Experimental study on the adsorption of dissolved heavy metals by nano-hydroxyapatite

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ABSTRACT

Bioretention system is an effective way to solve the problem of urban water environment pollution. In this paper, the difficulty of the existing biological retention system to effectively remove dissolved heavy metals was studied. By comparing the adsorption effect of acid quartz sand filler layers with nano-hydroxyapatite (N-HAP), medical stone, nano-carbon, and biochar, the conclusion is drawn from the static and cylinder dynamic experiments that N-HAP has the best effect of removing Cu^{2+} and Zn^{2+}, and the effect is long lasting. The scanning electron microscopy results showed that the N-HAP particles were rough and the surface was more rod-shaped, which increased the specific surface area of the N-HAP particles, promoted the complexation and electrostatic interaction of the additives and heavy metal solutions, and facilitated the adsorption of heavy metals. The research results help to improve the technology of filler matrix modification.

Key words | adsorption, bioretention, filler, heavy metal pollution, nano-hydroxyapatite, pollutant removal

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HIGHLIGHTS

- Bioretention system is an effective way to solve the problem of urban water environment pollution.
- The research results help to improve the technology of filler matrix modification in bioretention systems.

INTRODUCTION

In recent years, the progress of urbanization has been accelerating, urban roads and other impervious areas have rapidly increased, leading to a rapid decrease in drainage volume and causing damage to the hydrological cycle process in cities. The resulting environmental pollution has also become increasingly serious (Wang *et al.* 2015a, 2015b). Urban surface runoff has become the focus of current water environmental pollution research due to its wide geographical range, strong randomness, and complex causes (Deletic & Maksimovic 1998; Yin *et al.* 2005). However, in urban surface runoff, the most important part is the urban road runoff. Frequent traffic activities cause a large amount of pollutants such as suspended solids and heavy metals to accumulate on the pavement. These pollutants enter the water body with road runoff, which in turn affects the urban water environmental ecosystem (Kayhanian *et al.* 2007; Line & White 2007).

In order to achieve sustainable urban development, it is necessary to strengthen the regulation and purification of urban water resources. Recently, bioretention systems are gradually being widely researched and applied due to good runoff retention, peak flow regulation, and water purification effects (Wang 2011; Wang *et al.* 2015a, 2015b). Bioretention facilities mainly use filler layers to adsorb, precipitate, perform microbial action and ion exchange with

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pollutants in rain runoff, thereby removing pollutants (Peng *et al.* 2014). The bioretention system can also regulate the hydrology and water quality of rain runoff, so that the construction area can restore its natural state.

Various production activities such as industry and transportation generate a large amount of heavy metals, causing heavy metal pollution to be one of the main parts of urban water environmental pollution. In addition, Yue Jiang *et al.* sampled and analyzed the urban road runoff produced by 17 rainfall events in a city and found that Cu and Zn are the main heavy metal pollutants (Jiang 2012). The bioretention system has a small footprint and flexible layout, and can be used in conjunction with other water treatment systems. Therefore, using a bioretention system to remove heavy metals from urban rain runoff is a good choice (Roy-Poirier *et al.* 2010). In bioretention systems, fillers are a key factor in their functioning.

In this paper, the efficiency of removal of major heavy metal ions in the bioretention system under different packing conditions is evaluated, and the optimal filler for the bioretention system is selected. On this basis, the adsorption characteristics and removal rules of N-HAP for heavy metal ions in wastewater were studied. Furthermore, the removal effect of N-HAP on Zn^{2+} and Cu^{2+} was investigated in a dynamic cylinder simulation experiment, and it was tested whether the removal effect of N-HAP on heavy metal ions is persistent.

METHODS

Basic filler performance experiment

The permeability coefficient of acid-washed quartz sand is 0.037–0.089 cm/s through permeation experiment, which meets the international permeability requirements for fillers of bioretention facilities and verifies its feasibility as a basic filler.

