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Immobilization of nitrifying/denitrifying bacteria onto construction waste and the elimination of pollutants from stormwater runoff

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ABSTRACT

In this study, to enhance the removal efficiency of nitrogen in runoff, construction waste (CW) was used for immobilization of nitrifying and denitrifying bacteria. The efficiency and mechanism of the removal of runoff pollutants by immobilized-bacteria construction waste (ICW) were systematically investigated in column experiments. The results indicated that the nitrifying and denitrifying bacteria could be immobilized onto CW successfully. The highest removal efficiencies of total nitrogen (TN) and ammonia nitrogen (NH_4^+–N) were 91.97% and 78.82%, which could be attributed to the nitrification and denitrification caused by the immobilized microorganisms. Furthermore, the microorganisms played an important role in the removal of other pollutants in stormwater runoff. Comparing the pollutant concentrations in influent and effluent, the highest removal efficiencies of chemical oxygen demand (COD) and total phosphorus (TP) of nearly 100.00% and 80.33% could be achieved after a period of instability. ICW showed higher removal efficiency for nearly all runoff pollutants after the experiments were conducted for a long time (67 d). This study offers a new approach for the reuse of CW in bioretention systems and suggests a useful method for the removal of pollutants in runoff.

Keyword: Construction waste; Stormwater runoff; Nitrogen; Pollutants

1. Introduction

In recent years, as an important water quality issue, eutrophication, which is mostly attributed to the excessive release of nitrogen and phosphorus (P) into the environment, has drawn attention all over the world [1]. Furthermore, excess nitrogen in aquatic ecosystems can cause a series of problems such as altering the structure of the ecological community, deterioration of habitat quality, or even harm toward organisms [2].

As an identified major nitrogen pollution source, stormwater runoff contributes more than 50% of the nitrogen pollution in many countries [3]. Due to widespread urbanization, the increase in impervious areas has induced the discharge of stormwater runoff directly into aquatic ecosystems [4,5]. With the rapid development of urbanization in China, the contribution of urban stormwater runoff to nitrogen pollution has become more prominent [6]. Hence, the development of appropriate methods for decreasing nitrogen loads into aquatic environments is particularly important.

In order to reduce the pollutants loads in stormwater runoff, a number of stormwater control measures have been employed such as constructed wetlands, sedimentation ponds, sand filters, infiltration and bioretention systems [7].

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Among these measures, bioretention systems have attracted great attention due to their special ability to improve water quality and hydrologic conditions. Although results showed that bioretention systems could effectively eliminate heavy metals, total suspended solids (TSS) and grease in runoff, the nutrient degradation effect was not ideal, especially regarding nitrogen removal [8–10]. In recent years, many methods have been used to enhance the removal efficiency of bioretention systems such as establishing saturated zones [11], changing plant species [12], adding additional organic carbon [13] and introducing special materials [14]. However, the nitrogen removal efficiency by bioretention systems was still inconsistent. For example, some researchers found that the nitrogen removal efficiency from stormwater runoff could be more than 90% or less than 20%, and that nitrogen might even leach in bioretention systems with saturated zones [15–17]. Moreover, appropriate plants have always been considered to play the most important role in nitrogen removal, but plants can even release nutrients due to seasonal senescence [18]. Due to the highly unstable nitrogen removal efficiency in bioretention systems, it was very important to develop an efficient removal method for nitrogen by these systems.

As the key factors in bioretention systems, the filler and microorganisms play an important role in the removal of pollutants. The filler can offer enough useful sites for the adsorption of pollutants and immobilization of microorganisms. The activity of microorganisms can eliminate the pollutants in runoff further. Bioaugmentation is a promising technology, which introduces proper and sufficient microorganisms into bioretention systems. Due to its eco-friendly features and low cost, bioaugmentation has become a novel and popular alternative method in recent years. As one of the optimal bioaugmentation technologies, immobilization has been widely used in various areas due to its advantages of high biomass density, enhanced microbial stability and easy separation. Liu et al. immobilized bacterium D47 onto nanocellulose and used it for the removal of diuron [19]. Elgueta et al. found that immobilized white-rot fungus could improve the degradation of atrazine and reduce its migration in surface and groundwater [20]. Fu et al. demonstrated that the immobilized microbial activated beads were more efficient for improving the quality of contaminated water and sediment. The experiment results showed that the removal efficiencies of total nitrogen (TN), NH_4^+–N and COD in overlying water reached 87.5%, 61.8% and 87.1%, respectively [21]. Moreover, immobilization also could be used in other refractory wastewaters, such as landfill leachate, heavy metal wastewater, oil field wastewater, coking effluent, and phenol and dye wastewater [22].

