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Runoff regulation and nitrogen and phosphorus removal performance of a bioretention substrate with HDTMA-modified zeolite

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As a commonly used material in bioretention substrates, natural zeolite (NZ) provides decent adsorption capacity for cation pollutants and heavy metals, but limited ability to remove anion pollutants. Hexadecyltrimethylammonium bromide (HDTMA)-modified zeolite (MZ) was used as the bioretention substrate material. The performance of the media including runoff reduction, nitrate nitrogen (NO_3^--N) removal, ammonium nitrogen (NH_4^+-N) removal, and total phosphorus (TP) removal was assessed by the column experiment. The effects of different levels of modification, ratio of zeolite in the substrate, and rainfall intensity on media performance were investigated. The results indicate that HDTMA-modified zeolite significantly improves the NO_3^--N (up to 38.2 times of NZ) and TP (up to 17.5 times of NZ) removal rate of media and slightly increases the NH_4^+-N (up to 1.5 times of NZ) purification performance of the substrate. Compared with the media with NZ, decline on both runoff volume reduction (maximum decline up to 32.9%) and flow rate reduction (maximum decline up to 29.9%) of the media with MZ were observed. Based on multiple regression analysis, quantitative relationship models between influencing factors and response variables were established ($R^2 > 0.793$), the level of the effect of influencing factors on response variables was investigated, and the interactions between influencing factors were explored. The main effect analysis found that the degree of modification affects NO_3^--N and TP removal rate of the substrate the most, and when the amount of HDTMA molecules loaded on the zeolite surface exceeds 0.09 meq/g, the modification can no longer improve NO_3^--N removal efficiency.

1 Introduction

The increasing quantity and deteriorating quality of urban stormwater come with the rapid urbanization process (Fletcher et al., 2014; Chen et al., 2017), mainly because of the increasing impervious areas in the urban area (Li et al., 2018). Impervious areas such as roads and buildings not only block the infiltration process of rainwater but also accumulate various pollutants such as nutrients (nitrogen and phosphorus), organic matters, and heavy metal. The blocked infiltration process could increase flood risk, and accumulate pollutants would be washed into the receiving water bodies by stormwater runoff, which will cause water contamination (Walsh et al., 2012). Among these pollutants, nitrogen and phosphorus play significant roles in eutrophication, and relevant studies indicate that the majority of the nitrogen and phosphorus in stormwater runoff come from developed areas (Line and White, 2007; Davidson et al., 2010; Gao et al., 2019). A series of urban stormwater control measures have been adopted in response to these issues, such as bioretention, stormwater wetland, pervious pavement, and sedimentation ponds (Davis et al., 2009; Hatt et al., 2009; Baek et al., 2015).

Bioretention is an effective stormwater management technology that has been widely used to mitigate urban flooding risk and improve stormwater quality (Davis et al., 2009; DeBusk et al., 2011; Goh et al., 2019). The primary function component of bioretention is the substrate, which is commonly composed of topsoil (a general term for the upper or outmost layer of soil), compost, and aggregate amendments such as zeolite, biochar, and pumice (Jia et al., 2015; Liu and Fassman-Beck, 2016; Liu J. et al., 2017). The purpose of adding aggregate amendments in bioretention media is to adjust its saturated hydraulic conductivity (K_s) to address stormwater management objectives (Liu and Fassman-Beck, 2016). In addition to regulating K_s, different amendments were used in bioretention media to improve its water purification ability. Studies showed that amendments such as blast furnace slag, biochar, water treatment residuals (WTRs), and iron filings could improve the total phosphorus (TP) and total nitrogen (TN) removal ability of the bioretention media (Li et al., 2016; Chang et al., 2019; Poor et al., 2019; Zhou et al., 2022).

Zeolite is widely used in water treatment and environmental remediation as an adsorber or filler, due to its porous structure and cation exchange ability (Misaelides, 2011; Reddy et al., 2014). It is also a common material used for bioretention substrate (Jiang et al., 2019). Studies show that using zeolite as bioretention substrate media could achieve satisfying results in stormwater purification performance. Sari et al. (2019) investigated the treatment performance of bioretention media using quartz sand and zeolite, the results indicate that adding zeolite in substrate could significantly improve the removal efficiency of ammonium nitrogen (NH_4^+-N), Pb, and Zn. Wang et al. (2021) assessed three different mixtures of bioretention media, the

media contain zeolite demonstrated better performance in the removal of the total nitrogen (TN) and NH_4^+-N than other medias without zeolite; however, results also pointed out that the media with zeolite has limited ability for the removal of total phosphorus (TP). Other researches also reported that substrate media using zeolite exhibited satisfactory effect on removing TN, NH_4^+-N, and heavy metals, but showed poor performance on TP and nitrate nitrogen (NO_3^--N) removal (Jiang et al., 2019; N. Seelsaen et al., 2006; Wang et al., 2017).

Zeolite is a type of aluminosilicate mineral, due to its unique structure and chemical composition, zeolite possess negative charge and cation exchange properties, which is the reason it has limited effect on anionic pollutants (such as phosphate and NO_3^--N) removal, but shows high adsorption capacity for cationic pollutants such as NH_4^+-N (Ejhieh and Masoudipour, 2010; Misaelides, 2011; Sharafzadeh and Nezamzadeh-Ejhieh, 2015). Because of the unique porous structure, high cation exchange capacity and high adsorption ability, zeolite has various applications, it has been used for the removal of Pb (II), the removal of Cu (II), and the modification of carbon paste electrode (Heidari-Chaleshtori and Nezamzadeh-Ejhieh, 2015; Alidusty and Nezamzadeh-Ejhieh, 2016; Tamiji and Nezamzadeh-Ejhieh, 2019; Nasiri-Ardali and Nezamzadeh-Ejhieh, 2020). Moreover, the cation exchange ability of zeolite also makes it available for surface modification by cationic surfactant, which could significantly enhance its capacity to adsorb anionic pollutants (Bowman, 2003; Shi et al., 2009; Nezamzadeh-Ejhieh and Mirzaeyan, 2013; Nezamzadeh-Ejhieh and Tavakoli-Ghinani, 2014). Studies indicate that when surfactant concentrations are higher than the critical micelle concentration (CMC), a bilayer of surfactant molecules will form on zeolite surface. The double layer of surfactant molecules reverses the charge of zeolite from negative to positive, which enable modified zeolite with the ability to adsorb anions, cations, and non-polar organic species simultaneously (Nezamzadeh-Ejhieh and Afshari, 2012; Nezamzadeh-Ejhieh and Shahanshahi, 2013; Saadat and Nezamzadeh-Ejhieh, 2016; Mahdavi and Nezamzadeh-Ejhieh, 2017). Naghash and Nezamzadeh-Ejhieh (2015) compared the removal efficiency of natural zeolite, hexadecyltrimethylammonium bromide (HDTMA)-modified zeolite, and hexadecylpridinium bromide (HDP)-modified zeolite, results show that under the same condition, phosphate adsorption capacity of zeolite was significantly improved by modifications, form 16 mmol/kg (natural zeolite) to 376 mmol/kg (HDP-modified zeolite) and 675 mmol/kg (HDTMA-modified zeolite). In the area of water treatment and environmental remediation, researches have provided convincing evidence and satisfactory results for using modified zeolite (MZ) to enhance the treatment performance of NO_3^--N, phosphate, organic contaminants, and Pb (Yusof and Malek, 2009; Schick et al., 2011; Zhan et al., 2011; Anari-Anaraki and Nezamzadeh-Ejhieh, 2015; Tao et al., 2015; Liu et al., 2016). Additionally, surfactant-

modified zeolite can be used to make nitrate selective electrode, and it shows satisfactory ability for quantification of nitrate in water and industrial products (Nezamzadeh-Ejhieh and Nematollahi, 2011; Nosuhi and Nezamzadeh-Ejhieh, 2018).