Filler selection experiment

Static adsorption experiment

In this experiment, the static adsorption capacity of four materials to heavy metal ions was investigated. With 4 mg/l solution of $Zn(NO_3)_2$ and $CuSO_4$ solution, 30 250 mL conical bottles were taken and numbered A1–A5 and B1–B5.150 ml of 4 mg/L Zn^{2+} and Cu^{2+} solutions were added to Erlenmeyer flasks numbered A and B, respectively. In A1(B1), A2(B2), A3(B3) and A4(B4) Erlenmeyer flasks, 5 g of N-HAP, medical stone, nano-carbon, and biochar were added, respectively. A5 and B5 were blank control groups. The Erlenmeyer flask was placed on an oscillating shaker and oscillated for 60 min with the rotating speed set to 200 r/min and the temperature set to 25 °C. Then a sample was taken. With the same experimental conditions and variables, the oscillation time was set as 120 min. The flask was sampled again. With the same experimental conditions and variables, the oscillation time was set as 180 min.

After the oscillation, the sample was filtered (using a disposable sterile syringe with a 0.45 μm filter, and the same is true for the filtering process below) and the heavy metal concentration was measured. The removal rate of heavy metals was calculated according to formula (1).

$$R = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

where R = each of the characteristics of pollutants' removal rates, C_0 = initial heavy metal ion concentration, and C = sampling point concentration.

Cylinder dynamic experiment

In this experiment, the dynamic removal ability of heavy metal ions was investigated by simulating the rainfall environment. Ten test columns numbered A1, A2, A3, A4, B1, B2, B3, B4, C, D were prepared. This experiment chose to add filler in the middle of the test column (near sampling hole no. 3). Firstly, 170 g acid-washed quartz sand was added twice to each test column, and each time, it was shock compacted. Then, 160 g acid-washed quartz sand was added again to A1, A2, A3, A4, B1, B2, B3 and B4 test columns. 170 g acid-washed quartz sand was added to the C and D test columns for shock compaction, and then 10 g N-HAP, medical stone, nano-carbon, and biochar were respectively added to the A1(B1), A2(B2), A3(B3) and A4(B4) test columns. Then 170 and 160 g acid-washed quartz sand were added to each test column, and shock compaction was performed each time. The total weight of acid-washed quartz sand and filler for each test column was 840 g. After the filler addition was completed, the top of the test column was sealed with screws, and the experiment began after 24 hours of standing. The filled test column was placed on the test rack, the test column, water tank and peristaltic pump were connected with a hose, and the inlet water flow rate of each test column was controlled to be 10 ml/min, and water poured in from the lower part. The sampling point was designed as follows: a rubber plug was used as stop-water and the needle was inserted deep into the middle of the test column. The outside of the needle was connected to the hose. Water intake was controlled by a stop clamp on the hose. At the beginning of the experiment, water was poured into the test column at a constant speed. After the filler was fully wetted and the air between the pores of the filler was removed, the timing was started. After 60, 120 and 300 min, the top sampling point was sampled for water. The water samples were filtered to determine the concentration of heavy metals. The removal rate of Zn^{2+} and Cu^{2+} was calculated according to formula (1). The setup of the experiment column is shown in Figure 1. Simulated wastewater containing Zn^{2+} and Cu^{2+} was injected into the experiment columns in groups A, C, B and D, respectively. The experiment was repeated 3 times, and the average value was taken as the final experimental result.

Cylindrical experiment on removal of heavy metal ions by N-HAP

As a filler, a single removal of heavy metal ions is not enough. Therefore, in this study, the persistence of removal of heavy metal ions by N-HAP was detected by dynamic cylinder experiment.

