

Design and operation of submerged layer in bioretention for enhanced nitrate removal

Junyu Zhang , Rajendra Prasad Singh , Yunzhe Liu and Dafang Fu 

ABSTRACT

Bioretention, initially designed for treating discontinuous runoff pollution, faces considerable challenges in its trade-off between the hydraulic retention time (HRT) and its treatment capacity. In this study, six enhanced submerged media together with four HRTs were designed for bioretention cells to treat the highly nitrogenous river water in Tai lake basin in Yangtze River delta, China. Results revealed that bioretention with activated carbon has the highest removal of nitrate (NO_3^- -N) (93–96%) compared with surfactant-modified activated carbon (SMAC), surfactant-modified zeolite (SMZ), zeolite, fly ash and ceramsite. Although the SMAC had the best absorption for NO_3^- -N and could desorb NO_3^- -N when its concentration was low in the submerged layer, the desorbed surfactant could inhibit the growth of denitrifying bacteria, which leads to low removal efficiency (49–66%). The dynamic balancing of NO_3^- -N desorption and denitrifying system restrain in the SMAC device was observed and explained. The best activated carbon-gravel proportion in the submerged layer was 1:1 (150 mm). Such design could ensure the stable and efficient NO_3^- -N removal rate (93–94%) under high inflow concentration (28.9 mg/L) and high hydraulic loading (8.2 cm/h).

Key words | bioretention, NO_3^- -N, river treatment, submerged zone, surfactant modification, Tai lake basin

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INTRODUCTION

Due to the continuous deterioration of the water environment across China, the government carried out the action plan for 'Prevention and Control of Water Pollution' in 2015 to enhance the efforts for water quality improvement towards a long-term national strategy. This action plan aimed to restore all the contaminated water bodies in the Yangtze River delta by 2020. However, the inflowing rivers and tributaries of Tai lake (a major freshwater resource in the Yangtze River delta) are facing serious problems with pollution. Most of these rivers would not meet the National Standard for Surface Water Quality of China, especially on the total nitrogen (TN) (She *et al.* 2017; Tao *et al.* 2018). The annual average TN concentration

for the 15 inflowing rivers ranges from 4.5 to 6.0 mg/L, which is 2–3 times the minimum standard, and 70–92% of the TN is composed of dissolved nitrogen (DN), in which 41–77% is NO_3^- -N.

Bioretention systems have been studied and applied for removing pollutants, such as nitrogen, from runoff since the 1990s (Liu *et al.* 2014). The removal of ammonia nitrogen (NH_3 -N) is mainly through adsorption or ion exchange in the soil and filler. Reports indicated that a regular bioretention system can remove 60–90% of NH_3 -N (Davis *et al.* 2001; Bratieres *et al.* 2008; Hunt *et al.* 2008; Zinger *et al.* 2013) and 45–75% of total kjeldahl nitrogen (Davis *et al.* 2001). The removal of NO_3^- -N was generally poor, ranging from –4.7

to 24% due to its non-absorbability by the filler as well as the transformation from ammonia and organo-nitrogen between rainfall events (Davis *et al.* 2001; Kim *et al.* 2003; Hunt *et al.* 2008). Kim *et al.* (2003) conducted a study on the design of the submerged anaerobic zone (SAZ) and noted that bioretention systems with SAZ could remove 70–80% of NO_3^- -N while the pre-added carbon source could ideally last 20 years. Further studies also proved that SAZ can provide a suitable environment for denitrifying bacteria and significantly improve the NO_3^- -N removal rate (Ming & Chan 2012; Palmer *et al.* 2013). A recent study has also proved that most of the NO_3^- -N from the inflow as well as that transformed from NH_4^+ -N will be retained in SAZ.

However, SAZ also has negative impacts for bioretention systems. The anaerobic environment in the system will cause the leaching of phosphorus due to the pre-added carbon source (Zinger *et al.* 2013) or transformation of the undissolved phosphorus into dissolved ones (Correll 1998; Clark & Pitt 2012). The anaerobic zone also slows down the process of ammonification of organo-nitrogen as well as nitrification of ammonia (Zinger *et al.* 2007, 2013; Li *et al.* 2014; Ribas *et al.* 2015). Therefore, the removal rate of NH_4^+ -N and organo-nitrogen is reduced to some extent. Nevertheless, the bioretention systems, especially those with SAZ, is originally designed for treating runoff, which takes advantage of the interval between two events to biodegrade or biologically uptake the nitrogen (N) (Davis *et al.* 2006, 2009; Palmer *et al.* 2013). Earlier studies suggested the capacity of removing NO_3^- -N in the inflow water mainly depends on the size and hydraulic retention time (HRT) of SAZ, as the free-state NO_3^- -N does not absorb on traditional bioretention media nor natural soil (Kim *et al.* 2003; Zinger *et al.* 2007; Blecken *et al.* 2009; Passeport *et al.* 2009; Lucas *et al.* 2010; Chen *et al.* 2013; Lefevre *et al.* 2015; Lynn *et al.* 2015). Therefore, to design a bioretention system for treating polluted rivers in Tai lake basin, the major challenge lies in the balance between HRT and treatment capacity. There are many well established evaluation methods available regarding bioretention design as the optimization of HRT or nitrogen removal capacity in the submerged layer has been investigated by many researchers.

This study is aimed at finding a practical long-term treatment method for the high nitrate river water in the Taihu basin other than traditional emergency methods

(e.g. water diversion) or short-term methods (e.g. sediment dredging). The following work has been conducted: (1) selection and modification of six filter media in the submerged layer to provide NO_3^- -N immobilization, enabling efficiency and continuous NO_3^- -N removal; (2) monitor both the long-term and single-event performance to select the best modified filler; (3) monitor the vertical diversity of NO_3^- -N removal performance to optimize the bioretention structure design; (4) monitor the performance under different hydraulic loadings to analyze the feasibility of treating river water using bioretention systems.