With the rapid development of urbanization in China, the amount of construction waste (CW) has increased greatly and exceeded 1.5 billion tons in 2015 [23]. Due to the low rate of utilization and processing, the large amount of CW in the environment could cause a serious problem and increase the consumption of natural resources [24]. Therefore, it is urgent to find useful methods for the reuse of CW as a resource from the aspect of both economics and the environment. Results showed that CW could be used as filler in bioretention systems due to its proper hydraulic conductivity values [25]. Furthermore, results also showed that the CW could be used for the removal of various contaminants by adsorption processes, including fluoride, phosphate, dye, detergents and heavy metals [26–29]. Due to its favorable characteristics, CW could provide an ideal environment for the immobilization and growth of microorganisms [30,31]. Thus, as a potential filler with the advantages of proper porosity, low cost and stable structure, CW could be used for the immobilization of microorganisms and removal of runoff pollutants in bioretention systems. Nevertheless, most studies have focused on the reuse of CW in civil engineering applications. Few reports have investigated the reuse of CW as a filler in bioretention systems. No mention has been made on the study of CW colonized with proper microorganisms and its use in bioretention systems for the removal of pollutants in runoff.

To increasing the removal efficiency toward pollutants (especially for nitrogen), immobilized-bacteria construction waste (ICW) was prepared by a simple method and used for the removal of pollutants in column experiments. In this study, industrialized nitrifying and denitrifying bacteria (including *Nitrobacter*, *Nitrosomonas*, *Pseudomonas* and *Alcaligenes*) were selected as microorganisms due to their high nitrogen removal efficiency and low cost. The prepared ICW samples were characterized by X-ray fluorescence (XRF) and scanning electron microscope (SEM). The efficiency and mechanism of the removal of runoff pollutants were calculated based on long-term (67 d) column experiments. This study could provide a new method for utilization of CW and offer new insight into the elimination of pollutants in runoff.

2. Materials and methods

2.1. Materials and chemicals

The industrialized nitrifying and denitrifying bacteria employed were obtained from ZhenQing Environmental Protection Technology Co., Ltd. in Guangzhou, China. The biological glue was bought from WeiPu Chemical Technology Service Co., Ltd. in Shanghai, China. Other chemicals, including ascorbic acid, hydrochloric acid, $K_2S_2O_8$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, HgI_2, $K_2Cr_2O_7$, Ag_2SO_4, H_2SO_4 and NaOH, were all of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared in high-purity water (Milli-Q).

2.2. Immobilization of microorganisms on CW

The CW used in this study was prepared in Lu Cheng village near Beijing University of Civil Engineering and Architecture in Beijing, China. The CW were mechanically crushed to small particles, followed by sieving to 0–2 mm and 2–5 mm sizes, washed several times with distilled water to remove the surface dust and soluble ions, dried overnight at 105°C, and stored at room temperature for further use.

The immobilization of microorganisms onto CW was carried out as follows: First, CW were sterilized by high pressure steam at 121°C for 20 min. Biological glue (starch glue) was placed in an oven and dried at 80°C for 4 h. Second, the sterilized CW was mixed with the biological

glue and stirred evenly, wherein the mass fraction of biological glue was 10%. Third, the mixed materials (10 g) were added to a 500 mL Erlenmeyer flask containing 200 mL of a cell suspension of industrialized nitrifying and denitrifying bacteria and placed on a rotary shaker at 180 rpm and 25°C for 24 h, until the bacteria were adsorbed onto the surface of the CW. Finally, the prepared materials were filtered and washed several times with deionized water to remove the non-adsorbed bacteria, and the obtained ICW were then dried before use. The ICW were stored in a dark, ventilated and dry place, where the temperature was maintained at 25°C–30°C, which was proper for maintaining the biological activity of the bacteria. Furthermore, the safety characteristics of the CW and ICW were measured and the results are listed in Table S1.

2.3. Experimental setup

In order to investigate the removal efficiency of ICW, a series of column tests were conducted. The laboratory apparatus was assembled, and the schematic diagram is shown in Fig. 1. A 20 L bucket was used as the raw water bucket, and two experimental columns were used in the whole experiment. A peristaltic pump (BT100-1F, LongerPump, China) was used for the input of raw water to the experimental columns. The column was made of polymethyl methacrylate and had an effective volume of 0.25 L, diameter of 40 mm and height of 200 mm. Columns I and II were filled with 0–2 mm or 2–5 mm ICW materials, respectively. Each column consisted of 10 mm glass beads on the bottom, 180 mm of the modified materials, 10 mm of glass beads on the top and four pieces of gauze placed between the different layers. The role of the glass beads and gauze was to keep the water evenly distributed. In order to avoid the side-wall effect and make the operation more stable, the inlet of the experimental column was at the bottom and the operation mode was from bottom to top. The porosity of the columns (0–2 mm and 2–5 mm) was 47.06% and 50.20%, respectively. During the whole experiment, raw water was continuously pumped into the experimental columns and the hydraulic retention time of the systems was 5.5 h, which met the requirements of permeability in filter media obtained by the city sponge construction guide in China. The concentration of pollutants in the influent and effluent of the column was measured daily in the beginning and the entire experiment operated for 67 d.

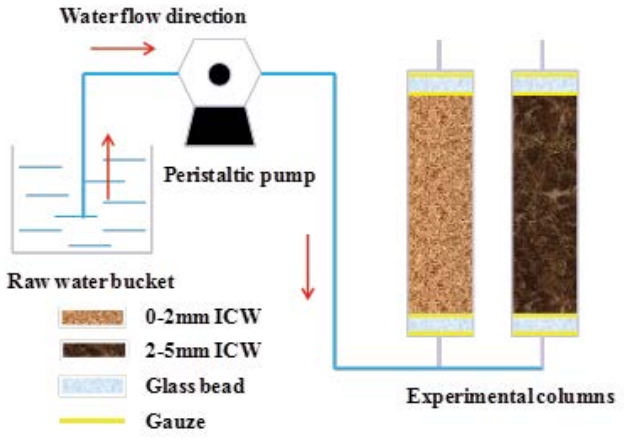

Fig. 1. Schematic diagram of the experimental setup.