The inlet water flow rate in the test column is controlled by the peristaltic pump to be 10 ml/min, and water continues to flow. When the solution is fully saturated in the test column and starts to flow from the top (sampling point 6), the timing starts, as the zero point of the sampling timing. Water samples were collected at 60, 150 and 300 min from the beginning of the timing. After filtering the obtained water samples, the concentration of heavy metals was measured, and the removal rate was calculated according to formula (1). After the test column had run for 360 min, the peristaltic pump was shut off to stop the water inflow, and the water inlet hose removed to let the test column dry naturally. After the test column had dried naturally for 24 hours, the above operation was repeated to calculate the removal rate. The removal effect of N-HAP on pollutants at different times was compared under the conditions of drying and re-watering.

Study on the adsorption characteristics of heavy metals by N-HAP

After confirming the feasibility of N-HAP as filler, field emission scanning electron microscope (SEM) of JEOL was used to obtain the SEM images amplified before and after the adsorption of N-HAP, so as to further analyze and explain the adsorption characteristics of N-HAP on dissolved heavy metal ions.

RESULTS AND DISCUSSION

Filler selection experiment

Static adsorption experiment

According to the concentration of Zn^{2+}/Cu^{2+} measured after 60, 120 and 180 min, the removal rate was calculated according to formula (1). Three groups of parallel experiments were designed to take the average value of the measured data, and the removal effect of different materials on Zn^{2+}/Cu^{2+} was obtained according to the static

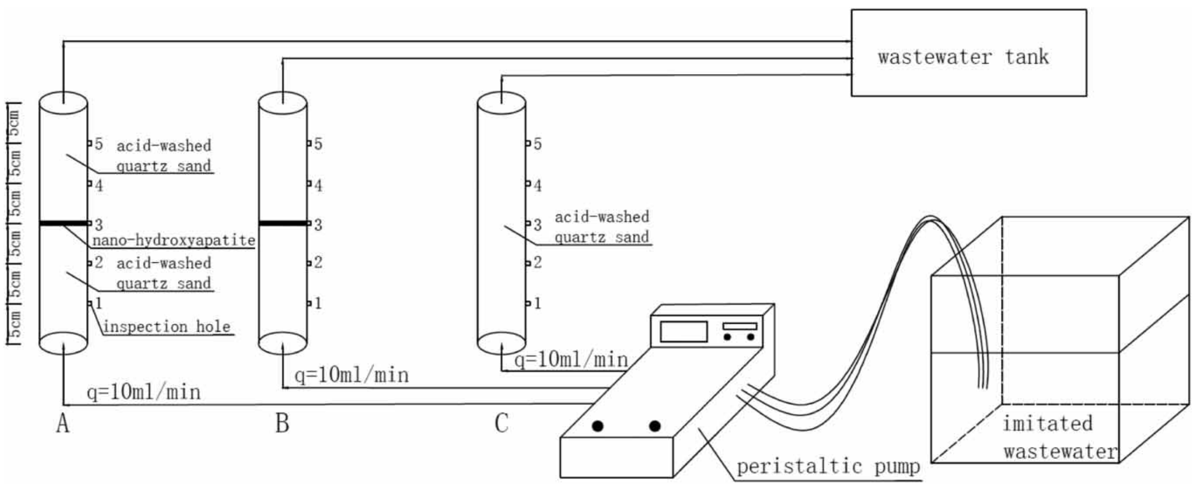

Figure 1 | Setting of test column and sampling point.

adsorption experiment results of each experimental material on Zn^{2+}/Cu^{2+}, as shown in Figure 2.

As can be seen from Figure 2, the removal rate of Zn^{2+} and Cu^{2+} in the blank group was almost zero, indicating that acid-washed quartz sand had a poor effect on the removal of heavy metal ions, which verified its feasibility as the foundation filler for the cylindrical experiment. After the static adsorption reached 60 min, the removal rate of Zn^{2+} and Cu^{2+} by N-HAP was close to 100%. With the extension of time, the removal rate was still 100% after 180 min. The removal rate of Zn^{2+} and Cu^{2+} for medical stone increased with time, reaching nearly 100% at 180 min. Although nano-carbon and biochar also had a certain removal effect on Zn^{2+} and Cu^{2+} in solution, and the removal rate increased with reaction time, the removal rate was relatively low, reaching only about 70% by 180 min.