MATERIAL AND METHODS

Experimental device

In order to compare the performance of bioretention cells under different design features, a parallel experiment was carried out by designing and constructing a series of bioretention units, as shown in Figure 1. These units were created using polyvinyl chloride (PVC) tubes (250 mm in diameter, 1,200 mm in height, and 10 mm in thickness). The overflow outlet was set at 100 mm from the top (valve A) while the outlets were set at 0 and 450 mm from the bottom (valve E and valve F). Three sampling outlets were set at the height of 250, 500 and 700 mm from the bottom (valve D, valve C and valve B, respectively). Two transparent glass ports were placed at valve B and C for the piezometer.

Filter media

The detailed design of bioretention cells varied from case to case while the basic structure always stays the same and the size of each layer remains in a certain range. Thus, referring to current design guidelines could ensure the performance comparison with existing guidelines as there is no excessive difference in design. The experimental devices in this study were designed to be a typical bioretention system with a SAZ of 450 mm depth. The filter media was chosen from locally available materials and overlaid according to the design guidelines (Hatt *et al.* 2009). The setting of layers and composition of filler materials are presented in Tables 1 and 2. A mixture of 150 g wood shavings and 150 g recycled

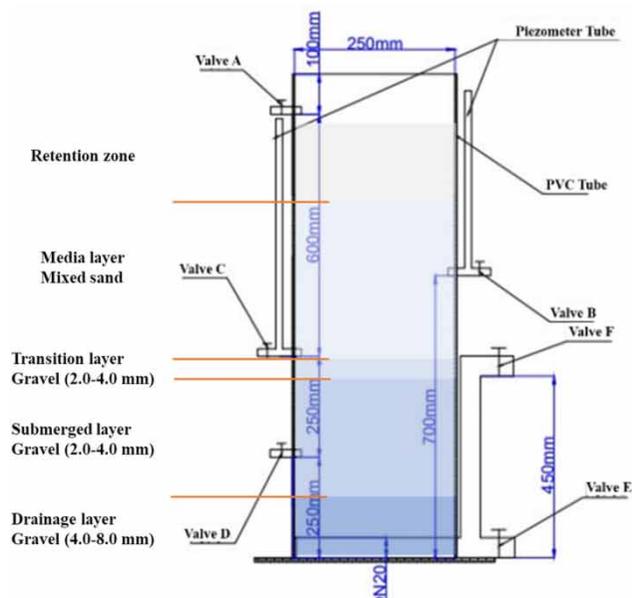


Figure 1 | Schematic design of bioretention unit.

newspaper was added in the submerged layer for extra carbon source.

Inflow water

As the concentration of pollutants in the river fluctuate dramatically across the year, it is very difficult to collect and store natural river water for the experiment. Therefore, the inflow water of the system was prepared by mixing

pollutants with tap water according to a given concentration (Table 3). To ensure the reliability of the result, these standards were determined by investigating the highest annual average value of each indicator in all inflowing rivers in Tai lake basin.

Filler modification

According to existing studies, six NO_3^- -N removal enhanced media were selected in this study due to their promising removal capacities in wastewater/runoff treatment: activated carbon (AC), surfactant-modified activated carbon (SMAC) (Choi *et al.* 2008, 2009; Hong *et al.* 2008), zeolites, surfactant-modified zeolites (SMZ) (Haggerty & Bowman 1994; Li 2003; Schick *et al.* 2010), fly ash, and ceramsite. The adoption of these media from literature could form a reliable base of modification options as well as offer comparability of results to existing studies.

A lab-scale application was primarily carried out to select feasible media for further experiments. The number of test sets was determined based on the minimum and maximum dosage as well as common intervals in the literature. Following the existing studies (Choi *et al.* 2008, 2009; Hong *et al.* 2008; Sarina *et al.* 2010), the SMAC used in this study was made up of particle activated carbon (2.0–4.0 mm) modified by cetylpyridinium chloride (CPC). Eight sets of SMAC: (1) for each set, 15 g activated carbon and 45 mL deionized water were added into a 250 mL conical flask; (2) 3.0, 6.0, 9.0, and 12.0 mmol technically pure CPC and analytically pure CPC were added into eight flasks, respectively (CPC concentration: 200, 400, 600, and 800 mmol/kg activated carbon); (3) the flasks were sealed and vibrated in a vapor-bathing vibrator at 150 r/min under 30 °C for 24 h; (4) the mixture in each flask was centrifuged at 4,000 r/min for 30 min to separate the solid and liquid; (5) the remaining solid was washed with deionized water repeatedly until no precipitate emerged when testing with AgNO_3 ; (6) the SMACs were dried at 60 °C for 12 h.

The SMZ used in this study was made up of zeolites (2.0–4.0 mm) modified by Hexadecyl trimethyl ammonium Bromide (HDTMA) according to existing studies (Haggerty & Bowman 1994; Li 2003; Schick *et al.* 2010). Twelve sets of SMZ were prepared: (1) for each set, 10 g zeolites and

Table 1 | Physical properties of filling materials

Layer	Depth (mm)	Filler	
		Traditional	Enhanced
Retention zone	200	–	–
Media layer	400	Mixed sand	
Transition layer	50	Gravel (1.0–2.0 mm)	
Submerged layer	300	Gravel (2.0–4.0 mm)	100 mm enhanced filler (2.0–4.0 mm) 200 mm gravel (2.0–4.0 mm)
Drainage layer	150	Gravel (4.0–8.0 mm)	

Table 2 | Composition of mixed sand in media layer

Particle size (mm)	< 0.15	0.15–0.30	0.30–0.55	0.55–1.00	1.00–2.00
Mass ratio	5%	10%	35%	35%	10%

45 mL deionized water were added into a 250 mL conical flask; (2) 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 mmol technically pure HDTMA and analytically pure HDTMA were added into the 12 flasks, respectively (HDTMA concentration: 100, 150, 200, 300, 400, and 500 mmol/kg zeolites); (3) the flasks were sealed and vibrated in a vapor-bathing vibrator at 150 r/min at 30 °C for 24 h; (4) the mixture in each flask was centrifuged at 4,000 r/min for 30 min to separate the solid and liquid; (5) the remaining solid with deionized water was washed 10 times; (6) the SMZs were dried at 60 °C for 12 h.

