oven at 105 °C for 24 h.

Water quality assessment

The measured values of water samples collected at each period were averaged and recorded as the final measured values. The interception rates and removal rates of different pollutants in the stormwater by permeable pavement system before and after modification were calculated according to Equation (4):

\[ \eta_i = \frac{C_{oi} - C_{ei}}{C_{oi}} \times 100\% \]

where \( \eta_i \) is the removal rate for nitrogen and phosphorus with different forms in rainfall runoff by permeable pavement.
Domestic and foreign researchers have proposed a method for assessing the comprehensive pollution indexes based on multiple indicators (Lei et al. 2018). Water pollution indicators can be comprehensively analyzed based on this method, and the evaluation results obtained from mathematical calculations can indicate the comprehensive pollution degrees of multiple pollution factors in water bodies. The equations for calculations are listed as Equations (5) and (6):

\[ P_i = \frac{C_i}{C_{si}} \]  
(5)

\[ PI = \frac{1}{n} \sum_{i=1}^{n} P_i \]  
(6)

where \( P_i \) is the pollution index of the assessment factor \( i \), \( C_i \) is the measured value of the assessment factor \( i \) (mg/L), and \( C_{si} \) is the standard value of the assessment factor \( i \) (mg/L):

The calculations were based on Grade V water quality standard of Environmental Quality Standard for Surface Water (GB3838-2002) in China. Water qualities can be classified into several grades according to the comprehensive pollution index method (Table 3), which provides a basis for water quality assessment (Zhu et al. 2010).

**RESULTS AND DISCUSSION**

**Performance of regulated zeolites**

**SEM-EDS characterization of natural zeolites and regulated zeolites**

The natural zeolites were featured by a rough surface and a relatively compact structure with the presence of particulate debris. After modification by sodium hydroxide, the particle fragments disappeared, making the surface of the regulated zeolites become relatively porous, coarse, and heterogeneous. Plentiful porous channels were formed due to the decrease in impurities on the surface and the corrosive effect of dissolved sodium hydroxide amorphous substance on the surface of the zeolites, providing a larger specific surface for loading. A large amount of fine sheet-like structures was observed in the porous channels on the surface of the zeolites, which could be a result of zirconium loading on the surface of the sodium-regulated zeolites. EDS spectrum was used to detect the Zr element on the surface of the zeolites. The analytic results showed that the element content of the natural zeolites originally constituted by Al\(_2\)O\(_3\), SiO\(_2\) and alkali metal ions (Mg\(^{2+}\) and Ca\(^{2+}\)) was altered by sodium hydroxide modification. The relative content of the Na element increased from 0.37% to 5.78%. The relative content of Al decreased from 10.6% to 4.98%, and the relative content of Ca decreased from 0.2% to 0.04%. These changes could be caused by the replacement of Al\(^{3+}\) and Mg\(^{2+}\) in the zeolites by Na\(^{2+}\) in the solution during the process of sodium hydroxide modification. The content of Zr in the zirconium oxychloride-regulated zeolites was 7.83%, while the content of the Na element was unchanged, indicating that the Zr element was successfully loaded onto the surface of the zeolites during the regulation (Figure 3).

**XPS characterization of natural zeolites and regulated zeolites**

To gain further insights into the composition to be modified, the XPS spectra of zeolite before and after were analyzed. Compared with the wide-scan XPS of natural zeolite (Figure 4), new peaks appeared on the surface of Zr/Na/Zr at 1,071.8 eV, 180.8 eV, and 182.8 eV, which corresponded to Na 1s, Zr 3d\(_{5/2}\)/5 and Zr 3d\(_{3/2}\)/2, proving the successful loading of Na and Zr elements. The sodium...
species on the surface of Z/Na and Z/Na/Zr were further investigated and Na 1s was decomposed by XPS PEAK, and the results indicated that the area of Na of Z/Na and Z/Na/Zr samples were stable in the modification. The large portion of Zr existence in Z/Na/Zr might be explained by the presence of partially small particles over the surface of zeolite, which were located deeper (3–5 nm) than the XPS sampling depth.