Comparing the removal effects of the four materials on Zn^{2+} and Cu^{2+} under the same conditions, it can be seen that N-HAP has the highest removal rate for heavy metal ions and the strongest static adsorption capacity, followed by medical stone, and the weakest nano-carbon and biochar.

The Freundlich model was used to fit the experimental results of N-HAP, which had the best removal effect on Zn^{2+} and Cu^{2+}. The sorption coefficient of N-HAP on Zn^{2+} and Cu^{2+} was 55.31 and 59.03 respectively. It can be seen that the sorption effect of N-HAP on Cu^{2+} was slightly higher than that of Zn^{2+}.

Cylinder dynamic experiment

Water samples were collected from the top sampling point at different times and filtered to measure the concentration of heavy metals. The removal rate of Zn^{2+} and Cu^{2+} was calculated according to formula (1). Groups A and C, and groups B and D were treated with Zn^{2+} and Cu^{2+} solutions, respectively. The experiment was repeated 3 times, and the average value was taken as the experimental result. The removal rates of different fillers in each time period are compared as shown in Figure 3.

According to the comparison analysis of removal rates among different fillers in Figure 3, it can be seen that N-HAP has a good removal effect on two kinds of heavy metal ions, and the removal rates in different time periods can reach 100%. Compared with the other three alternative materials, the removal effect is the best and the removal effect is the most stable. The removal rate of Zn^{2+} and Cu^{2+} was about 80%, but the removal rate increased first and then decreased with time. The removal rate of Zn^{2+} is about 60%, which increases and then decreases with time. However, the removal rate of Cu^{2+} can only reach about 40%, which decreases and then increases with time. The removal rate of biochar for both kinds of ions after 180 min was less than 20%, and both increased and then decreased with time, with the worst effect.

Brief summary

By static adsorption experiments, the removal effects of Zn^{2+} and Cu^{2+} on four materials at different times were compared. After 60 min, the removal rate of Zn^{2+} and Cu^{2+} by N-HAP reached 100%. After 180 min, the removal rate of Zn^{2+} and Cu^{2+} by medical stone began to approach 100%. The initial removal rates of the two ions by nano-carbon were very low, but after 180 min the removal rates

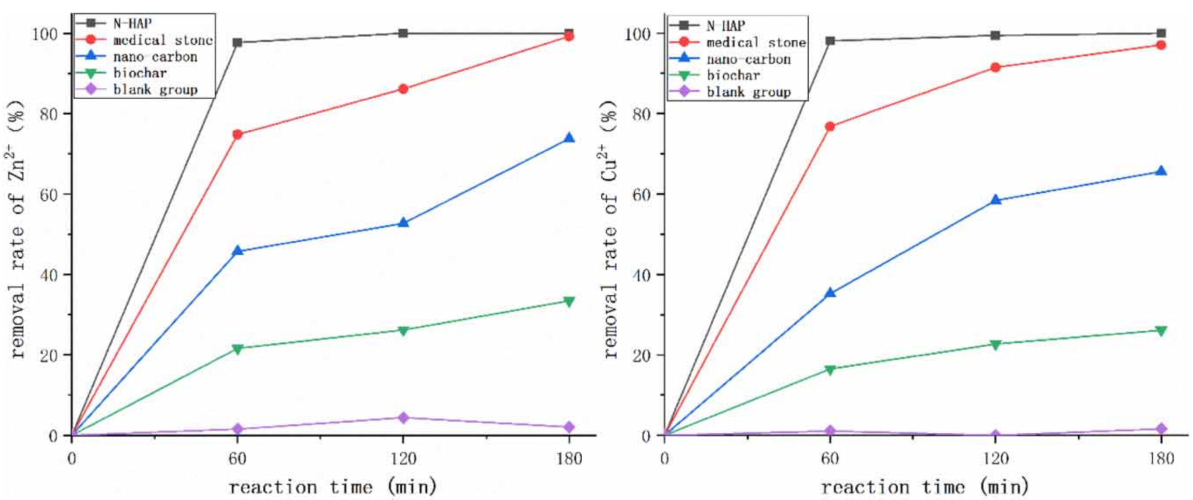

Figure 2 | Static removal of Zn^{2+} and Cu^{2+} by nano-hydroxyapatite, medical stone, nano-carbon, biochar and blank group.