Filler selection

Enhanced filler selection

The performance of the modified fillers was tested and compared to determine the better modified pattern for different

fillers. The experiment was carried out under the following procedures: (1) 1 g modified filler was added into a conical flask together with 20 mL standard potassium nitrate (KNO₃) solution (100 mg/L); (2) the flasks were sealed and vibrated in a vapor-bathing vibrator at 150 r/min at 30 °C for 24 h; (3) the supernatant was collected and the concentration of NO₃⁻-N was measured through ultraviolet (UV) spectrophotometry, the best performed SMAC and SMZ were selected as the candidate fillers. The performance of all fillers was tested and compared following the procedures as above. The better performed fillers were adopted in the practical experiments.

Performance of pollutant removal

After selecting the enhanced filler, the bioretention units were built according to Tables 1 and 2. The following preconditioning process was carried out to stabilize the structure of each layer as well as the properties of media, and to initiate the microbial community in the units. (1) The units were flushed with tap water four times per day for 7 days to simulate the saturation process during operation, as well as to precipitate fillers in each

Table 3 | Pollutant concentration in inflow water and monitoring method

Indicator	Target concentration (mg/L)	Source	Quantity (mg/L)	Monitoring method
COD	8	Glucose	8	Acidic potassium permanganate method
TN	8	–	–	UV spectrophotometry
ON (organic nitrogen)	1.6	C ₆ H ₅ O ₂ N	14.07	
NH ₄ ⁺ -N	2.4	NH ₄ Cl	9.17	Nessler's reagent colorimetry
NO ₃ ⁻ -N	4	KNO ₃	28.89	UV spectrophotometry
TP	0.4	KH ₂ PO ₄	1.76	Phosphovanadomolybdate spectrophotometric method

layer to ensure stable structure in the following experiments and to wash out the salt and unsteady organics in the media. (2) The units were saturated with natural river water, which would be kept in the units for 48 h and drained out before the next saturation. The process was repeated for 2 weeks to initiate the relevant microbial community.

The long term performance of the bioretention units was monitored by the following procedure. (1) Units were saturated with inflow water (room temperature, 10–20 °C). The inflow rate (peristaltic pump) and the outflow rate (valve F) were adjusted to 4 L/h. (2) Systems were kept running while the outflow water quality was being monitored, the systems were stopped until the water quality remained stable for 4 h. (3) The experiments were repeated once or twice a week for 7 weeks.

Extra samples were taken during weeks 1, 3 and 7 to investigate the vertical diversity of NO_3^- -N removal in the units. The samples were taken at the end of each experiment, from inflow, valve B, C, D and E (200, 400, 650, and 900 mm, respectively, from the surface of media layer).

Optimization of design and operation

After the selection of the best filler, the design of SAZ composition as well as the operation pattern were investigated by evaluating the system performance of bioretention units with various proportions of enhanced filler (Table 4) in SAZ under different hydraulic loading (4, 6, 8, and 12 L/h). After considering the similar preconditioning process mentioned in the section ‘Performance of pollutant removal’, the following procedures were carried out for the optimization of system operation: (1) the outflow valve F was fully opened to prevent saturation in media layer, providing the environment for the aerobic reaction; (2) the units were operated under a hydraulic loading of 4 L/h for 24 h and stopped for 48 h, and repeated five times to allow for system stabilization and adaptation of

the microbial communities to such a loading environment; (3) the units were operated under 4 L/h loading for 24 h, and the outflow water quality was monitored during the experiment; and (4) the hydraulic loading was adjusted and steps 1–3 were repeated.

RESULTS AND DISCUSSION

Enhanced filler selection

The NO_3^- -N removal capacity of the eight sets of SMACs and 12 sets of SMZs was first investigated to determine the better modifying pattern for activated carbon and zeolites (Figure 2). For SMAC, the non-modified activated