In addition to enhanced pollutant removal efficiency, the surface modification process would also change hydrophilicity and hydrophobicity properties of zeolite (Nezamzadeh-Ejhieh and Raja, 2013). Hydrophilicity/Hydrophobicity of the material is the key factor which determines its interactions with water (Gray et al., 2014; Kameyama et al., 2019). Research suggests that hydrophobicity play fundamental roles in water movement and retention of material, and consequently affects its hydraulic properties (Edeh and Mašek, 2022). Hydraulic properties of substrate material were identified as important factors that affect the hydrological performance of bioretention (Liu and Fassman-Beck, 2016; Liu and Fassman-Beck, 2017a). Studies suggest that K_s and water retention characteristic (WRC), as the basic hydraulic properties of bioretention substrate, would affect overall hydrologic performance of the media (Lucas and Greenway, 2011; Paus et al., 2014; Fassman-Beck et al., 2015; Liu and Fassman-Beck, 2018, 2016). Moreover, different K_s indicate different hydraulic conductivity (K) of the media, and K can be predicted from measured data of the WRC and K_s (van Genuchten, 1980; Palla et al., 2009; Liu and Fassman-Beck, 2018). The previous research confirms that HDTMA modification would alter properties such as K_s and WRC of zeolite (Qin et al., 2022). Changes in WRC and K_s of the media will alter the hydrological performance of substrate, (Liu and Fassman-Beck, 2017a;Liu and Fassman-Beck, 2017b), therefore, more information regarding the hydrological performance of bioretention media with MZ is needed.

In the water treatment and environmental remediation area, HDTMA-modified zeolite is widespread used and has been considered to be safe for the environment, it also has been proved to be effective at TP, NO_3^--N and NH_4^+-N removal (Li et al., 1998; Bowman, 2003; Schick et al., 2010). However, few researches explore the possibility of using HDTMA-modified zeolite as bioretention media. As mentioned earlier, HDTMA modification would not only improves pollutant adsorption capacity of zeolite, but also affect its hydraulic properties, which would impact hydrological performance of bioretention media with MZ. In this context, this paper investigated the runoff regulation ability and the NO_3^--N, NH_4^+-N, and TP removal performance of bioretention media with HDTMA-modified zeolite. The effect of different influencing factors (level of modification, zeolite ratio, and rainfall intensity) on hydrological and pollutant removal performance of substrate was studied. The level of modification and percentage of zeolite are substrate factors that directly affect media performance, rainfall intensity was included as environmental factor, to evaluate the substrate performance of stormwater management under different rainfall conditions. Through multiple regression analysis, the correlations between

influencing factors and stormwater regulation performance (runoff reduction, NO_3^--N, NH_4^+-N, and TP removal rate) were established, and the interaction between influencing factors was studied.

2 Materials and methods

2.1 Materials

Natural zeolite (NZ), specifically, natural clinoptilolite (a type of zeolite) was used in this study. The clinoptilolites was sourced from Jinyun, Zhejiang, China, graded for 2–8 mm. The chemical compositions of NZ were 68.07% SiO_2, 12.12% Al_2O_3, 2.37% CaO, 2.06% Na_2O, and 1.01% Fe_2O_3. Peat soil and quartz sand were purchased from local horticulture company in Shanghai, China. Hexadecyltrimethylammonium bromide (HDTMA) was analytical grade reagents from Fisher Scientific, other chemical reagents involved in the experiments were analytical grade reagents purchased from Sinopharm.

2.2 Preparation of HDTMA-modified zeolite

Modified zeolite (MZ) in two levels of modification was prepared, 10% modified zeolite (ZHD10) and 50% modified zeolite (ZDH50). The level of modification was determined based on the percentage of the cation exchange capacity (CEC) of NZ, and the mass of HDTMA used for the modification was calculated by the equation suggested by Zohra et al. (2008):

$$f = \frac{M_{cation}}{CEC \cdot M_Z \cdot GMW_{cation} \cdot X},$$

where f is the portion of CEC satisfied by cation surfactant (dimensionless), M_{cation} is the mass of surfactant required for desired portion of CEC (g), CEC is the cation exchange capacity of zeolite (mol/g), M_Z is the mass of NZ (g), GMW_{cation} is the Gram molecular weight of HDTMA cation (g/mol), and X is the moles of charge per equivalent, which is 1 mol/equiv. for the HDTMA.

The CEC of NZ was calculated using the method introduced by Endo et al. (2013). The CEC value determined for the NZ used in the research is 164.75 cmol/kg. Based on the CEC value of NZ, required mass of HDTMA for the modification was calculated, which are 0.06g and 0.3 g for every 1 g of ZHD10% and ZHD50%.

NZ was washed by deionized water vigorously and dried in an oven at 105°C for 12 h. Washed NZ and deionized water in a solid-liquid ratio of 1:10 (w/w) were put into a chemical mixing tank, and the amount of HDTMA required for the modification was added, the blender of the mixing tank was set at 180 rpm.

The mixing tank was placed in a water bath heater with a constant temperature of 40°C for 24 h. After 24 h, the zeolite was washed with deionized water until AgNO$_3$ test indicate no bromide ions in the supernatant solution, then zeolite was dried in an oven at 105°C for 12 h.

After the modification, the Fourier transform infrared (FTIR) spectra of NZ and MZ were obtained in the region of 4,000 to 400 cm^{-1} by a Thermo Scientific Nicolet 6700 spectrophotometer. FTIR data were used to confirm whether the modification is successful. Thermogravimetric analysis (TGA) was conducted by a thermogravimetric analyzer, PerkinElmer, Pyris1. Based on the TGA data, the amount of surfactant loaded on zeolite surface were calculated using the thermogravimetric method (volatilization method), which are 0.05meq/g for ZHD10 and 0.09meq/g for ZHD50. Detailed discussion on the effect of HDTMA modification on zeolite characteristics can be found in the previous study (Qin et al., 2022).

2.3 Preparation of a bioretention substrate

Normally, a bioretention substrate is a mixture of various materials; the main component is soil (promotes infiltration and evapotranspiration of rainwater runoff), and other materials such as zeolite, coal slag, biochar, and perlite are added to improve the hydraulic and runoff treatment performance of the substrate (Davis et al., 2009; Brown and Hunt, 2011; Goh et al., 2019). In this research, the main purpose is to investigate the effect of HDTMA-modified zeolite on the runoff regulation performance of the substrate, to explore the possibility of using HDTMA-modified zeolite as bioretention substrate material, therefore, the substrate media used in this study were consist of only peat soil and zeolite. Peat soil is a general term for the soil formed by the natural accumulation of partially decayed biomass (Stracher et al., 2015). It is a dual-porosity material, makes it has relatively high K_s and high water retention ability (Hyväluoma et al., 2020).

A total of six substrate media were prepared by mixing NZ and MZ with peat soil in different ratio by percent volume. Detailed percentages of zeolite and peat soil were (1) 25% zeolite +75% peat soil (25% Z+75% S); (2) 50% zeolite +50% peat soil (50% Z+50% S); (3) 25% ZHD10 + 75% peat soil (25% ZHD10 + 75% S); (4) 50% ZHD10 + 50% peat soil (50% ZHD10 + 50% S); (5) 25% ZHD50 + 75% peat soil (25% ZHD50 + 75% S); and (6) 50% ZHD50 + 50% peat soil (50% ZHD50 + 50% S).