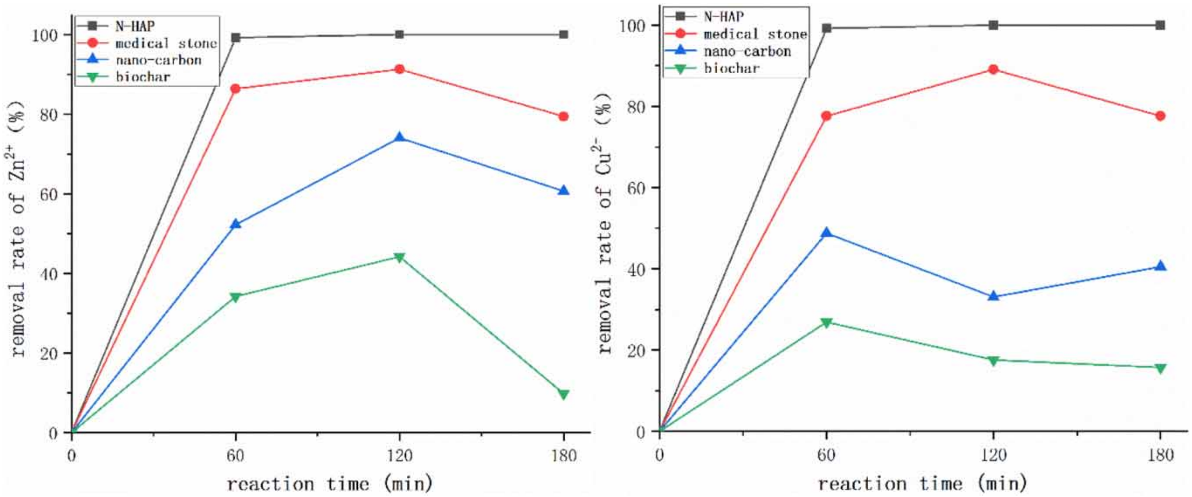

Figure 3 | Dynamic removal of Zn^{2+} and Cu^{2+} by nano-hydroxyapatite, medical stone, nano-carbon and biochar.

of Zn^{2+} and Cu^{2+} were increased to 70 and 65%, respectively. Biochar has a poor removal rate for both.

The removal rates of Zn^{2+} and Cu^{2+} were obtained by cylinder experiment. Compared with the other three fillers, N-HAP showed a more significant removal effect on Zn^{2+} and Cu^{2+}. With the increase of time, the removal rate of 180 min could still reach 100%.

Combined with static and dynamic experiments, it is concluded that N-HAP has a good removal effect for both Zn^{2+} and Cu^{2+}, and the removal effect remains constant over time, indicating the superiority of choosing N-HAP as biological retention facility filler.

Cylindrical experiment on removal of heavy metal ions by N-HAP

In this experiment, the removal of Zn^{2+} and Cu^{2+} by N-HAP under the condition of drying and re-watering is shown in Figure 4.