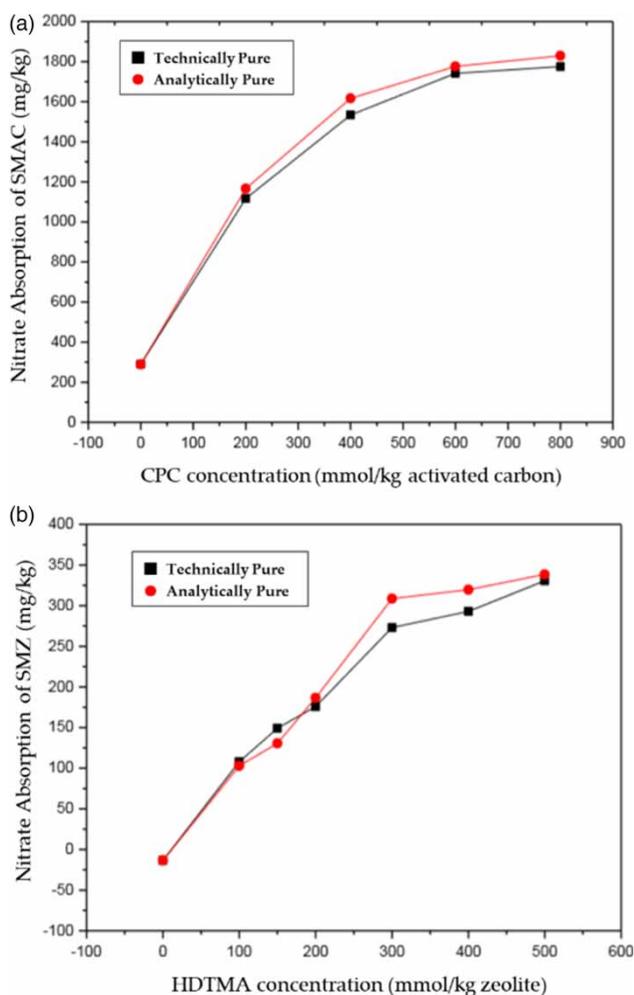


Figure 2 | NO_3^- -N absorption capacity for different modifier concentrations: (a) activated carbon modified by CPC; (b) zeolite modified by HDTMA).

Table 4 | Composition of submerged layer

Layer	Media	Composition			
		A (mm)	B (mm)	C (mm)	D (mm)
Submerged layer	Enhanced filler	50	100	150	200
	Gravel	250	200	150	100

carbon has an NO_3^- -N absorption capacity of 290 mg/kg. The capacity rises dramatically with the CPC concentration increasing from 0 to 400 mmol/kg and gradually declined after 400 mmol/kg. The improvement of NO_3^- -N absorption from 600 to 800 mmol/kg was only 30 mg/kg (1.7%). The difference between modification by technically pure and analytically pure modifier was less than 85 mg/kg (5.6%). Thus, the efficient pattern of SMAC modification was 600 mmol technically pure CPC/kg activated carbon.

For SMZ, the non-modified zeolite has no NO_3^- -N absorption capacity. The SMZs modified by analytically pure HDTMA perform better than those modified by technically pure HDTMA in most cases. For SMZs modified by analytically pure HDTMA, their capacity enhanced dramatically with the modifier concentration increasing from 0 to 300 mmol/kg and gradually slowed down after 300 mmol/kg. The improvement of NO_3^- -N absorption from 300 to 500 mmol/kg was only 23 mg/kg (7.3%). Thus, the efficient pattern of SMZ modification was of 300 mmol analytically pure HDTMA/kg zeolite.

After determining the efficient modification pattern of SMAC and SMZ, the NO_3^- -N absorption capacities of fillers were analyzed. As shown in Figure 3, SMAC has the highest absorption capacity (1,742 mg/kg) which was more than five times compared to the second ranked SMZ (311 mg/kg) and the third ranked activated carbon (290 mg/kg). The remaining three fillers have very limited capacity in NO_3^- -N absorption. The result suggests higher absorption capacity of SMAC compared to SMZ, which is

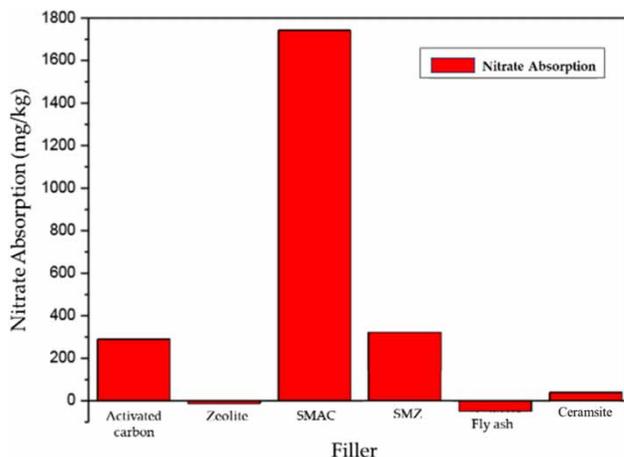


Figure 3 | NO_3^- -N absorption capacity for different enhanced fillers.

consistent with existing studies (Li 2003; Schick *et al.* 2010). Compared to previous studies, the SMAC and SMZ modified in the study have a lower capacity of NO_3^- -N absorption capacity, which may be due to the larger particle size, smaller specific surface area, as well as higher pollutant concentration. Based on the absorption capacity, the SMAC, SMZ, activated carbon and zeolite (as compared to SMZ) were selected as the potential enhanced filler for further operation and experiments.

Performance of bioretention units

Five bioretention units were built with the traditional sand filler and four enhanced fillers were selected after evaluation of their performance in primary stage experiments. Long-term performance as well as single-event performance of the units at the end of the experiment was investigated (Figure 4). At the initial stage, the SMAC device had the highest NO_3^- -N removal efficiency (71%) while the other four devices had very poor performance (non-modified: 18%; zeolite: 16%; activated carbon: 32%; and SMZ: 12%). Such a difference could be due to the extraordinary absorption capacity of SMAC. The results show that after the 3-week preconditioning, SMAC units still had the capacity for effective removal of NO_3^- -N.