XRD characterization of natural zeolites and regulated zeolites

The XRD diffraction patterns of Z/Na and Z/Na/Gr are shown in Figure 5. The natural zeolites used in this study were mainly made up of clinoptilolite ((NaKCa)4Al6Si30O72·18H2O), heulandite (Ca3.6K0.8Al8.8Si27.4O72·26.1H2O), and silica. Both the zeolites before and after modification showed a typical crystal structure with similar characteristic diffraction peaks, indicating that the modification had few impacts on the crystal structure of the zeolites. The diffraction peaks appeared at the diffraction angles 2θ involving 21.8°, 27.1°, 36.2°, 49.9°, 59.3°, and 67.4°. As well, the diffraction peaks coincided with the characteristic peaks of the natural zeolites. Zr element was detected on the surface of Z/Na/Gr by EDS spectrum, whereas the characteristic diffraction peak of zirconium oxychloride was not found in the diffraction spectrum of XRD. Previous studies have indicated that the chemical action between selected cations and zeolites mainly occurred on the surface of zeolites (Zamparas et al. 2013). Test results demonstrated that there were no peaks related to zirconia or zirconium oxychloride, suggesting that the zirconium element was well dispersed in the regulated zeolites. Moreover, it was also possible that the characteristic diffraction peak of zirconium oxychloride (21.8°, 27.1°, and 32.6°) coincided with that of zeolites.
Adsorption kinetics

The kinetic curves of adsorption for ammonium and phosphorus by Z/Na/Zr are shown in Figure 6. Z/Na/Zr adsorbed both ammonium and phosphorus, which was rapid initially and then slowly reached the adsorption equilibrium. The adsorption efficacy of Z/Na/Zr improved with the increase of the initial mass concentrations of ammonium and phosphorus under the same reaction conditions. The quasi-first order kinetic adsorption model and quasi-second order kinetic adsorption model are common methods for describing the adsorption kinetics of adsorbates by adsorbents (Lin et al. 2019).

The adsorption kinetics curves for ammonium and phosphate with different initial concentrations by Z/Na/Zr are shown in Figure 6. Most of the ammonium and phosphate were adsorbed by Z/Na/Zr in the first 80 min. Then, the adsorption tended to become slowly balanced and complete adsorption equilibrium was approached at 5 h. This is due to high concentrations of ammonium and phosphate in the solution and the abundant active sites and exchangeable cations in Z/Na/Zr which lead to the rapid adsorption of ammonium or ion exchange on the surface of Z/Na/Zr. With the reaction progressing, the active sites for adsorption...
were occupied and the exchangeable cations were replaced, leading to the decrease in the concentrations of ammonium. The results of nonlinearily fitting the quasi-first order and the quasi-second order kinetic models are shown in Figure 6. The quasi-first order kinetics of adsorption for ammonium and phosphate by Z/Na/Zr, the equilibrium adsorption capacity was obtained by fitting quasi-secondary kinetics, theoretical equilibrium adsorption capacity, adsorption rate constant, and fitting correlation coefficients were obtained by model fitting, which are listed in Table 4. The nonlinear fitting correlation coefficient \( R^2 \) of Z/Na/Zr against adsorption kinetics of ammonium and phosphate was greater than 0.9. The maximum equilibrium adsorption capacity calculated according to the quasi-first order kinetic model was significantly different from that obtained from the experiment, while the equilibrium adsorption capacity calculated based on the quasi-second order kinetic model was similar to that obtained from the experiment. These results indicated that the quasi-secondary kinetic model could better describe the kinetic characteristics of ammonium and phosphate absorption. Chemisorption involves electron sharing or transfer (Lin et al. 2019). This study showed that chemisorption was a critical regulator of the adsorption rates of Z/Na/Zr on ammonium and phosphate, which was consistent with previous studies (Deng et al. 2016).