2.4 Experimental setup

The hydrological and pollutants removal performance of different substrate was evaluated by laboratory column experiments. In filed application, bioretention system includes
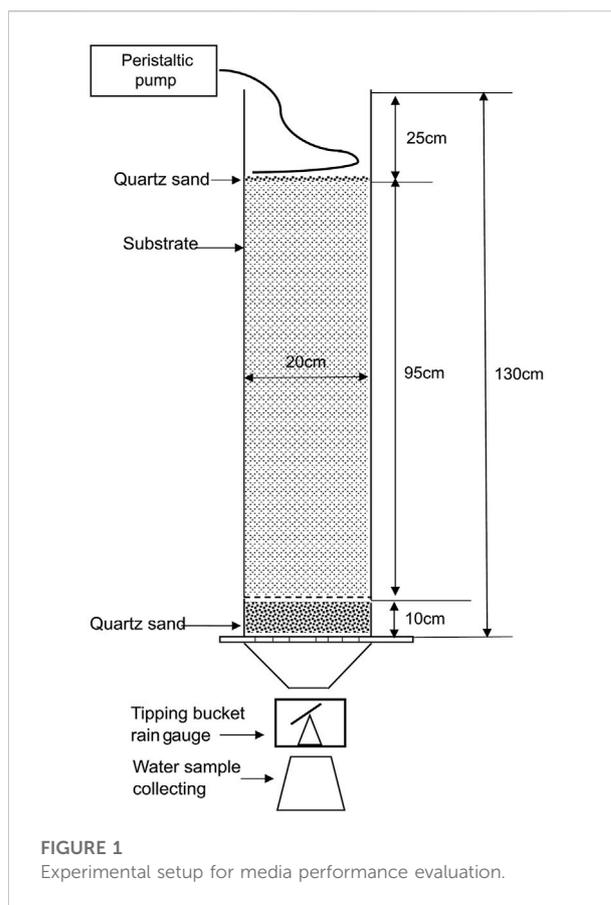
FIGURE 1
Experimental setup for media performance evaluation.

plants, but plants were not included in this study. Several studies indicate that plants have notable influence on bioretention media's hydrological and pollutants removal performance (Lucas, 2010; Le Coustumer et al., 2012; Hua et al., 2017). This study aims to investigate the relationship between media factors and substrate performance under different rainfall conditions, therefore, no plants were included to limit the influence from other factors. As shown in Figure 1, a polymethyl methacrylate column with 20 cm inner diameters and 130 cm height was packed with three layers: (1) 10 cm of quartz sand (graded for 5–10 mm) as the drainage layer at the bottom; (2) 95 cm of the tested media at the middle; and (3) 2–3 cm layer of quartz sand (graded for 5–10 mm) at the top to prevent the media scoured by inflow. It should be noted that this is not a typical bioretention substrate structure. Such experimental setup is to explore the possibility of HDTMA-modified zeolite as bioretention media, not to evaluate its performance as the actual bioretention media.

NZ, MZ, and peat soil were dried in an oven for 24 h at 105°C before mixing, then peat soil and zeolite were blended in a drum mixer. While mixing, 100 g water was added for every 1 L media to prevent the possible hydrophobicity. Before packing the material into the column, a thin layer of Dow Corning high

FIGURE 2
Photo of the inflow distribution tube.

vacuum grease was applied in the interior of the column to reduce the water flow along the side of the column. The high vacuum grease is a silicone metalloid complex, which is insoluble in water, chemically resistant, and maintains its consistency over a wide temperature range (-40–$204°C$). Therefore, the application of high vacuum grease would not affect the chemical analysis results. When every 10 cm material in depth was filled, a 4.5 kg proctor hammer was dropped six times from 45 cm height to achieve compaction, which is a compaction procedure suggested by Liu and Fassman-Beck (2016).

Inflow was steadily supply by a peristaltic pump (Longer, BT600-2J) through silica gel tube, outlet of the tube was clamped by tubing clamp, from that end, about 30 cm of the tube was punctured with a needle (1.6 mm inner diameters) in every 1 cm, and put on the top layer of quartz sand in spiral shape to evenly distribute the inflow (Figure 2). The outflow from the column was recorded continuously by a tipping bucket rain gauge, and a glass beaker was placed under the rain gauge to collect runoff sample.

2.5 Experimental procedure and analytical methods

The main objective of the experiments was to investigate the effect of HDTMA modification on runoff reduction and NO_3^--N, NH_4^+-N, and TP removal of media with zeolite on. The hydrological and pollutants treatment performance of all six

substrates were tested under three rainfall intensities, which were 1-, 10-, and 100-year average recurrence interval (ARI) events of Shanghai, the corresponding rainfall depth are 36.5, 67.3, and 98.1 mm/h (SBQTS, 2017). The rainfall intensities were converted to inflow rates by rational method (Dooge, 1957), which were 19.17 ml/min (low inflow rate, 1-year ARI), 37.17 ml/L (medium inflow rate, 10-year ARI), and 51.33 ml/min (high inflow rate, 100-year ARI). Under each inflow rate condition, three replicas were conducted.

Synthetic stormwater was prepared by the mixture of municipal tap water with NO_3^--N (KNO_3), NH_4^+-N (NH_4Cl), and TP (KH_2PO_4), and the concentrations of earlier pollutants were 5, 5, and 1 mg/L. Pollutants concentrations were set based on the average surface runoff quality of Shanghai (Han, 2015; Liu J. et. al., 2017). Synthetic stormwater was supplied by the peristaltic pump for 24 h under each rainfall intensity scenario. Outflow from the column was monitored by a tipping bucket rain gauge, which was connected with a computer that continuously works (1 min logging interval) since the pump was turned on. Water samples were collected by a borosilicate glass beaker in every 30 min since the outflow occurs, and stops when no outflow occurs from the column. Each sampling period last 15 min. The collected effluent sample was filtered with a 0.45 μm membrane filter.

Concentration of TP was determined using the ammonium molybdate spectrophotometric method, the Nessler's reagent spectrophotometry method was used to test the NH_4^+-N concentration, and the ultraviolet spectrophotometer method was applied to analyze the NO_3^--N concentration. The aforementioned methods are from Monitoring and Analysis Method of Water and Wastewater (Fourth Edition), and test procedures were conducted accordingly (MEEPRC, 2002). Event mean concentration (EMC) was used as the analytical parameter to evaluate the purification efficiency of the media. The average concentration of pollutants and the pollutant removal efficiency are calculated by the following equations:

$$EMC = \frac{\sum_{n=1}^{n} v_i \cdot c_i}{\sum_{n=1}^{n} v_i},$$

$$P = \frac{EMC_{in} - EMC_{out}}{EMC_{in}} \cdot 100\%,$$

where P is the efficiency of media pollutant removal; v_i is the total inflow/outflow volume during the sampling period (L); c_i is the pollutants concentration of inflow/outflow during the sampling period (mg/L); EMC_{in} and EMC_{out} are the mean concentrations of inflow and out flow pollutant.

During the experiment period, three rounds of experiments were conducted. In every round, each substrate was tested under different inflow rate conditions. Table 1 lists the test schedule of the first round. Schedules of round 2 (from 25th, Jan. 2021 to 12th, Mar. 2021) and round 3 (from 15th, Mar. 2021 to 13th, May. 2021) were arranged same as the first round, therefore, they were not listed here. One column was used for experiment. After

TABLE 1 Test schedule of the first round of experiment.