With time, denitrification processes in the devices gradually occurred and stabilized at week 3. The NO_3^- -N removal efficiency of SMAC device continuously decreased and reached 37% at day 21, while the other four devices had significant improvement on their performance (non-modified: 69%; zeolite: 52%; activated carbon: 73%; and SMZ: 29%). The decrease in performance of the SMAC device suggests that the high removal capacity at the initial stage was mainly due to the absorption of SMAC rather than denitrification. Notably, the modified fillers performed poorer than the non-modified fillers and the non-enhanced filler. The possible reason for such a phenomena may be the existence of cationic surfactant in the submerged area coming from the residual or desorb of the modifier which could restrain the denitrification process (Schick *et al.* 2010) in the submerged area. In this case, although the modified fillers can desorb the NO_3^- -N during the operation interval, it could hardly be removed. Thus, the modified

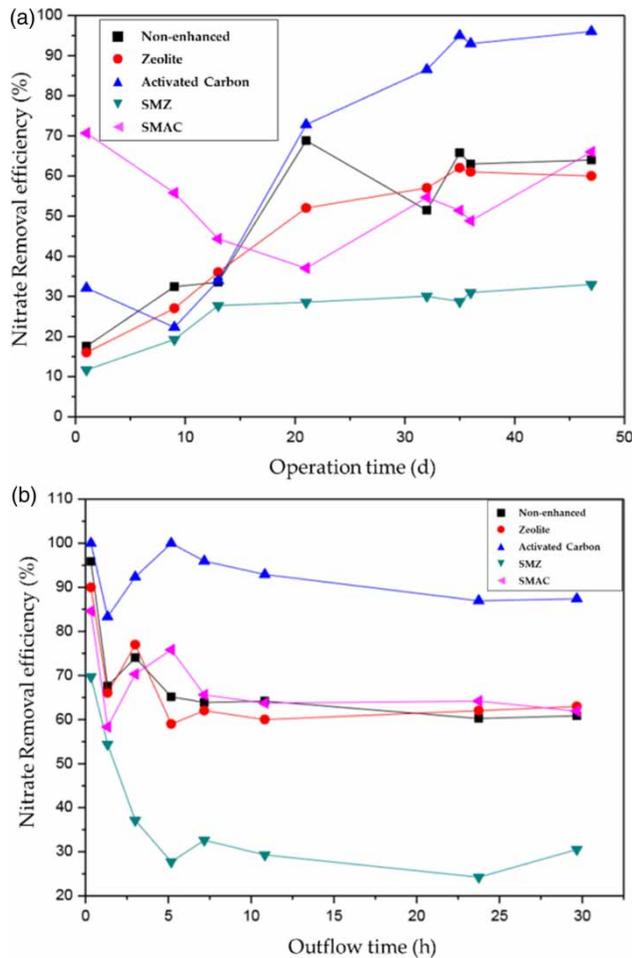


Figure 4 | NO_3^- -N removal performance for candidate fillers: (a) long-term performance and (b) single event performance at week 7.

fillers could not provide satisfying performance due to the restrain of denitrification from modifiers.

At the later stage, the well-developed denitrification processes resulted in the stable performance of five devices. The activated carbon device had the highest NO_3^- -N removal efficiency (93–96%) while the non-enhanced, SMAC and the zeolite device could remove 60–66% of the inflow NO_3^- -N. The SMZ had the lowest performance since the beginning of the experiment and the final removal efficiency was only 29–33%. The SMAC device suffered a dramatic decrease on removal efficiency where its removal efficiency fluctuated and increased throughout the experiment period. According to the denitrification restrain phenomena (Schick *et al.* 2010), the reason for such fluctuations could be explained as follows. (1) Operation of the

unit could flush out the dissolved surfactant which stopped restraining the denitrification process. (2) After the SMAC turned saturated, desorption may happen and the desorbed NO_3^- -N could be denitrified in the submerged area. Desorption offers more absorption capacity in the next operation which made the NO_3^- -N removal efficiency rise again. (3) With enhancement in the denitrification process, more NO_3^- -N could desorb in one operation interval, which could enhance the surfactant desorption into the submerged area. This again restrained the denitrification system and reduced the NO_3^- -N removal efficiency. Such processes will repeat until no more surfactant could be desorbed, and the final performance of the SMAC device will be the same as the activated carbon device (Schick *et al.* 2010).

The stabilized performance of the non-modified cell (63% removal) was consistent with existing studies (Randall & Bradford 2013), which indicates the NO_3^- -N remove rate of traditional sand mix bioretention cells ranging at $62.7 \pm 18.8\%$. Considering the material of the stabilized performance of SMZ cells (33%), zeolite cells (60%) and SMZ cells (66%) were also consistent with the earlier findings ($-118.0 \pm 55.6\%$) for sorbtive cells (Randall & Bradford 2013). While considering the cell structure, these cells performed relatively weakly compared to traditional anoxic cells ($99.3 \pm 0.55\%$). The difference was caused by the running pattern where the performance system proposed in this section was monitored under continuous operation, which is not a strictly anoxic environment, while Randall & Bradford (2013) monitored their anoxic cells 24 hours after operation, which offered a sufficient anoxic environment for denitrification.

Notably, the activated carbon cells showed far better performance (96% removal efficiency) compared to the sorbtive cells in this study as well as in the literature. The extraordinary performance may be due to the high specific surface area of activated carbon which offered preferred conditions for simultaneous nitrification and denitrification (Mousavi *et al.* 2012). This may be due to the higher specific surface area of activated carbon which provided better NO_3^- -N absorption capacity.

For a single event, the activated carbon device had the best NO_3^- -N removal performance (stable at 87–96%) throughout the event followed by the non-enhanced, zeolite and SMAC devices having a similar performance (stable at

60–66%). The SMZ device had the poorest performance, stabilizing at 24–31%. The high removal efficiency at the beginning indicates that NO_3^- -N could be efficiently denitrified within a 24 h operation interval and the dramatic performance drop could be due to: (1) NO_3^- -N flushed out from the media layer, which was nitrified from ammonia during the operation interval; (2) inflow with high NO_3^- -N had reached the outlet; and (3) the denitrifying bacteria in the SAZ were restrained due to lack of NO_3^- -N at the end of the interval. With time, the NO_3^- -N in the media layer being fully flushed out and the denitrifying bacteria being activated, the removal efficiency was gradually increased. With the continued inflow, the carbon source could not supply the consumption from denitrification and the removal rate was gradually decreased until stable.