2.4. Test methods

As shown in Table 1, the raw water was prepared for the simulation of urban road stormwater runoff in this study [32]. The raw water in the bucket was often stirred to confirm that the chemicals were mixed uniformly. The samples of the influent and effluent were collected at different times and tested for COD, NH_4^+–N, TN and TP to evaluate the transformations of pollutants in the columns. The removal efficiency of pollutants was calculated as below:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e are the concentrations of pollutants in influent and effluent, respectively.

All pollutants were measured in accordance with standard methods. The COD, NH_4^+–N, TN and TP were measured by the fast digestion-spectrophotometric method (HJ/T399-2007), Nessler's reagent spectrophotometry (HJ 535-2009), alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012) and ammonium molybdate spectrophotometric method (GB 11893-89), respectively. The pH values of solutions were measured by using a laboratory pH meter (Thermo Scientific Orion 9157BNMD, USA). The entire experimental process was kept at room temperature (about 25°C). All the water samples were stored in a freezer at 4°C with special bottles and analyzed within 48 h after sampling.

2.5. Characterization

In this study, three kinds of materials (2–5 mm) were characterized, including CW, ICW, and ICW in the column at the 67th day (ICW-67). All three materials were pretreated by freeze-drying by the same process before characterization. The surfaces of the samples were examined by an SEM (Hitachi SU8010, Japan). The chemical analysis of materials was carried out by XRF (PANalytical Axios–mAx, Netherlands). The specific surface area, pore volume and pore size distribution were measured using N_2 Brunauer–Emmett–Teller isotherms obtained on a

Table 1
Raw water quality

Water quality indicators	Source	Typical road runoff (mg L^{-1})	Raw water used in study (mg L^{-1})
COD	Glucose	308.26 ± 115.80	403.37
TP	KH_2PO_4	1.03 ± 0.49	1.18
NH_4^+–N	NH_4Cl	2.96 ± 2.24	4.07
TN	NH_4Cl and KNO_3	7.73 ± 4.54	9.10
pH	–	–	7.20

TriStar II 3020 instrument (Micromeritics, USA) and calculated with built-in software. Pore size distributions were calculated from the desorption branch of the N_2 isotherm data by the Barrett–Joyner–Halenda method [33].

3. Results and discussion

3.1. Characteristics of materials

Representative SEM micrographs of the three samples are depicted in Fig. 2. As shown in Fig. 2(a), the surface morphology of the CW was rough and porous, indicating that the CW could provide enough useful sites for the immobilization of microorganisms. Furthermore, the porous structure could provide pathways for the transfer of oxygen and other substances into the CW, which was very useful for the growth of microorganisms. After the incorporation of bacteria, it appeared that there were some bacteria on the surface of CW (Fig. 2(b)), which suggested that the bacteria were successfully immobilized on the surface of CW. The CW in the column remained intact during the experiment. As showed in Fig. 2(c), after the treatment of runoff for 67 d, a large number of oval microorganisms appeared on the surface of ICW-67, which showed that the modified CW provided an ideal structure for microbial colonization. These results illustrated that the bacteria flourished in the experimental column might play an important role in the removal of pollutants in runoff.

To investigate the characteristics of materials, XRF was used to evaluate the main chemical composition. As shown in Table 2, the major constituents of CW were SiO_2, Al_2O_3 and CaO, with the contents of 56.96%, 15.20%, and 10.42%, respectively. After the immobilization of bacteria, the contents of the main components were changed, which might be attributed to the presence of the biological glue. The content of Al_2O_3 was reduced from 15.20% to 5.22%, while the content of MgO increased from 2.08% to 17.20%. The major components of ICW and ICW-67 were SiO_2, CaO and MgO with contents of 36.00%, 32.31%, and 17.20%, and 40.50%, 25.92% and 15.70%, respectively. Furthermore, all the materials also contained other low-content components such as Fe_2O_3, K_2O and SO_3. The different components contained in the materials might have a great influence on pH, microbial growth and removal of contaminants in stormwater runoff [30,34,35].

The specific surface areas of the three materials were determined by a nitrogen physical adsorption apparatus. The specific surface area, pore volume and pore size were 2.35 $m^2\ g^{-1}$, 0.006 $cm^3\ g^{-1}$ and 10.21 nm for CW. The specific surface area became smaller after immobilization because microorganisms and biological glue were loaded on the surface of CW and blocked some channels. Compared with other reported materials with specific surface areas of 0.19–0.36 $m^2\ g^{-1}$ [36], the CW in this study could provide sufficient area for microbial growth and attachment.