Nitrogen and phosphorus removal by PAPS with regulated-zeolites reservoir under a rainfall event

Dynamic reducing capability for \( \text{NH}_4^+ \)-N in stormwater runoff

In the simulated rainfall experiment, the concentration of \( \text{NH}_4^+ \)-N in the outflow water showed an increasing trend with the duration of the rainfall (Figure 7(a)). The zeolite

Table 4 | Kinetic parameters for ammonium and phosphate adsorption by Z/Na/Gr (pH = 7.0, dosage = 5.0 g L\(^{-1}\), reaction time = 24 h, T = 30 \(^\circ\)C)

| Pollutant | \( c_0 \) (mg/L) | \( q_e \) (mg/g) | Pseudo-first order kinetics equation | Pseudo-second order kinetic equation |
|-----------|-----------------|----------------|------------------------------------|--------------------------------------|
| \( \text{NH}_4^+ \)-N | 20 | 4.5 | 0.989 | 0.912 |
| | 40 | 5.7 | 0.97 | 0.912 |
| TP | 20 | 7.2 | 1.45 | 0.986 |
| | 40 | 10.9 | 3.4 | 0.989 |
reservoir showed promising effects on \( \text{NH}_4^+ \)-N removal. The average removal rate during the whole process of the rainfall remained above 40%. The removal of \( \text{NH}_4^+ \)-N mainly involved filtration, retention, adsorption, and ion exchange in structural layers. Results also showed a similar variation trend in \( \text{NH}_4^+ \)-N removal efficacies between the regulated and the unregulated permeable pavement systems. With the duration of sampling, the removal efficacy circuitously decreased in the first 60 min and gradually stabilized in the last 30 min.

For the PAPS using natural zeolites as the reservoir, the concentration of \( \text{NH}_4^+ \)-N in the initial outflow was only 2.48 mg/L and the removal rate was 51.4%, indicating that the PAPS with zeolites as the reservoir had a favorable removal capacity for \( \text{NH}_4^+ \)-N in rainfall runoff. Notably, such effect gradually weakened in later periods, which could be caused by the initial erosion effect of the rainfall on the pavement during the initial stage and the saturation of the adsorption sites of layers with the duration of the rainfall (Chen et al. 2019; Jayakaran et al. 2019). For the PAPS with regulated zeolite as the reservoir, the concentration of \( \text{NH}_4^+ \)-N in the initial outflow water was only 1.01 mg/L. Notably, the removal rate of \( \text{NH}_4^+ \)-N reached up to 80.1%, which was significantly greater than that in the pavement.
with natural zeolite reservoir and in accordance with the Grade IV standard for surface water quality. These results demonstrated that the zirconium–sodium-regulated zeolite reservoir improved the quality of runoff in the pavement.

**Dynamic reducing capability for TP in stormwater runoff**

Figure 7(b) shows that the concentration of TP in the outflow water, analogous to NH$_4$-N, increased with the progress of the artificial rainfall event, which could be related to saturated adsorption of asphalt mixture and zeolites (Sounthararajah et al. 2017). For the water quality of initial outflow, the concentration of TP in the unregulated-zeolite reservoir was 0.63 mg/L. The removal rate was 47.3%, slightly lower than that for NH$_4$-N in the same period of sampling, which could be mainly caused by the concentration of NH$_4$-N in the synthetic stormwater being higher than TP. For the PAPS using modified-zeolite as a reservoir, the average reduction of TP in the initial rainfall was 1.15 mg/L, while the average reductions of TP in the later two stages of rainfall were 1.09 mg/L and 1.04 mg/L, respectively.

**Efficiency of nitrogen and phosphorus removal by PAPS with regulated-zeolite reservoir with temporary storage**

The curves describing the variations of removal rates on nitrogen and phosphorus in runoff by PAPS with the regulated zeolite reservoir during temporary storage are shown in Figure 7(c) and 7(d). Obvious decreases in the concentrations of nitrogen and phosphorus in the outflow were observed at 1 h after PAPS entered the storage stage. The average removal rates of the regulated zeolite permeable pavement system structure on NH$_4$-N and TP were up to 77.9% and 88.6%, respectively, reaching 1.48 and 1.73 times of the PAPS with unregulated zeolite reservoir. The removal rate on pollutants in the effluent was over 90% after 24 h of storage. More importantly, all cases met the Grade III standard for surface water. When the pavement structure transformed into the storage stage from the permeation stage, the regulated zeolite aggregates were fully immersed in stormwater runoff with constant increases in the saturation degree of the reservoir, effectively enhancing the interaction between aggregates and stormwater runoff.