No. (YYYY/MM/DD)	Substrate	Rainfall intensity (inflow rate)
1 (2020/12/02)	25% Z+75% S	1a (36.5 mm/h)
2 (2020/12/05)	25% Z+75% S	10a (67.3 mm/h)
3 (2020/12/08)	25% Z+75% S	100a (98.1 mm/h)
4 (2020/12/11)	50% Z+50% S	1a (36.5 mm/h)
5 (2020/12/15)	50% Z+50% S	10a (67.3 mm/h)
6 (2020/12/18)	50% Z+50% S	100a (98.1 mm/h)
7 (2020/12/22)	25% ZHD10 + 75% S	1a (36.5 mm/h)
8 (2020/12/24)	25% ZHD10 + 75% S	10a (67.3 mm/h)
9 (2020/12/26)	25% ZHD10 + 75% S	100a (98.1 mm/h)
10 (2020/12/29)	50% ZHD10 + 50% S	1a (36.5 mm/h)
11 (2021/01/02)	50% ZHD10 + 50% S	10a (67.3 mm/h)
12 (2021/01/05)	50% ZHD10 + 50% S	100a (98.1 mm/h)
13 (2021/01/08)	25% ZHD50 + 75% S	1a (36.5 mm/h)
14 (2021/01/11)	25% ZHD50 + 75% S	10a (67.3 mm/h)
15 (2021/01/14)	25% ZHD50 + 75% S	100a (98.1 mm/h)
16 (2021/01/16)	50% ZHD50 + 50% S	1a (36.5 mm/h)
17 (2021/01/19)	50% ZHD50 + 50% S	10a (67.3 mm/h)
18 (2021/01/21)	50% ZHD50 + 50% S	100a (98.1 mm/h)

one substrate was tested under one inflow rate condition, the column was emptied, and DOWSI Cleaner and Surface Prep Solvent was used to clean the high vacuum grease on the inner surface of the column, then high pressure water cleaner was used to wash the column with tap water. Finally, O.R. towel was used to wipe the column surface dry, and the column was ready to use for the next test.

The purpose of column experiment is characterizing the effect of different influencing factors on media's stormwater regulation performance. The designed experiment has two factors with three levels (level of modification and rainfall intensity) and one factor with two levels (zeolite ratio), all possible combinations of different levels across these three factors for each response variable (runoff reduction, NO_3^--N, NH_4^+-N, and TP removal rate) were tested, the effects of each factor on the response variables were investigate, and the quantitative models between factors and response variable were established. One-way analysis of variance (ANOVA) was performed to investigate statistical significance of factors on response variable. The multivariate regression analysis was used to establish quantitative relationship between factors and response variable. The data analysis was conducted by Minitab 19 Statistical Software.

3 Results and discussion

3.1 Runoff reduction performance

Figure 3 shows the outflow rate of all media under the three tested inflow rate conditions. Table 2 lists the time of occurrence and flow rate for first flow, peak flow, and steady flow of tested media under the different inflow rate conditions. Three influencing factors examined in the experiments have significant effect on the runoff rate reduction of media with zeolite ($p < 0.05$).

When the percentage of zeolite in substrate is the same, under all inflow rate conditions, the time of the appearance of first flow, peak flow, and steady flow were reduced as the level of modification increased. For example, when zeolite ratio in substrate was 25%, under low inflow rate condition, first flow, peak flow, and steady flow of media with NZ were reached at 425 min, 731 min, and 1193 min, for media with ZHD10, these flow conditions occurred at 408 min, 606 min, and 1163 min, and for media with ZHD50, these flow conditions were reached at 361 min, 475 min, and 972 min. In terms of the outflow rate, when the same amount of zeolite was added in substrate, under all inflow rate conditions, the modification increases the outflow rate of media for first flow and steady flow, and the rates

FIGURE 3
Outflow rate variation over time of different media under different inflow rate **(A)** 25% Z+75% S, **(B)** 50% Z+50% S, **(C)** 25% ZHD10 + 75% S, **(D)** 50% ZHD10 + 50% S, **(E)** 25% ZHD50 + 75% S, and **(F)** 50% ZHD50 + 50% S.
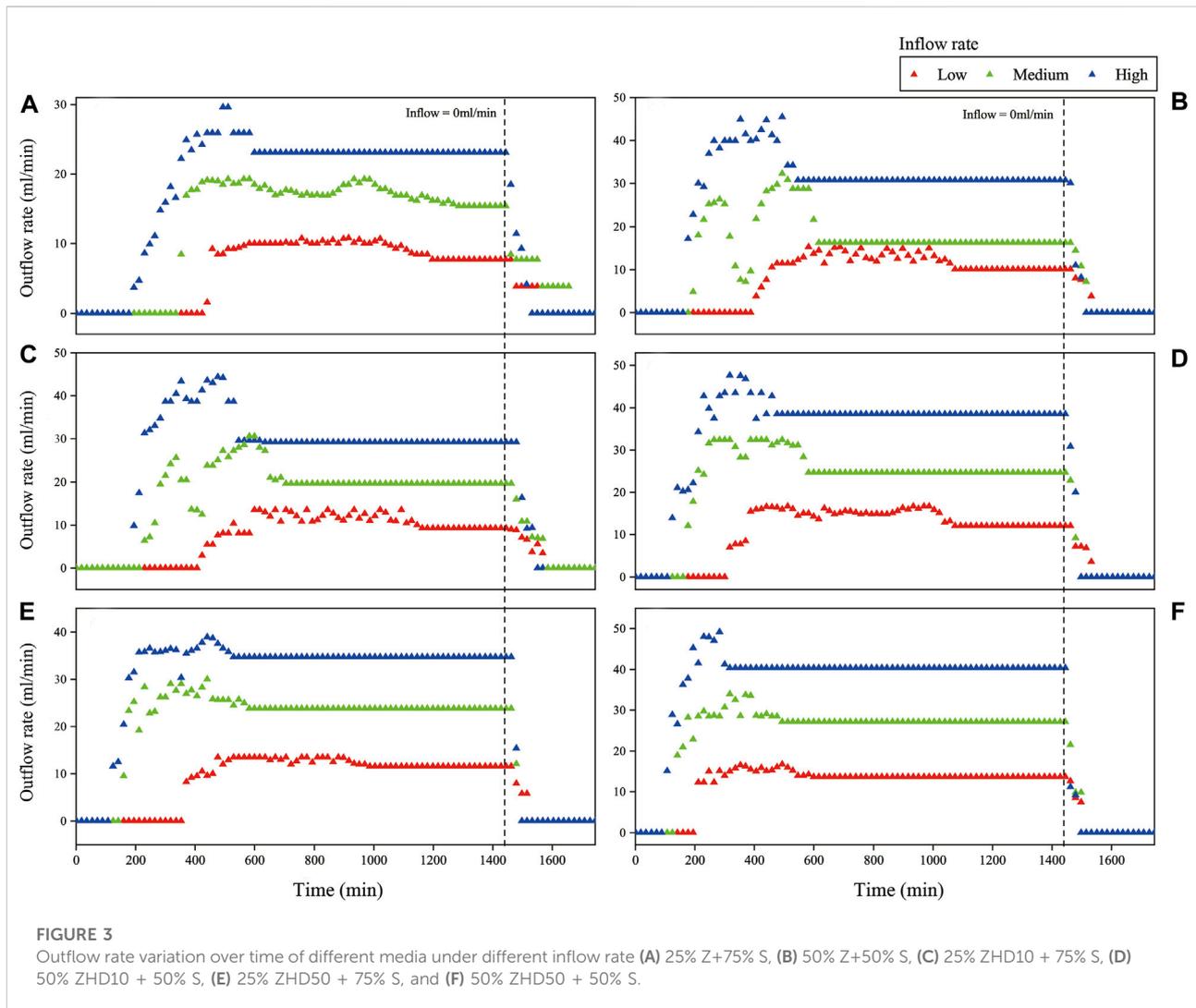
increased when the degree of modification increases. Except when the inflow rate was 37.17 ml/min, 25% zeolite was added in the media, the first flow rate of NZ, ZHD10, and ZHD50 were 8.5, 6.3, and 9.5 ml/min. This might cause by the preferential flow which was discussed later in this section. These patterns might be the results of decreased water retention ability of the media. In previous study, HDTMA modification was reported to alter the hydraulic properties of substrate media with zeolite, including WRC. Based on the effect of HDTMA modification on WRC of zeolite media, the water retention ability of media with zeolite decreases with the increased level of modification (Qin et al., 2022), lower the water retention ability, quicker the water flows through the media. In general, the HDTMA modification decreases the outflow rate reduction of the substrate with zeolite, but media with MZ could reach steady flow sooner than that of media with NZ.