3.2. Changes of pH values in the effluent

The pH value is an important indicator of water quality. Higher or lower pH values than optimal could inhibit microbial activity in water, resulting in the deterioration of water quality. Fig. 3 shows the pH values in the effluent for different particle sizes of CW. As shown in Fig. 3, the difference in particle size had little effect on the effluent pH values of ICW. The pH values in the effluent increased sharply at the beginning, followed by some fluctuation and finally reaching stability. Compared with the influent pH values of 7.20, the ICW could increase the solution pH values due to the alkaline materials in the structure of the CW (Table 2; Fig. S2). During the experiments, some alkaline materials such as lime might be dissolved into the aqueous solutions, causing the increase of pH values in the effluent. Although the pH values increased in the experiment, the final effluent pH values were maintained at about 8.20, which is still in the range of the standards for surface water environment quality [34].

Table 2
Chemical composition of different samples as determined by XRF

Element	% Weight		
	CW	ICW	ICW-67
SiO_2	56.95	36.00	40.50
Al_2O_3	15.20	5.22	7.29
CaO	10.42	32.31	25.92
Fe_2O_3	6.94	4.09	5.04
K_2O	3.78	2.39	2.73
MgO	2.08	17.20	15.70
SO_3	1.79	0.33	0.53
P_2O_5	1.67	1.38	1.43
TiO_2	0.84	0.32	0.47
MnO	0.13	0.06	0.07
Other	0.17	0.67	0.36

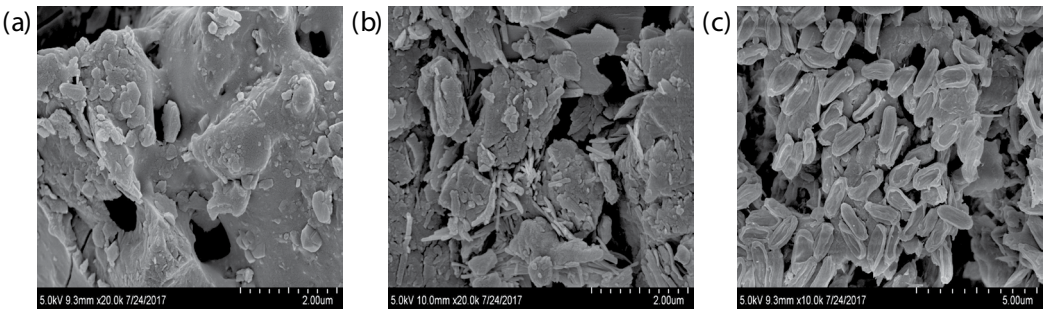

Fig. 2. Representative SEM images of materials. (a) CW, (b) ICW and (c) ICW-67.

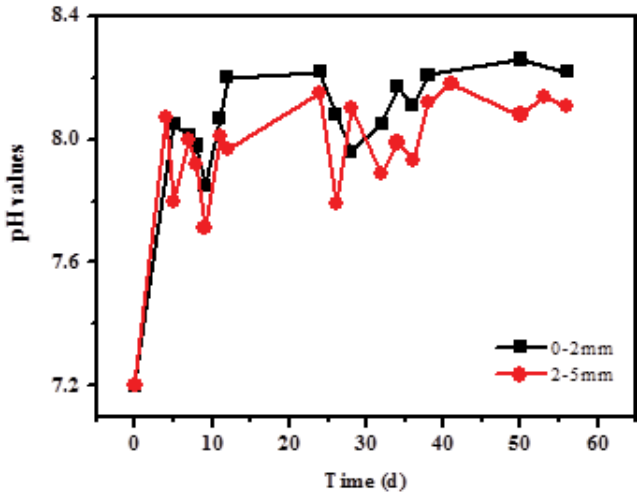

Fig. 3. Changes of pH values in the effluent of the column.

3.3. Changes of COD in the effluent

As one of the major pollutants in stormwater runoff, higher values of COD would increase the degradation of water quality. Fig. 4 shows the changes of COD concentration in the effluent and removal efficiency of the experimental column (2–5 mm). Compared with the influent concentration (403.37 mg L^{-1}), the effluent concentration of COD was almost the same as the influent concentration during the first 9 d, which suggested that the ICW had little effect on the removal of COD in runoff. As the contact time increased, the removal efficiency increased rapidly to nearly 100.00% on day 14. With further operation of the system, the removal efficiency showed fluctuation. The effluent concentration of COD climbed to about 82.12 mg L^{-1} and the removal efficiency decreased to 79.91% on day 28. After the adaptation of microorganisms, the effluent concentration reduced to 30.25 mg L^{-1} with the removal efficiency of 93.27% on day 41. Finally, the effluent concentration of COD was stabilized and the removal efficiency was maintained at about 90.00%.

The removal mechanism for COD was mainly attributed to adsorption and microbial degradation in the column [37,38]. At the beginning of the experiment, the removal was mainly due to adsorption as the microorganisms had not fully adapted to the environment. The biological glue might occupy some part of the adsorption sites on the surface of the CW and decrease the removal efficiency of COD. At the same time, some of the COD might be due to the release of organic components from the biological glue (Table S3). With the contact time increasing, the microorganisms multiplied quickly and became dominant, resulting in a rapid increase in the COD removal efficiency [21]. Studies have shown that biotransformation is the main mechanism for the reduction of soluble COD and that an attached biofilm could greatly promote the removal efficiency for soluble organic compounds [37]. Therefore, microorganisms attached to the CW played a key role in the COD degradation efficiency. However, the biofilm formed at this time was unstable and could easily fall off, which induced an increase in the concentration of effluent COD. When the system reached a stable state, the COD removal efficiency gradually increased and reached stability. In the present study, the COD removal level was efficiently maintained at about 90.00%, which was similar to the results reported by Sun et al. [39] and Schmitt et al. [40].