Nitrogen removal efficiency distribution

The vertical diversity of NO_3^- -N removal efficiency was also investigated to identify the effective part of the system.

The media layer offered relatively stable but limited capacity of NO_3^- -N removal (13–20% at the bottom of the layer) throughout the experiment (Figure 5). In most cases, the removal capacity at the middle section of the layer was very similar to the bottom section. In some cases, such as the activated carbon device (week 7) and the SMAC device (week 7), the removal efficiency at the middle section was even higher than that at the bottom, which may be due to the flushing of ammonia-transformed NO_3^- -N in the media layer. Such phenomena have also been monitored and verified in a runoff treatment case in the latest research.

At week 2, the non-enhanced, zeolite and SMZ devices had no significant change on removal efficiency in the submerged layer and the drainage layer, proving the denitrification systems were not formed yet and providing no contribution to NO_3^- -N removal. This suggests that the removal of NO_3^- -N in activated carbon and the SMAC device were mainly through absorption of the enhanced fillers. Notably, the well performed SMZ in the lab-scale experiments had a poor performance which indicates that the absorption power of SMZ was not strong enough under the hydraulic loading of 4 L/h and desorption occurred during the operation.

At week 4, the non-enhanced, zeolite and activated carbon devices had significant improvement on removal efficiency in the submerged layer. The increasing removal efficiency from the bottom of the media layer, through two-thirds of the submerged layer, to the bottom of the drainage layer is rather linear, indicating that the NO_3^- -N in this area should be removed by the same route (denitrification). This suggests the formation of the denitrification system had been completed at week 4. The SMZ device had very limited improvement which indicates that the denitrification system had been restrained. Notably, the SMAC device had a dramatic decrease of removal efficiency compared to week 2. The upper two-thirds submerged layer had notably higher removal efficiency than the combination of the lower one-third submerged layer and the drainage layer. This suggests that the NO_3^- -N removal in the SMAC device still depended more on the absorption of SMAC while the absorption capacity had a significant decrease over the past 2 weeks. The denitrification system was also restrained in the SMAC device, proving the cationic surfactant had a negative impact on denitrifying bacteria.

At week 7, the denitrification system had been stable for most devices besides the SMAC unit. The non-enhanced devices had a moderate decrease on the removal efficiency stabilizing at around 64% while the zeolite device slightly increased to 61%. The activated carbon cell had the highest removal capacity of 93% and the SMZ cell had the lowest at 28%. Remarkably, there was an increase of NO_3^- -N removal in the SMAC device and the efficiency increment from the bottom of the media layer to the bottom of the drainage layer became more linear than in week 4. This proves that the denitrification system in the SMAC device had a dynamic balance between desorption of NO_3^- -N (with cationic surfactant) and the activation of denitrifying bacteria, as discussed above.

Although the non-enhanced device had a similar performance compared to the zeolite and SMAC device at week 7, the overall trend of its performance was decreasing while the other two revealed increasing trends. This trend suggests a shorter life cycle and more careful maintenance of the non-enhanced units. Considering the long-term performance as well as the single-event performance, the activated carbon was selected as the enhanced filler for further experiments in the current study.