The time of peak flow was reached and the peak flow rate of different media under different inflow rate did not exhibit

obvious pattern. For instance, when inflow rate was 19.17 ml/min, the peak flow rate for media with 25% of NZ, ZHD10, and ZHD50 were 10.8, 13.5, and 13.5 ml/min. For substrate with 50% zeolite ratio, under the rainfall condition of 37.17 ml/min, the peak flow rate for NZ, ZHD10, and ZHD50 were 32.4, 31.3, and 34.3 ml/min. This might be attributed to the preferential flow, which is when water transport through soil or porous materials, it would travel through the material in the path with least resistance. Under saturated condition, it mainly associates with inflow volume and flow rate, under unsaturated status, it mostly associates with pore structure and hydrophobicity of the material (Flury, 1996; Uhlenbrook, 2006; Nimmo, 2012; Beven and Germann, 2013). Despite the same procedure was applied to prepare and pack the substrates, parameters such as interaggregate pores and soil hydrophobicity of the materials cannot be maintained as the same for each experiment. For the first flow, the WRC of substrate also plays an important role in water movement, thus most of experiments demonstrated the

TABLE 2 Time of occurrence and flow rate for first flow, peak flow, and steady flow of different media under different inflow rates.

Media label	Parameter	Low inflow rate (19.17 ml/min)			Medium inflow rate (37.17 ml/min)			High inflow rate (51.33 ml/min)		
		First flow	Peak flow	Steady flow	First flow	Peak flow	Steady flow	First flow	Peak flow	Steady flow
25% Z+75% S	Time (min)	425	731	1193	347	476	1269	191	484	593
	Rate (ml/min)	1.6	10.8	7.5	8.5	19.3	15.4	3.7	29.6	23.1
50% Z+50% S	Time (min)	394	514	1067	197	427	611	162	346	533
	Rate (ml/min)	4.8	15.2	10.7	5.2	32.4	16.2	16.7	45.6	30.8
25% ZHD10	Time (min)	40	606	1163	221	455	699	184	468	633
+75% S	Rate (ml/min)	3.7	13.5	9.2	6.3	23.8	19.6	9.8	44.4	29.3
50% ZHD10	Time (min)	318	486	1096	168	399	577	115	306	491
+50% S	Rate (ml/min)	7.7	12.1	10.6	12.1	31.3	24.7	13.8	48.1	38.5
25% ZHD50	Time (min)	361	475	972	152	396	576	120	421	515
+75% S	Rate (ml/min)	8.3	13.5	11.6	9.5	30.7	23.8	11.6	39.3	34.7
50% ZHD50	Time (min)	196	306	591	128	392	488	93	243	316
+50% S	Rate (ml/min)	12.4	16.8	13.7	18.7	34.3	27.1	14.7	49.2	40.3

same pattern, and only one experiment condition did not fit in the pattern (25% zeolite ratio, medium inflow rate). As the experiment process continues, the water content in substrate had increased but yet saturated, interaggregate pores and material hydrophobicity have significant impact on water flows at this stage, due to the different pore structure and hydrophobicity in each column, preferential flow might causes the irregular peak flow rate for each set of experiment. Finally, when the media in the column reaches near saturated status, inflow volume and rate were steadily controlled, which limited the effects of preferential flow. Additionally, the preferential flow was suggested to be introduced by the bimodal pore structure of the media (Liu Y. et al., 2017a), substrate with zeolite was found to have such pore structure (Qin et al., 2022).

Under the condition of the same modification degree, with more zeolite added in the substrate, the earlier the time that first flow, peak flow, and steady flow appears, the higher the rate of these flow statuses. When material with different particle shapes and relatively larger particle size such as zeolite was mixed with soil, it would alter medias' particle size distribution, increases its K_s and decreases water retention ability (Liu and Fassman-Beck, 2016; Qin et al., 2022), which makes the velocity of water flow through the substrate positively correlated with zeolite ratio in media.

When level of modification and percentage of zeolite were fixed, with the increased rainfall intensity, the time of production for first flow, peak flow, and steady flow were reduced and flow rates were increased. Except for 25% Z+75% S, the first flow rate
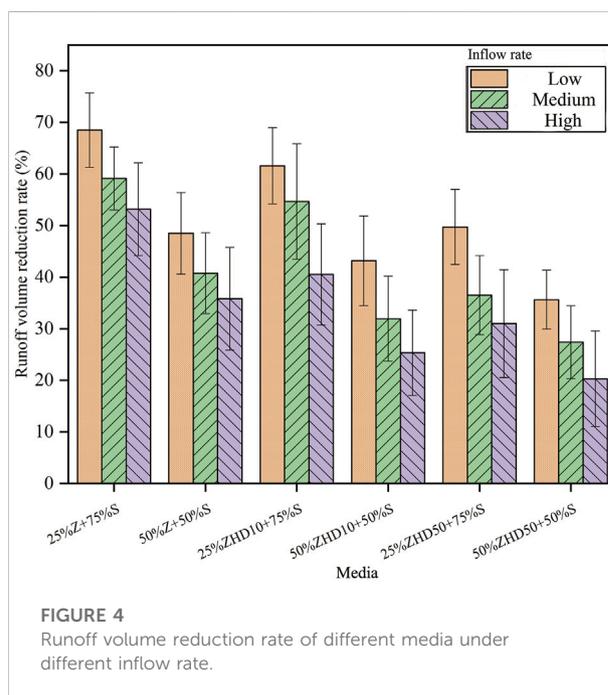
FIGURE 4
Runoff volume reduction rate of different media under different inflow rate.

of high inflow rate was the lowest (3.7 ml/min), which might be the result of preferential flow as well.

The runoff volume reduction rate is shown in Figure 4. It can be observed that three influencing factors examined in the experiments were all negatively correlated with the runoff