3.4. Changes of NH_4^+–N in the effluent

Excess NH_4^+–N in the water could easily cause the multiplication of algae and induce eutrophication. Fig. 5 shows the concentration and removal efficiency of NH_4^+–N in the effluent during the whole experiment (2–5 mm). The removal efficiency of NH_4^+–N increased gradually from 14.62% to 65.91% during the first 3 d. In addition, the removal efficiency of NH_4^+–N varied greatly and was unstable (from 32.21% to 63.55%) between days 4 and 22. After the system operated for 22 d, the removal efficiency of NH_4^+–N increased rapidly and the effluent concentration of NH_4^+–N was stabilized gradually. The highest removal efficiency of NH_4^+–N reached nearly 78.82%.

In this study, the removal mechanism of NH_4^+–N was mainly attributed to adsorption and nitrification by

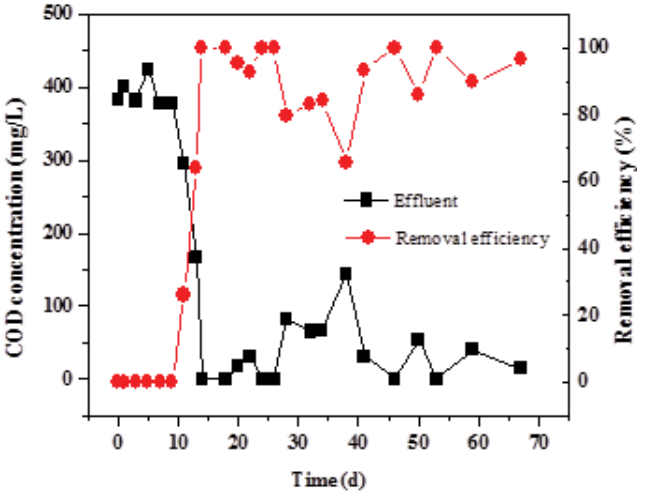

Fig. 4. Changes of COD in the effluent of the column.

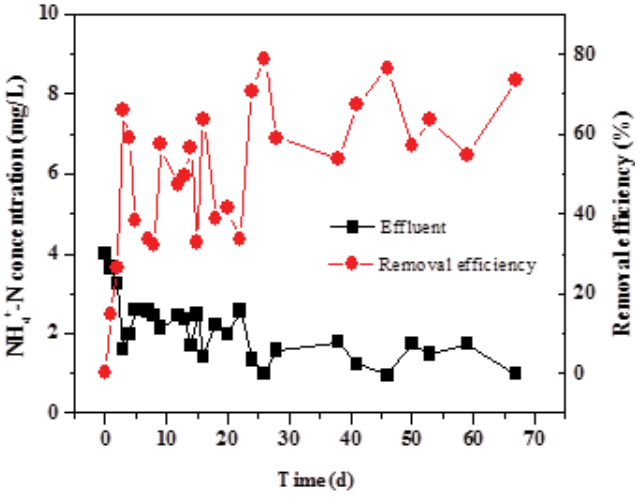

Fig. 5. Changes of NH_4^+–N in the effluent of the column.

microorganisms [41]. The initial NH_4^+–N removal efficiency was not stable, probably due to the combined effects of adsorption and nitrification. At the beginning of the experiment, as the microorganisms in the column had not fully adapted and the system was still in the microbiological acclimation stage, adsorption might be the main reason for the removal of NH_4^+–N, such as by ion exchange [42]. Previous studies have also shown that the ion exchange capacity could be enhanced between NH_4^+–N and materials by the presence of monovalent cations, such as K^+ (Table 2) [43]. With the contact time increased, adsorption and nitrification would affect the removal together, inducing instability in the removal efficiency. With the contact time increased further, the useful adsorption sites decreased and nitrification became more important, so that the entire system operated stably [38,44]. As shown in Eq. (2), nitrifying bacteria attached to the ICW in the aerobic state convert NH_4^+ to NO_3^- eventually.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (2)$$

The solution pH value is one of the most important factors influencing the nitrification process; higher or lower pH values than the optimal range would induce the decline of nitrification and inhibit the growth of microorganisms [45]. The nitrification process could consume the alkalinity of the water Eq. (2), which affects the reaction efficiency. However, in this study, the pH of the effluent could be stabilized around 8.20 eventually (Fig. 3), which is similar to the optimal pH for nitrification (8.25) [45]. Results indicated that ICW could provide a suitable environment for nitrification. The final (at day 67) concentration of NH_4^+–N was 0.97 mg L^{-1}, and the removal efficiency reached 73.52%. These values are similar to other reported results and met the criteria of the standards for surface water environment quality [42,46].