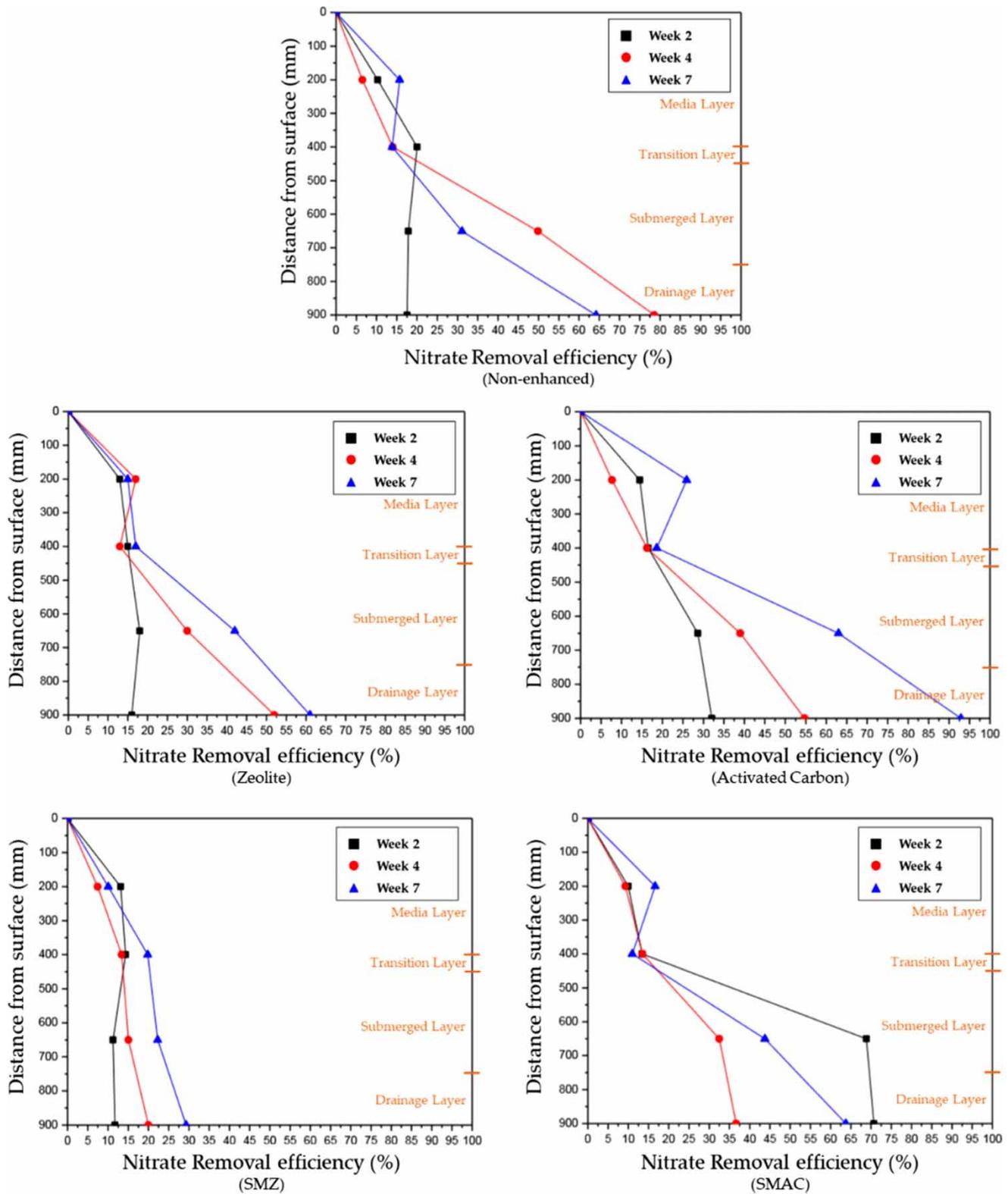


Figure 5 | Vertical diversity of NO_3^- -N removal performance for candidate fillers.

Design and operation optimization

Hydraulic loading is the most influencing factor to adapt bioretention techniques to treat river water. Higher loading ensures the efficiency and feasibility of such treatment methods but can also disturb the performance of bioretention. Thus, different proportions of enhanced filler (50, 100, 150, and 200 mm) in the submerged layer were evaluated under different hydraulic loading rates (4, 6, 8, and 12 L/h) to determine a feasible design and operation pattern of application.

As shown in Figure 6, the NO_3^- -N concentration in the outflow decreased with the proportion of activated

carbon in the submerged layer increasing. The differences between 150 and 200 mm under different hydraulic loadings were -0.004 ± 0.109 mg/L ($p < 0.05$), which suggests limited improvement by replacing more gravel with activated carbon after the proportion reached 50%. Such a performance limit was due to the removal route of the NO_3^- -N. The addition of activated carbon not only provided space for denitrifying bacteria but also absorbed NO_3^- -N for more efficient denitrification. At the beginning of adding more activated carbon, the denitrification process worked together with the absorption. With more activated carbon added, more NO_3^- -N was absorbed, and its concentration in the submerged layer became low enough to start

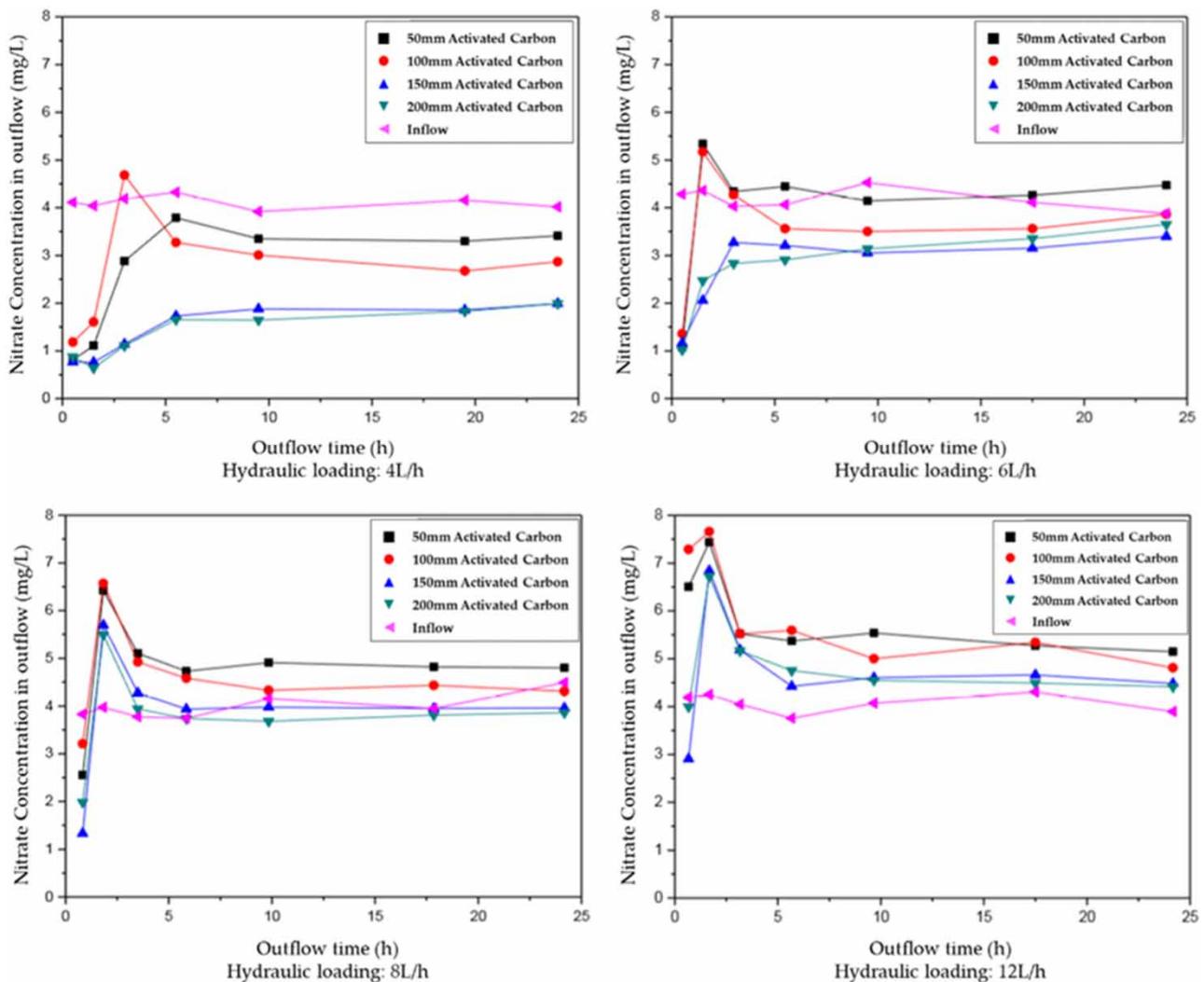


Figure 6 | NO_3^- -N concentration in outflow under different filler layer designs and hydraulic loadings.