As can be seen from Figure 4, the removal rate of N-HAP for Zn^{2+} and Cu^{2+} can still reach 100% in the case of re-watering after drying, and can still be completely removed at a high solution concentration, indicating that N-HAP has a good removal effect on Zn^{2+} and Cu^{2+}. The removal effect of N-HAP on Zn^{2+} and Cu^{2+} did not

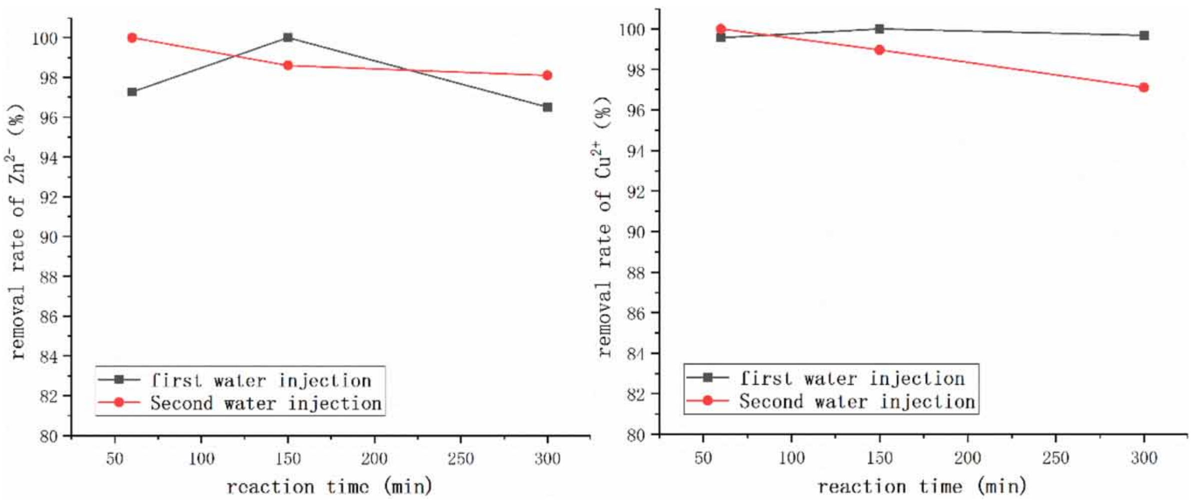

Figure 4 | Two removal effects (first water injection and second water injection) of N-HAP on Zn^{2+} and Cu^{2+}.

change significantly compared with the first water injection under the condition of the second water injection 24 h after the natural drying of the experimental column, and the removal rate fluctuated within a small range below 100%, indicating that N-HAP has a long-lasting removal effect on Zn^{2+} and Cu^{2+}.

The removal effect of N-HAP on heavy metals decreases slightly over time (second water injection). According to the analysis, at the beginning, there were many active sites on N-HAP, which could rapidly adsorb heavy metals in the wastewater. Later, due to a slight decrease of the adsorption sites, the removal effect of N-HAP on heavy metals was also weakened.

Study on the adsorption characteristics of heavy metals by N-HAP

It can be seen from Figure 5 that the surface of N-HAP particles is rough and more rod-shaped, which increases the specific surface area of N-HAP particles and is conducive to the adsorption of heavy metals. Compared with N-HAP particles with a magnification of 50 μm before and after the experiment, it was found that the size of N-HAP particles increased to different degrees after the experiment. By comparing the N-HAP particles with a magnification of 1 μm before and after the experiment, it was found that the pores on the surface of the particles decreased in visibility after the experiment, indicating that N-HAP adsorbed a large number of heavy metal ions during the experiment.

As shown in Figures 6 and 7, the scanning electron microscopy was used to analyze the elements of N-HAP before and after adsorption, and it was found that heavy metal elements in N-HAP increased while oxygen elements decreased, indicating that a large number of heavy metal ions are adsorbed on the surface of N-HAP. In the process of adsorption, the hydroxyl functional groups on the surface of N-HAP have complexation and electrostatic adsorption with heavy metals, which can effectively remove heavy metal ions from the solution.