3.5. Changes of TN in the effluent

TN is one of the main indicators reflecting the eutrophication of water. Fig. 6 shows the TN concentration and removal efficiency in the effluent (2–5 mm). The results showed that there was little removal on the first day; however, the TN removal efficiency increased rapidly to 87.00% on day 7, and more than 90.00% was eliminated on day 24. As the system operated, the TN concentration in the effluent gradually became stable and the removal efficiency was maintained (average 80.00%) until the end of the experiment. The highest removal efficiency reached nearly 91.97%.

The composition of TN was mainly composed of NH_4^+–N and nitrate nitrogen (NO_3^-–N) in this study. At the beginning of the experiment, the decrease in TN concentration might be due to the adsorption of NH_4^+–N, since microorganisms were still in the adaptation phase. However, comparing the NH_4^+–N effluent concentration (1.73 mg L^{-1}) and TN effluent concentration (2.04 mg L^{-1}) at 50 d of operation, NO_3^-–N was effectively removed and transformation occurred. As NO_3^-–N is not easily removed by adsorption, this suggested that denitrification occurred and to a large extent [37]. As reported by other researchers, TN removal could be mainly attributed to consumption or denitrification by the microbial community [47]. Eq. (3) shows that denitrifying bacteria transformed NO_3^- to N_2 under anoxic and anaerobic conditions.

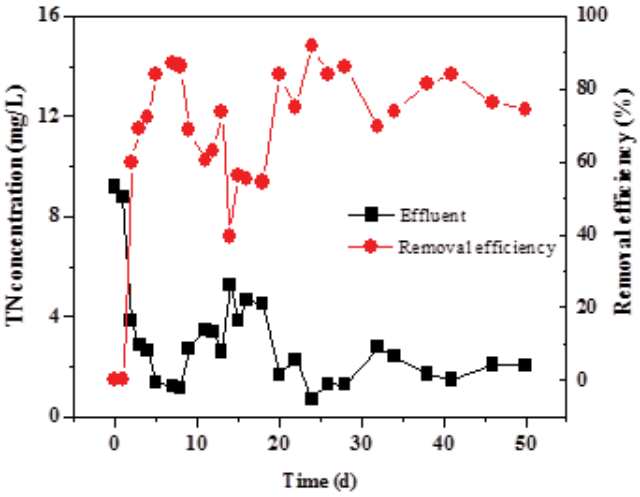

Fig. 6. Changes of TN in the effluent of the column.

$$NO_3^- + 5H(\text{electron supplier} - \text{organic matter}) \rightarrow \frac{1}{2}N_2 + 2H_2O + OH^- \quad (3)$$

In this study, the good TN removal efficiency was mainly attributed to the denitrifying bacteria incorporated onto CW. The immobilization was conducive to the degradation of pollutants, which had been verified by a previous study [19]. Good overall removal efficiency of TN (average 80.00%) was observed and this result was higher than the results (22.00%–55.00%) of various types of stormwater management systems, which suggested that ICW had a good removal effect for TN [37,48]. In the experimental conditions, anoxic and anaerobic zones might have existed in upper filler for denitrification to occur. Moreover, the pores on the CW surface (Fig. 2) could form anaerobic microenvironments, providing space for denitrification [47]. In addition, biological glue as a carbon-rich material might be a potential carbon source, which could facilitate the denitrification. The concentration of TN (at day 50) was 2.04 mg L^{-1}, which basically met the requirements of the standards for surface water environment quality [46].

3.6. Changes of TP in the effluent

Excessive TP plays a dominant role in causing eutrophication, algal bloom and other serious environmental risks. Fig. 7 shows the concentration and removal efficiency of TP in the effluent (2–5 mm). Results showed that the effluent concentration of TP was almost unchanged during the first 8 d, but began to increase rapidly on day 9, and more than 75.00% of TP was eliminated on day 24. Moreover, the concentration of TP in the effluent remained stable between days 24 and 32. The highest removal efficiency reached nearly 80.33%.

The removal mechanism of TP was mainly attributed to adsorption and chemical precipitation in the matrix [49]. Shi et al. [30] verified that CW could be used as useful materials for the removal of TP in constructed wetlands. In this study, the low TP removal effect in the beginning might be attributed to fewer useful adsorption sites being present,

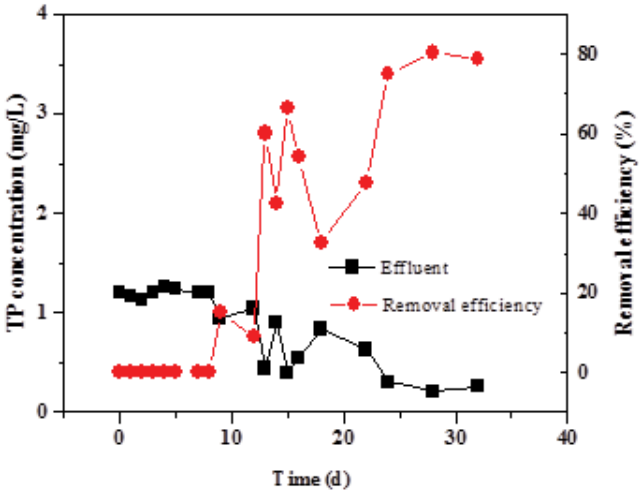

Fig. 7. Changes of TP in the effluent of the column.