restraining the denitrification. Thus, the total removal performance would reach a certain limit with the increasing proportion of activated carbon and the most cost-efficient design would be 150 mm activated carbon +150 mm gravel.

The best hydraulic loading rate was suggested to be 4 L/h which equals to 81.5 mm/h (2.0 m/d), almost double the loading of a vertical constructed wetland (lower than 1.0 m/d) (Saeed 2012). As the NO_3^- -N in the submerged layer could be fully denitrified within 24 h, the operation interval could be adjusted according to the need of the river water treatment or upcoming rainfall events. The overall hydraulic loading rate will be higher than a traditional vertical wetland and the location of the bioretention units could be decentralized along the river, providing more flexibility in design and construction.

Compared with existing studies (Table 5), the proposed design revealed a better and more stable performance than traditional enhanced bioretention designs. The results indicate that the proposed design could operate at a significantly higher hydraulic loading and NO_3^- -N concentration while maintaining its performance. The dominant difference of the proposed design and an enhanced vertical wetland is that such a bioretention system can operate intermittently to ensure the proper removal of TN. Such a pattern enables the flexible operation between river treatment and runoff reduction, as well as a robust performance for both.

PRACTICAL APPLICATIONS AND FUTURE RESEARCH PERSPECTIVES

In application to river treatment, the proposed devices could be implemented on both sides of the river, integrated with the existing (distributed) landscapes or green areas along the river. As the bioretention cell systems are designed to be distributable, it could be easier and more flexible to allocate the systems than wetland systems. The two parts of the system could operate at intermittent conditions to provide enough operation time (to ensure treating volume) and sufficient interval time (to ensure nitrogen removal performance).

There are several limitations in this study which could be improved in future studies. First, although the SMAC showed a high capacity for absorbing NO_3^- -N and feasibility of desorbing NO_3^- -N during the operation interval for continuous denitrification, the conflict between the modifier and the denitrifying bacteria is the major problem in application. As found in the current study, the performance of the SMAC unit fluctuates but is improving, and future studies can be carried out on the life cycle of different enhanced bioretention units (total volume of river water that can be treated between maintenances). This study also shows the possibility of using the bioretention structure to treat highly nitrogenous rivers. Notably, the proposed design in this study was only focused on treating polluted water in the Taihu lake basin, therefore, future studies could be conducted on the improvement in design criteria

Table 5 | Performance of enhanced bioretention systems/wetlands for NO_3^- -N removal

Reference	System	Hydraulic loading	NO_3^- -N concentration (mg/L)	Removal efficiency
Kim et al. (2003)	Bioretention	6.0 h 4.0 cm/h	2.00	80%
Palmer et al. (2013)	Bioretention	3.2 h 13.3 cm/h	0.40–0.74	45.2% (mean)
Sun et al. (2018)	Vertical wetland	20 d 4.16 cm/h	10.04 ± 1.29	93.1–99.0%
Tian et al. (2019)	Bioretention	21.0 h 5.5 cm/h	10.7–12.4	66.2–92.9%
This study	Bioretention	24.0 h 8.15 cm/h	28.89	93.2–94.1%

or the optimization of bioretention units for river treatment in a wider sense.

Nevertheless, it was a limitation of the study that the data from the experiment could not carry out a reliable sensitivity analysis. This was due to the following. (1) The experiments were designed as a variable-controlled experiment instead of a comprehensive experiment. The parameters above were modified step by step and the poor performing parameters would not be adopted in the following steps. Thus, the data could not support a sensitivity analysis process. (2) The performance of bioretention cells is also strongly dependent on the construction quality (e.g. compactness uniformity), which is quite difficult to consider in the pilot-scale experiments. Further study could be carried out on the design parameters such as composition of the submerged zone, the enhancement pattern of the filler media, and the operation time and intervals to support more applicable and effective designs.

CONCLUSIONS

The current study was conducted to optimize the performance of a bioretention system in treating river water: (1) modification of filter media; (2) identify the best modified filler by monitoring the long-term and single-event performance; (3) optimize the bioretention structure design; and (4) identify the best operation pattern. The results reveal that the SMAC (modified with 600 mmol technically pure CPC/kg activated carbon) has the highest absorption capacity (1,742 mg/kg) which was five times higher than second ranked SMZ (311 mg/kg). For long-term performance, the activated carbon, non-modified, zeolite and SMZ gradually improved their NO_3^- -N removal efficiency due to the formation and stabilization of the denitrification system throughout the experiment. The SMAC device started with a high removal efficiency of 71% due to its strong absorption capacity. The most cost-efficient design would be 150 mm activated carbon +150 mm gravel operating under hydraulic loading of 4 L/h. Such loading equals to 81.5 mm/h (2.0 m/d) which is far higher than a traditional vertical wetland. The operation interval could be adjusted according to the need for river treatment or upcoming rainfall events.

ACKNOWLEDGEMENTS

This work was financially supported by the National Key Research & Development Program of China (Grant No. 2018YFC0809900).

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First received 21 April 2019; accepted in revised form 29 October 2019. Available online 2 December 2019