FIGURE 5
Removal rate of different media on different pollutants **(A)** NH_4^+-N removal rate of substrate with 25% zeolite, **(B)** NH_4^+-N removal rate of substrate with 50% zeolite, **(C)** NO_3^--N removal rate of substrate with 25% zeolite, **(D)** NO_3^--N removal rate of substrate with 50% zeolite, **(E)** TP removal rate of substrate with 25% zeolite, and **(F)** TP removal rate of substrate with 50% zeolite.
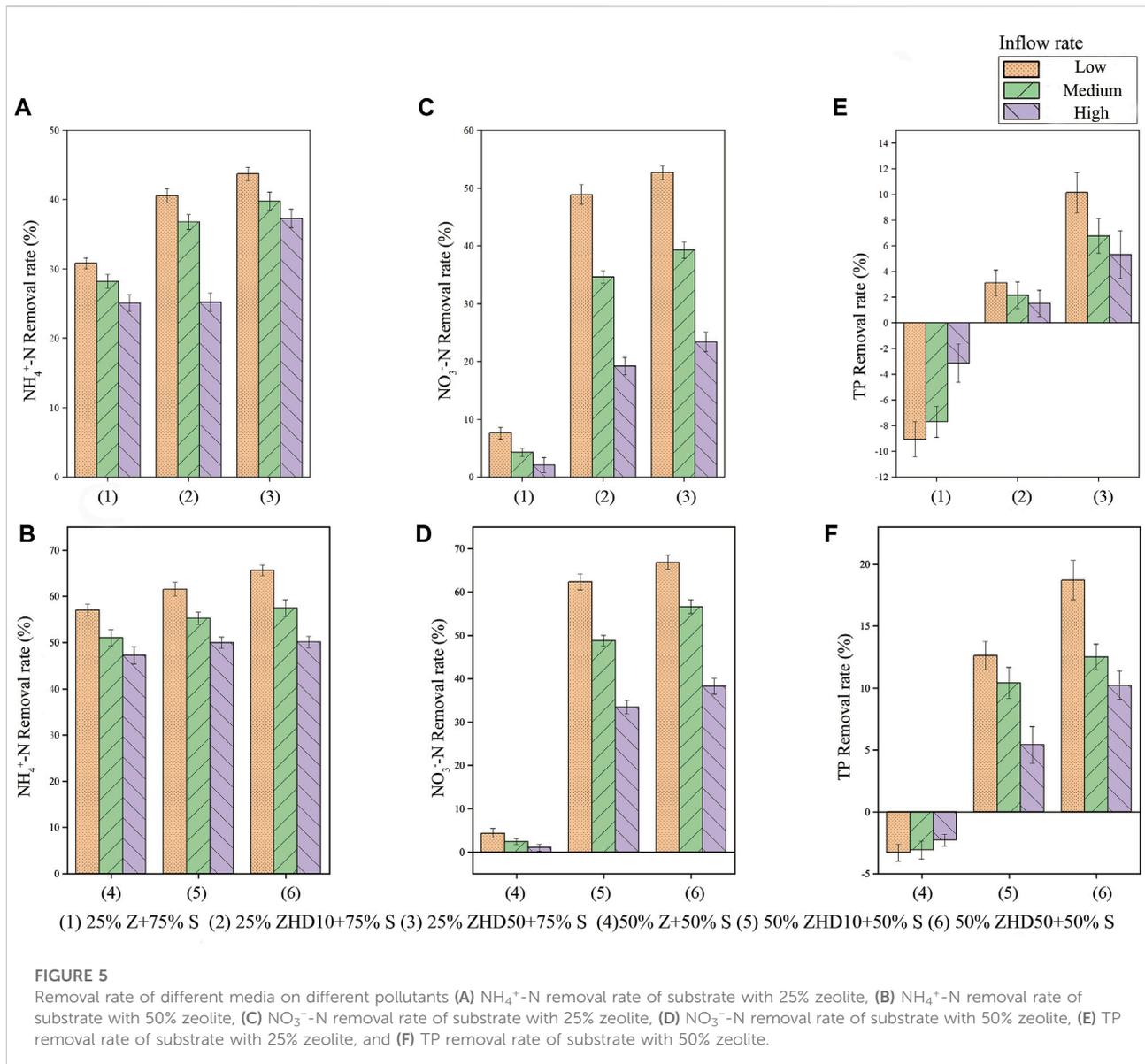
volume reduction rate of media, and the effect of these factors on media's runoff volume reduction rate were significant ($p < 0.05$). This result also is in accordance with the effect of HDTMA modification on WRC of the media with zeolite. Previous study indicates that substrates with MZ have poor water retention capacity than that of media with NZ, because of the HDTMA molecules loaded on the zeolite surface (Qin et al., 2022). The result from Figure 4 is consistent with findings in the previous study. The most significant decreases occurred when percentage of zeolite was 50%, under high inflow rate condition, the runoff volume reduction rate drops from 53.2% of NZ to 20.3% of ZHD50. The quantitative relationship between influencing factors with stormwater volume reduction rate and the

interaction between these factors were further discussed in multiple regression analysis section.

3.2 Nitrate, ammonium, and phosphorus removal performance

Figure 5 demonstrates the removal rate of different media under different inflow rare on NO_3^--N, NH_4^+-N, and TP. Three influencing factors examined in the experiments have significant effect on media's removal performance of aforementioned pollutants ($p < 0.05$). The substrate with NZ demonstrates decent removal efficiency on NH_4^+-N because of the cation exchange capacity of NZ. The MZ slightly increases the

NH_4^+-N removal ability of the substrate, because the HDTMA molecules can only load on the zeolite surface, the cation exchange property in the inner pore structure of zeolite remains intact (Nezamzadeh-Ejhieh and Raja, 2013). Additionally, during the modification process, some impurities inside the zeolite might be removed through the stirring and heating, so the removal ability of NH_4^+-N was enhanced. Moreover, loaded surfactant molecules on zeolite surface can interact with ammonium head groups (Sharafzadeh and Nezamzadeh-Ejhieh, 2015) and traps some of the NH_4^+-N molecules; therefore, the removal efficiency of NH4+-N increased as the modification degree increased.

Media with NZ barely shows removal ability for NO_3^--N, due to the negative charges carried by zeolite that make NZ not able to adsorb anionic pollutants. After the modification, the surfactant molecules loaded on zeolite surface gives MZ anionic exchange property, combined with the cation exchange capacity reserved in inner pores of zeolite, MZ can adsorb anions and cations pollutants simultaneously (Bowman, 2003; Nezamzadeh-Ejhieh and Tavakoli-Ghinani, 2014; Anari-Anaraki and Nezamzadeh-Ejhieh, 2015; Hasheminejad and Nezamzadeh-Ejhieh, 2015). As the results indicate, under all inflow rates, the modification of zeolite significantly enhances the NO_3^--N treatment performance of media. For instance, when percentage of zeolite was 25%, under low inflow rate condition, the removal rate for NO_3^--N increases from 7.6% (NZ) to 48.91% (ZHD10) and 52.7% (ZHD50). Positive correlation was found between NO_3^--N removal rate and level of modification. However, the degree of improvement is not high, given the fact that nearly twice of HDTMA molecules loaded on ZHD50 (0.09meq/g) than that of ZHD10 (0.05meq/g). This might attribute to some anions substances contained in the peat soil. When MZ and peat soil was mixed together and soaked in the water, some of the anions exchanged with cationic groups on the MZ surface, thus the improvement from the increased modification degree was relatively small.

As for TP removal, leaching of phosphorus was observed during the experiment when media with NZ was tested, which was up to 9.1% when percentage of zeolite was 25% under the low inflow rate condition. This phenomenon is common in the bioretention column study of non-vegetated substrate media (Hatt et al., 2009; Liu and Davis, 2014; Li et al., 2016), attribute to the phosphorus brought by the soil in the substrate. Without the plant uptake, phosphorus would leach from the column when other materials in the substrate have limited phosphorus removal efficiency. Phosphorus in the synthetic stormwater was dissolved phosphate, which is also anion pollutant like NO_3^--N, therefore, positive correlation was found between level of modification and TP removal rate as well. However, the effect of MZ on TP adsorption improvement was not as notable as that of NO_3^--N removal. For example, in substrate with 50% zeolite, under medium inflow rate, TP removal rate increased by 2.2% from ZHD10 to ZHD50, while NO_3^--N removal efficiency raised by

7.9% from ZHD10 to ZHD50. This is because when phosphorus and NO_3^--N were removed by MZ simultaneously, MZ would adsorb NO_3^--N molecules preferentially (Li et al., 2017).