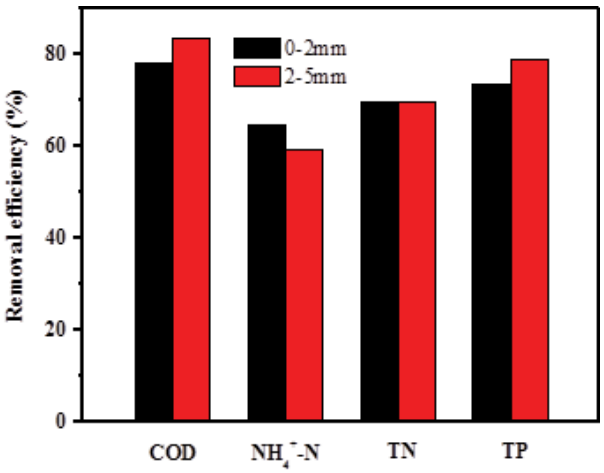

Fig. 8. Effect of particle size of ICW on the removal of different pollutants on day 32.

caused by the biological glue and microorganisms. On the other hand, although the calcium-containing components in CW could react with P to form a stable sediment (shown in Eq. (4)), the preparation process and the use of biological glue inhibited the removal efficiency of P in the beginning [38,50].

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \quad (4)$$

Some studies have shown that the removal of TP can also be linked to microorganisms [51]. Microorganisms could facilitate removal of P [30,37]. With the operation time increasing, the TP removal efficiency began to increase rapidly, which might be attributed to the combined effects of adsorption, chemical precipitation and microbial uptake. Compared with the influent concentration of TP (1.18 mg L^{-1}), the concentration of TP in the effluent was lower and kept at a relatively stable level (0.2–0.3 mg L^{-1}), which was similar to the results of Xia et al. [48]. These values met the criteria of the standards for surface water environment quality [46]. In addition, there was a coupling mechanism in the removal processes of nitrogen and P [14]. In this study, on the one hand, TP adsorbed on the materials further contributed to the abundance and activity of microorganisms, which facilitated the TN removal. On the other hand, effective nitrification–denitrification could increase the demand for TP by nitrifying and denitrifying bacteria, which was beneficial for TP removal.

3.7. Effect of particle size on the removal of pollutants

Differences in the particle size of materials could influence the removal of pollutants in the runoff. In this study, the effect of CW in two size ranges (0–2 and 2–5 mm) on the removal efficiency of different pollutants was studied and the results are shown in Fig. 8 (32 d). The results proved that the particle size had little effect on the removal of pollutants in runoff. The removal efficiencies of COD, NH_4^+–N, TN and TP in 0–2 and 2–5 mm ICW were 78.04%, 64.42%, 69.43% and 73.53%, and 83.22%, 59.13%, 69.55%, and 78.73%, respectively. It is widely accepted that the removal efficiency would be higher for smaller particles because of the larger surface area and better adsorption performance [28]. However, in this study, the removal efficiency was mainly attributed to the microorganisms, which might be little affected by the difference in particle size. The results showed that larger particle size (2–5 mm) ICW might have greater potential for the application due to the lower cost and reduced clogging effect.

4. Conclusions

In this study, ICW were prepared for enhancing the removal efficiency for pollutants (especially nitrogen) in runoff. Results showed that the CW could be used as a potential filler in bioretention systems and could be a good candidate as a bacteria-immobilizing carrier. In the column experiments, the prepared ICW had a good removal effect on nitrogen and other pollutants in runoff. The highest removal efficiencies of TN, NH_4^+–N, COD and TP reached about 91.97%, 78.82%, 100.00% and 80.33%, respectively. Moreover, the microorganisms immobilized on the CW played an essential role in the removal of contaminants from runoff. Results confirmed that ICW were efficient and could promote the quality of contaminated water. This research could offer a useful method for the utilization of CW and provide a new idea for the preparation of high-efficiency fillers in bioretention systems.

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Supplementary Information

I. Safety characteristics of the CW and ICW

To investigate the safety characteristics of CW and ICW, the two materials were immersed in water with a ratio of 1:10, the mixed solution was stirred for 5 d, the concentration of typical heavy metals were measured and the results were shown in Table S1. The concentration of typical heavy metals in mixed solution was low. Furthermore, as shown in Table S2, the concentrations of heavy metals in mixed solutions were in the range of the standard in surface water environment quality in China [46]. All these results showed that the prepared materials are safe for use in water environment.

II. Comparison of removal efficiency between CW and ICW

We conducted an experiment on the removal efficiency of CW on stormwater runoff pollutants. However, the aim of this study was investigated the removal efficiency of ICW and we paid more attention to the long-term treatment. Therefore, we did not show experimental data for CW in the manuscript. As shown in Fig. S1, the removal efficiency of ICW was better than CW. Some results confirmed that the CW could be used for the removal of contaminants and show good removal efficiency by an adsorption process. However, the removal of nitrogen was mainly dependent on micro-organisms degradation. Thus, in this study the removal mechanism was mainly attributed to the absorption and biotransformation processes.