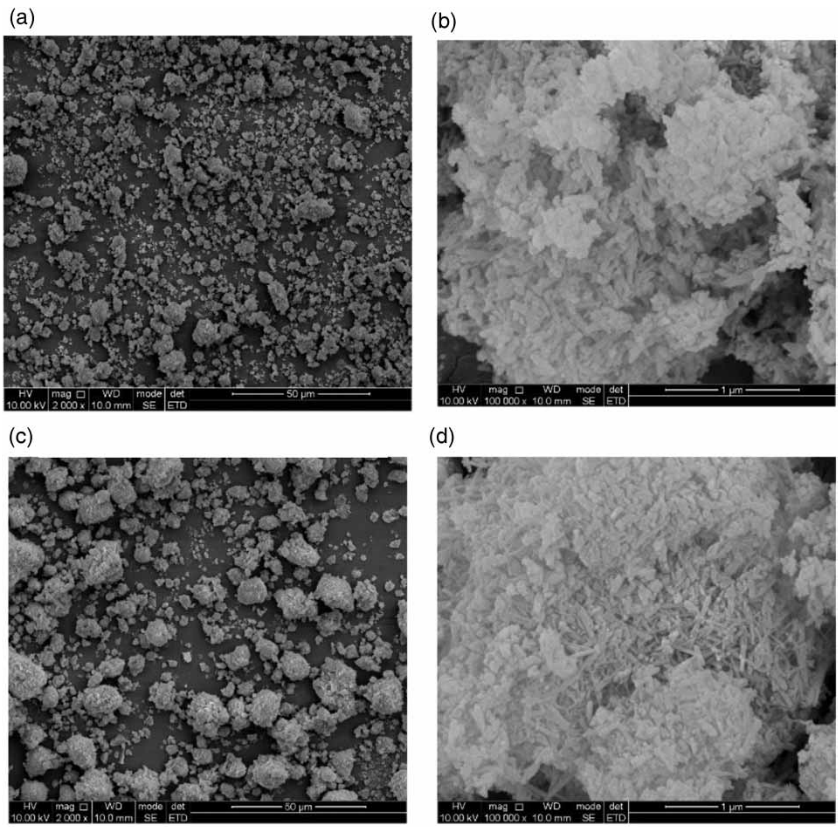

Figure 5 | Scanning electron microscopy before and after adsorption of N-HAP. (a) SEM spectra of N-HAP before experiment (×50μm), (b) SEM spectra of N-HAP before experiment (×1μm), (c) SEM spectra of N-HAP after experiment (×50μm), (d) SEM spectra of N-HAP after experiment (×1μm).

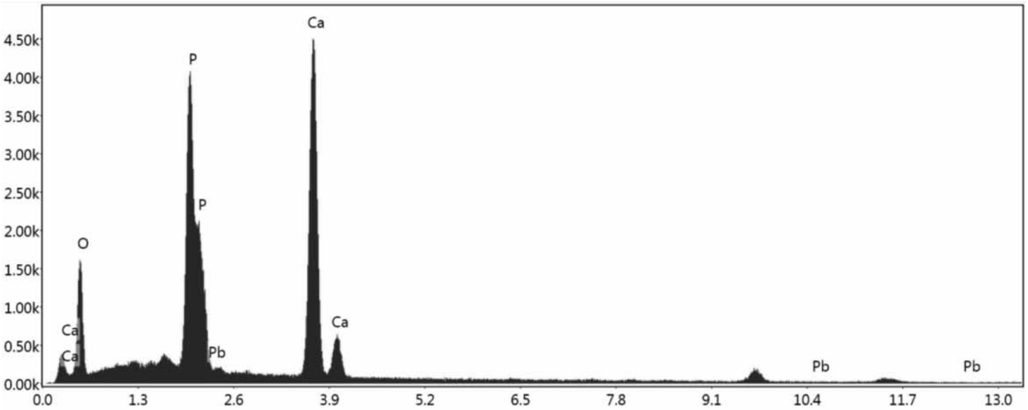

Figure 6 | Element analysis diagram of energy spectrometer before N-HAP adsorption.