Hydrolysis and ionization occurred on the surface of the zeolites and the regulated zeolites, generating a large amount of ions via ion exchange. Compared to the unregulated zeolites, the specific surface area and gross pore volume of the regulated zeolites were partially increased. The regulated zeolites mainly exchanged with Ca$^{2+}$ during the process of cation exchange (Jiang et al. 2015; Sounthararajah et al. 2017). The volume fraction of Na$^+$ in the modified zeolites was 14 times that in the unregulated zeolites. It was concluded that the purifying effect of the PAPS with modified zeolites under storage conditions on the effluent quality was significantly higher than that of the unmodified pavement. In addition, the regulation of NH$_4$-N and TP in the initial erosion runoff by PAPS mainly depended on the physical retention of microscopic void structure of materials inside the structural layer and the adsorption of particulate matters. Therefore, it was considered that ion exchange, electrostatic adsorption, and complexation reaction of reservoir particles built a good environment for controlling NH$_4$-N and TP when the pavement structure entered the temporary storage stage.

**Assessment of effluent quality from regulated pervious asphalt pavement**

In this study, the fifth level standard for surface water in China is defined as the basic category. The degrees of effluent pollution are determined by Equations (2) and (3) based on the comprehensive pollution index method. Results showed that during the simulated rainfall event, the quality of water collected from the permeable pavement system containing a natural zeolite reservoir during the six sampling periods was inferior, and the water storage was graded as the fifth level standard (Table 5). For the permeable pavement system with the regulated reservoir, the quality of effluent in the first 60 min met the fifth level standard for surface water but downgraded afterwards. Both the effluent quality of the unregulated or regulated reservoir permeable surface improved with the duration of storage. The TP content in the water layer of the double-regulated zeolites was merely 0.11 mg/L after 24 h of storage period, which was approximately 32% of that in the unregulated reservoir and close to the second level standard for surface water. The content of NH$_4$-N was only 0.31 mg/L, meeting the
second level standard for water quality. Results indicated that the removal effect on pollutants in runoff was more significant in PAPS with regulated zeolites as the reservoir than that in natural zeolite reservoir, whereas the effluents in the PAPS using zeolite, sand (Jiang et al. 2015), basalt gravel, and limestone gravel (Zhao et al. 2018) as the reservoir or the cushion were seriously polluted. Hence, single PAPS could not meet the initial rainwater treatment standards, which was consistent with the results of several previous studies suggesting that the intensified permeable pavement system reservoir could be a better tool for controlling the quality control of stormwater runoff (Sun 2017; Tong 2017; Wang 2017; Zhao et al. 2018). Several enhancement techniques and combination technologies became available for selection later, such as ecological ditches, bioretention, constructed wetlands, etc. (Lin et al. 2013).

CONCLUSIONS

The capacities of PAPS using a regulated and unregulated reservoir to remove NH$_4^+$-N and TP in stormwater runoff were compared in this study by designing and synthesizing zirconium–sodium-regulated zeolites. The removal efficiencies on pollutants during a rainfall event and a temporary storage were measured, and water qualities were assessed. The mechanisms for the regulated zeolite reservoir to purify stormwater runoff were investigated. Results showed that the removal efficiency for pollutants was significantly increased during the water storage period regardless of the regulation status. The efficiencies of the PAPS with regulated zeolites in removing NH$_4^+$-N and TP were above 90% with extension of the storage duration. The modification for zeolites increased porous sizes, specific surface areas, and gross pore volumes, facilitating the entrance of zirconium and sodium elements into zeolite pores and amplifying exchangeable cations in zeolites. The diffraction pattern by XRD suggested the crystal structure of zeolites remained unchanged during the process of modification. Ion exchange was the major method for the regulated zeolite reservoir to remove ammonium, and phosphate was mainly removed via complexation action. The effluent achieved the Grade V standard for PAPS with regulated zeolite as the reservoir in an artificial rainfall event. Therefore, it is recommended to further investigate various enhancement and combination technologies (e.g., ecological ditch, ecological slope, bioretention, constructed wetland, and other series and combined technologies) to practically minimize the impacts on pollutant removal involving nitrogenous and phosphorus compounds and other heavy metals.

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