Table S1
Concentration of heavy metals in mixed solution

	Cu (mg L^{-1})	Zn (mg L^{-1})	As (mg L^{-1})	Cd (mg L^{-1})	Cr (mg L^{-1})	Pb (mg L^{-1})
CW	0.003	0.011	0.057	0.000	0.000	0.000
ICW	0.006	0.018	0.035	0.000	0.001	0.001

Table S2
Standard values of heavy metals for environmental quality standard in surface water

Classification standard value items		Class I	Class II	Class III	Class IV	Class V
Concentration (mg L^{-1})	Cu	0.01	1.0	1.0	1.0	1.0
	Zn	0.05	1.0	1.0	2.0	2.0
	As	0.05	0.05	0.05	0.1	0.1
	Cd	0.001	0.005	0.005	0.005	0.01
	Cr	0.01	0.05	0.05	0.05	0.1
	Pb	0.01	0.01	0.05	0.05	0.1

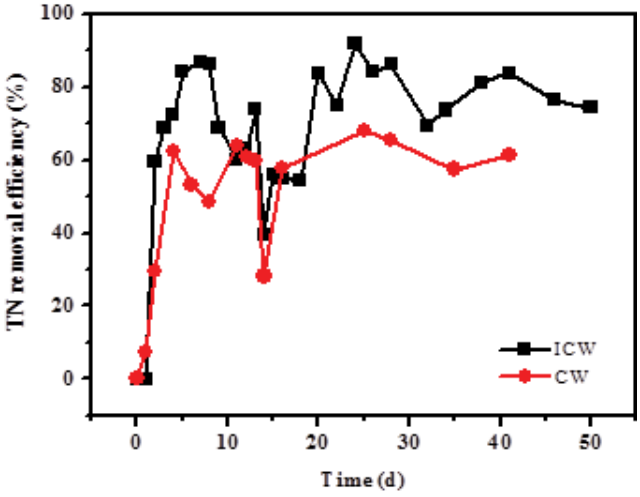

Fig. S1. Changes of TN in the effluent of the column.

III. Changes of pH values

Fig. S2 showed the pH values in the effluent of CW and ICW, results indicated that the effluent pH values of ICW was similar to CW. For CW and ICW, the pH values in the effluent increased sharply at the beginning and finally maintained at about 8.00. According to previous research and the results of XRF, the CW contained large amount alkaline materials which could be released into aqueous solution and increased

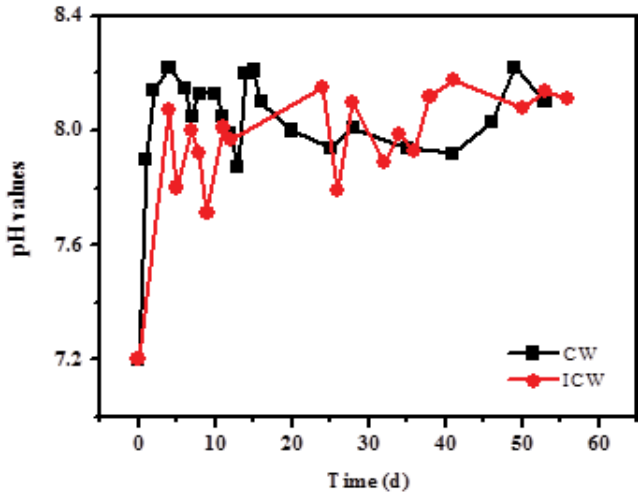

Fig. S2. Changes of pH values in the effluent of the column.

Fig. S3. A field study in China.

Table S3
Impact of biological glue on contaminants

Water quality indicators	Raw water concentration (mg L^{-1})	Final concentration (mg L^{-1})
COD	400.32	938.45
TP	1.32	1.37
TN	9.91	10.79
NH_4^+–N	4.60	5.53

Table S4
Influent and effluent concentration in a field study

Test items	Influent (mg L^{-1})	Effluent (mg L^{-1})
TP	1.32	0.10
NH_4^+–N	4.82	0.62
COD	49.00	12.00

the pH values. On the other hand, the nitrification could consume the alkalinity of the water, resulting in the decrease of pH. Thus, alkaline materials in the CW may be the main factors which increase the solution pH values.

IV. Impact of biological glue on contaminants

To verify the effect of biological glue on contaminants, batch experiment was carried out with the solid–liquid ratio of 0.5 g L^{-1} and the results were shown in Table S3. Table S3 revealed that biological glue had little effect on the removal of TP, TN and NH_4^+–N. On the contrary, biological glue could increase the concentration of COD in solution due to release of organic components. However, results confirmed that the removal efficiency of COD was mainly attributed to ICW.

V. Life-term of ICW

In order to verify the wide applicability of ICW, a field study was carried out to investigate the river bioremediation by ICW, as shown in Fig. S3. ICW showed a good removal effect for different contaminants, such as COD, NH_4^+–N and TP. Table S4 showed the concentration of different pollutants in the influent and effluent on day 15. The materials that were exposed to air for a long time would cause weathering, resulting in clogging effect and reducing treatment efficiency of the entire system. However, the life-term of ICW had not been determined at present.