The percentage of zeolite in substrate was positively correlated with NO_3^--N, NH_4^+-N, and TP removal rate, while negative correlation was found between rainfall intensities and the removal of these pollutants. In terms of pollutants removal, zeolite act as modifier in the substrate, it enhances the pollutants removal performance of substrate, therefore, with more zeolite used in the substrate, higher the pollutants removal rate of the media. Under the low inflow rate, highest NO_3^--N, NH_4^+-N, and TP removal efficiency were reached when substrate contain 50% of ZHD50, which were 65.3%, 65.6%, and 18.7%, respectively.

As the inflow rate increases, the velocity of water flow through media increments, thus the time for zeolite to adsorb pollutants was shorten, and stability for the adsorption process was comprised, the removal efficiency of substrate on all pollutants decreases consequently. However, when NZ was used in substrate, more phosphorus leached from the substrate as the inflow rate decreased, possibly because more phosphorus from the peat soil could be dissolved in water when water move through media slows down.

3.3 Relationship between influence factors and stormwater regulation performance

A total of 54 set of experiments data from column studies were used to conduct multiple regression analysis between influencing factors and response variables, with the objective to establish quantitative relationship model between level of modification (represented by amount of HDTMA molecules loaded on zeolite surface), percentage of zeolite in substrate, rainfall intensity (represented by the inflow rate), and substrate stormwater regulation performance. The main effect plot and influencing factor interaction plot were generate based on fitted means using the least squares model. The quantitative relationships are shown in following formulas:

$$R_r = 108.74 - 0.662I - 0.8826Z - 394.9M + 5.04ZM \ (R^2 = 0.892),$$

$$R_p(NO_3) = 7.46 - 0.066I - 0.034Z + 1066M - 5908M^2 - 9.16IM + 7.42ZM \ (R^2 = 0.798),$$

$$R_p(NH_4) = 22.66 - 0.3715I + 0.7729Z + 70M \ (R^2 = 0.805),$$

$$R_p(TP) = 0.0866I + 0.2372Z + 333.1M - 4.05IM - 15.95 \ (R^2 = 0.793),$$

where R_r is the runoff volume reduction rate (%); R_p (NO_3), R_p (NH_4), and R_p (TP) are the removal rate of NO_3^--N, NH_4^+-N, and

FIGURE 6
Main effect plot for different response variables **(A)** main effect plot for NH₄⁺-N removal rate, **(B)** main effect plot for NO₃⁻ removal rate, **(C)** main effect plot for runoff volume reduction, and **(D)** main effect plot for TP removal rate.
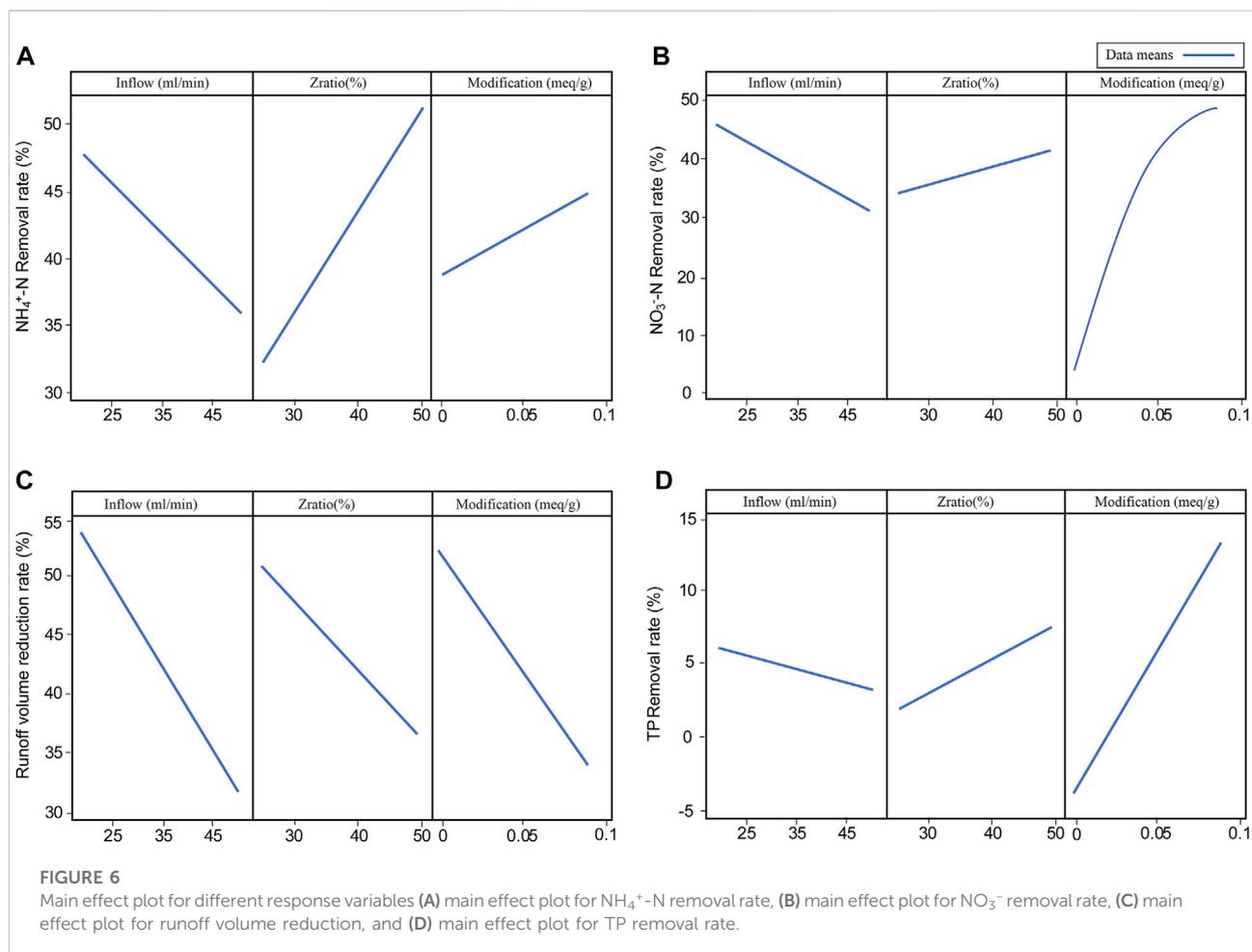
TP (%); I is the inflow rate (ml/min); Z is zeolite ratio in substrate (%); M is the amount of HDTMA molecules loaded on the zeolite surface (meq/g); R^2 is the coefficient of determination.

Figure 6 is the main effect plot of different response factors, which can be used to examine the levels of effect of influencing factors on response variables. The main effects plot graphs the response mean for each factor level connected by a line, levels of effect could be determined based on the slope of the line. Ratio of zeolite to the peat soil (Zratio) and level of modification of zeolite (Modification) were positively correlated with NO₃⁻-N, NH₄⁺-N, and TP removal rate, inflow rate (Inflow) was negatively correlated with the removal rate of these pollutants. All three factors were negatively correlated with the runoff volume reduction rate. The level of effect of different influencing factors on response variables are: (1) Zratio > Inflow > Modification for NH₄⁺-N removal rate; (2) Modification > Inflow > Zratio for NO₃⁻-N removal rate; (3) Modification > Zratio > Inflow for TP removal rate; and (4) Inflow > Modification > Zratio for the runoff volume reduction rate. HDTMA modification of zeolite has notable effect on all four response variables. When MZ is being considered as substrate material, its positive effect on water quality improvement and

negative impact on water quantity control should both be taken into account. Additionally, the level of effect of Modification on NO₃⁻-N removal rate reached the top when the amount of HDTMA molecules loaded on the zeolite surface was 0.09meq/g (ZHD50%), which means when the modification level of zeolite is beyond 50% of zeolite's CEC value, increasing modification degree of zeolite would no longer improves the NO₃⁻-N removal performance of substrate.