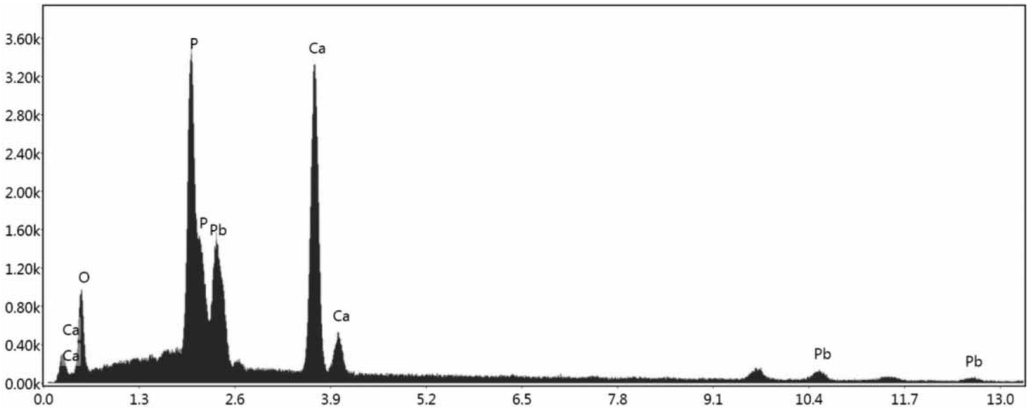

Figure 7 | Element analysis diagram of energy spectrometer after N-HAP adsorption.

CONCLUSIONS

1. Through filler selection experiment, the static adsorption and dynamic removal effects of N-HAP on heavy metal ions are the best, reaching 100%, far better than the other three fillers.
2. The removal effect of N-HAP on Zn^{2+} and Cu^{2+} was not significantly changed compared with the first water injection, and the removal rate was still 100%, proving that N-HAP has a long-lasting removal effect on Zn^{2+} and Cu^{2+}.
3. The rough surface of N-HAP particles is more rod-shaped, and the specific surface area is large, which is conducive to the electrostatic and complexation between additives and heavy metal ions and the adsorption of heavy metals.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Deletic, A. B. & Maksimovic, C. T. 1998 Evaluation of water quality factors in storm runoff from paved areas. *Journal of Environmental Engineering-ASCE* **124** (9), 869–879.

Jiang, Y. 2012 *Study on Mixed Toxicity of Surface Runoff From Urban Fast Dry Road*. Tongji University, Shanghai.

Kayhanian, M., Suverkropp, C., Ruby, A. & Tsay, K. 2007 Characterization and prediction of highway runoff

constituent event mean concentration. *Journal of Environmental Management* **85** (2), 279–295.
Line, D. E. & White, N. M. 2007 Effects of development on runoff and pollutant export. *Water Environment Research* **79** (2), 185–190.
Peng, S. H., Huang, J. J. & Li, T. 2014 Study on runoff pollution control effect of filter-type biological retention pool. *Water and Wastewater Engineering* **2014** (6), 38–42.
Roy-Poirier, A., Champagne, P. & Filion, Y. 2010 Review of bioretention system research and design: past, present, and future. *Journal of Environmental Engineering* **136** (9), 878–889.
Wang, W. L. 2011 *The Experiment and Application Research About Rainwater Bioretention Technology*. Beijing University of Civil Engineering and Architecture, Beijing, China.
Wang, J. L., Yang, L. Q. & Huang, T. 2015a Effect of composite bioretention media on heavy metals removal from urban stormwater runoff. *Chinese Journal of Environmental Engineering* **9** (7), 3086–3091.
Wang, S. M., He, Q., Xu, Q. & Song, L. 2015b Summary of nitrogen removal in surface runoff by bioretention system. *Advances in Water Science* **2015** (1), 140–150.
Yin, W., Li, P. J. & Ke, X. 2005 Control technologies on urban surface runoff pollution in China. *Chinese Journal of Ecology* **24** (3), 533–536.

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