Figure 7 shows the influencing factor interaction plot of different response variables. The effect of interaction between influencing factors exists on the runoff volume reduction rate, the TP removal rate, and the NO₃⁻-N removal rate, no effect of interaction between influencing factors on the NH₄⁺-N removal rate was found, which can also be observed from the relationship models. The interaction between Zratio and Modification suggests that when more zeolite with higher level of modification was added in the substrate, less runoff could be intercept by the substrate, but higher removal efficiency on NO₃⁻-N could be achieved. The effect of interaction between Zratio and Modification was not found on the TP removal rate, probably due to the preferential adsorption of MZ on NO₃⁻-N.

FIGURE 7
Influencing factor interaction plot of **(A)** runoff volume reduction rate, **(B)** TP removal rate, and **(C)** NO_3^--N removal rate.
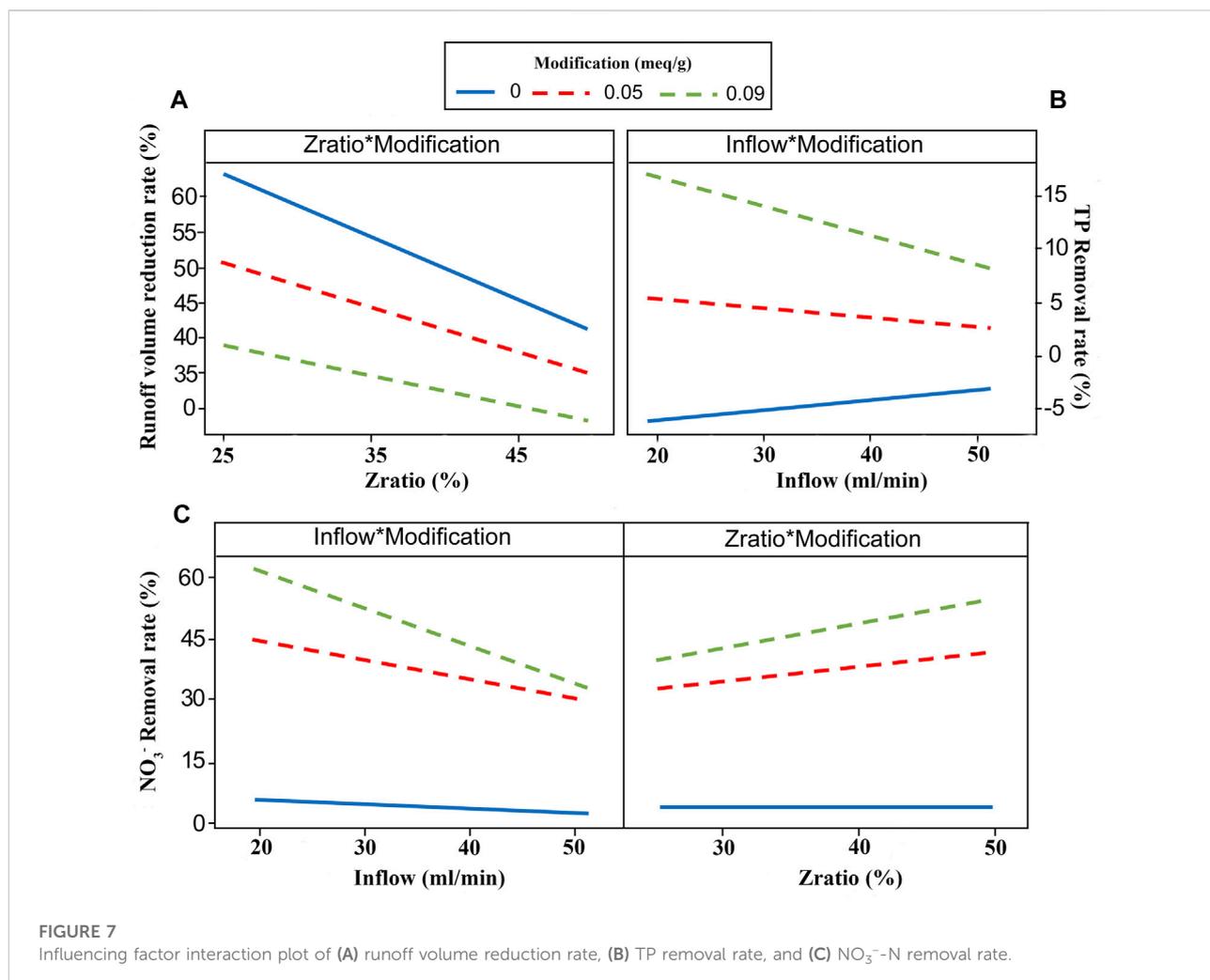
When most of the adsorption capacity of MZ on anionic pollutants was occupied by NO_3^--N, the interaction between substrate factors did not exhibit statistical impact on the TP removal rate. The interaction between Inflow and Modification appease to affect the TP and NO_3^--N adsorption performance, increased level of modification could mitigate the decline in TP and NO_3^--N removal rate of substrate as inflow rate raised, and with the increase of inflow, the improvement effect of increasing modification degree decreased.

4 Conclusion

This research has shown that HDTMA modification of zeolite could increases the NO_3^--N, NH_4^+-N, and TP removal rate of bioretention media with zeolite. Under different conditions, removal performance of NO_3^--N for media with MZ were 6.4–38.2 times than that of NZ, and NH_4^+-N removal rate increased by 1–1.5 times through the modification. The

modification improves the phosphorus adsorption ability of media, but not as notable as that of NO_3^--N adsorption. The highest TP removal rate was 18.7% ,while highest NO_3^-N removal rates was 65.3%. Percentage of zeolite and level of modification were found positively correlated with the removal rate beyond pollutants, while negative correlation was found between the inflow rate and pollutants removal efficiency. However, the modification was proved to reduce the reduction rate on runoff volume and outflow rate, because of the decreased water retention ability of media caused by the modification. Therefore, when hydrological regulation is the main control objective of the bioretention system, the negative effect of HDTMA-modified zeolite should be considered. In terms of outflow of the substrate, preferential flow was suggested to affect the time of peak flow was reached and peak flow rate, caused irregular fluctuation of peak flow status. Quantitative relationship model (R^2>0.793) among influencing factors, hydrological and pollutants treatment performance was given, which can be useful for modeling and predicting the performance of the bioretention

system, and for designing substrate media. Level of modification was found to have the most significant effect on NO_3^--N and TP removal rate of substrate. The inflow rate was negatively correlated with removal efficiency of all three pollutants, but the increases of modification level was found to reduces the decrease of NO_3^--N and TP adsorption efficiency while the inflow rate increases. Additionally, when loading amount of HDTMA molecules on zeolites exceeds 0.09meq/mg, increasing modification level cannot improve the removal efficiency of NO_3^--N. The results from column experiment cannot represent the actual behavior of bioretention media with MZ in field application. Therefore, filed experiment for substrate with HDTMA-modified zeolite is needed, as well as long-term monitoring of its performance, for in-depth evaluation of zeolite substrate performance under service condition and model validation.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

YQ developed the experiment procedures, collected and analyzed the data, and led the writing of the manuscript. MC and SL provided advice and background on zeolite modification and participated in the column experiments. YF contributed to the data analysis and modeling. XL and JQ reviewed and revised the manuscript and supervised the research project. All authors contributed to the design, implementation, and writing of the manuscript.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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