Enhanced removal of NH$_4^+$ in bioretention by sludge biochar

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Abstract: Both bioretention and sludge biochar have better effects to the removal of nitrogen and phosphorus removal in water. Combining them could improve the effect of bioretention on NH$_4^+$. After applying sludge biochar, the adsorption effect of filler on NH$_4^+$ was improved. When the sludge biochar was applied to the filler, on the top of the submerged area in the tank, the removal rate of NH$_4^+$ could reach 88.62%~94.48%.

At present, the process of urbanization is gradually accelerating, which makes the urban impermeable area increase$^{[1]}$. At the same time, due to the increase of the probability of extreme climate occurrence caused by greenhouse effect and so on, the urban drainage system is facing a severe test, and the concept of "Sponge City" came into being. As one of the main facilities of rain flood management, bioretention is widely used in Sponge City planning and design. The bioretention plays a role in slowing down urban rain pollution and controlling urban waterlogging. At present, bioretention research shows that it has a good effect on the removal of pollution in most runoff, such as particulate matter, heavy metals, petroleum hydrocarbon$^{[2]}$, pathogens and so on. But some organic nutrients are relatively good unstable, and sometimes even the pollutant concentration in the production flow is higher than the influent concentration$^{[3]}$, so the packing for the bioretention needs to be optimized and improved.

Sludge biochar is widely used in water treatment as an effective sludge resource utilization method. The adsorption and removal effect of heavy metals, nitrogen and phosphorus was remarkable, so sludge biochar was used as filler modifier in bioretention to strengthen the effect of ammonia nitrogen removal.

1. Materials and tests

1.1. Test materials

1) Sludge biochar

The sludge raw material is taken from the secondary settling tank sludge of Hengyang Jinda Water Co., Ltd. after 105°C of drying, ground into powder shape, over 100 mesh sieve, in a muffle furnace with 600°C pyrolysis 4h preparation completed.

2) Standard filler Soil

A standard filler soil ratio of 88%(w/w) of concrete sand, 8% of silt and clay, and 4% of organic matter (e.g. sawdust) was used in North Carolina, USA.

3) Improved filler soil

Add 4%(w/w) sludge biochar to the standard filler soil base and mix evenly.

1.2. Experiment equipment
The test device was fabricated according to the bioretention with lining and submerged area. The main body is DN300 rigid plastic pipe, the bottom plate is made of imitation marble PV plate and hot melt adhesive, the bottom is connected with DN20 perforated pipe for drainage, and the right side is connected with a riser to set the height of different submerged areas.

1.3. Ammonia nitrogen adsorption test
This experiment uses artificial simulated runoff rainwater to carry out ammonia nitrogen and phosphate adsorption experiments on sludge biochar, control filler soil and modified filler soil respectively. The three types of materials were rinsed with deionized water several times before the experiment, until the conductivity of the eluent did not change. So, the surface of the material was considered to be cleaned. The adsorption isotherm test was carried out at 20 ± 2 °C. The group repeats. The 0.1mg·L⁻¹NH₄Cl stock solution was diluted with simulated rainwater runoff to NH₄⁺ concentration of 0.0, 0.5, 1.0, 2.0, 5.0, 10.0mg·L⁻¹ solution. Simulated rainwater runoff is a mixed solution of 120mg·L⁻¹CaCl₂, 14mg·L⁻¹Na₂HPO₄ and 12.0mg·L⁻¹NaNO₃, the pH value is adjusted to 7.0±0.2. 0.4g sludge biochar, 10g control filler soil and 10g are weighed respectively put the modified filler soil in a 50ml centrifuge tube, add 20ml artificial simulated rainfall runoff with different concentrations, shake it at 150r/min for 24h, then centrifuge at 5000r/min at high speed for 20min, take the supernatant through 0.2μm pore size. After filtering the filter paper, the NH₄⁺ concentration was analyzed. The determination of NH₄⁺ refers to the spectrophotometric method of Nessler's reagent in "Water and Wastewater Monitoring and Analysis Method (Fourth Edition Supplement)". The measuring instrument is Shanghai Jinghua752 ultraviolet spectrophotometer.

1.4. Simulation rainfall infiltration test
Before the formal starting of the experiment, the system was inoculated and cultured with water from the school pond. Once every 3d, 40L each time to make the packing and microorganism in the device more mature, to establish the biological diversity of the packing in the bioretention, and to make it closer to the actual soil environment. Under the conditions of selecting the best inundation area (standard group: 300mm, modified group: 600mm), the synthetic rainwater with different pollutant concentrations was configured to investigate its treatment capacity for rainwater in different situations. The simulated rainfall infiltration tester was carried out six times, and its period was three days to ensure that the treatment effect between the front and back did not interfere with each other. The influent flow rate is set to 160 ml·min⁻¹. Then, the treated water quantity of a single bioretention is 80 ml·min⁻¹. The water distribution time is 4h, and the water sampling time is set to 4h. After the start of the test, the rainwater concentration of 6 water distribution is shown in Table 1.
Table 1  Application concentration of simulated rainfall infiltration test reagent/(mg.L⁻¹)

| Rainfall | COD  | TN  | NH₄⁺-N | NO₃⁻-N | TP | Niacin |
|----------|------|-----|--------|--------|----|--------|
| 1        | 150.0| 7.0 | 3.0    | 3.0    | 1.0| 1.0    |
| 2        | 200.0| 8.0 | 3.5    | 3.5    | 1.5| 1.0    |
| 3        | 250.0| 10.0| 4.5    | 4.0    | 2.0| 0.5    |
| 4        | 300.0| 12.0| 5.5    | 4.5    | 2.5| 2.0    |
| 5        | 350.0| 14.0| 6.0    | 5.0    | 3.0| 3.0    |
| 6        | 400.0| 15.0| 6.5    | 6.0    | 3.5| 2.5    |

2. Results and analysis

2.1. Ammonia nitrogen adsorption test

Adsorption isotherms are generally classified into six. As shown in Fig.2, different isotherms reflect the adsorption characteristics of adsorbates by different adsorbents.

When the NH₄⁺ concentration is low, the already washed sludge biochar still leaches a small amount of NH₄⁺; its adsorption amount is negative. The relationship between the NH₄⁺ equilibrium concentration and adsorption amount after the static adsorption of the three materials at 24h is shown in Fig.3. Its adsorption characteristics do not conform to the traditional single molecule adsorption curve, but conform to the trend of type III adsorption isotherm. The curve is concave and has no inflection point. All three materials have weak interaction with NH₄⁺. But it can be seen that the curve slope of the modified packed soil is slower. Its interaction with the NH₄⁺ is slightly stronger than that of the standard packed soil.
Fig. 3  Relationship between adsorption capacity and equilibrium concentration \( \text{NH}_4^+ \) of three materials

2.2. Analysis of simulated rainfall seepage test

From fig. 4, it can be seen that a single modified filler soil cannot use its own characteristics to improve the removal of \( \text{NH}_4^+ \). \( \text{NH}_4^+ \) removal rate of the standard group decreased by up to 10% with the increase of its initial concentration, which may be due to the decrease of internal oxygen with the continuous operation of the bioretention, and the continuous ammoniation reaction of nicotinic acid into \( \text{NH}_4^+ \) to reduce the removal rate. Improved group’s removal rate of \( \text{NH}_4^+ \) is relatively poor, mainly:

1. Because the height of the submerged area is 600mm, the whole device is almost immersed in water and lacks aerobic environment, so it is difficult to achieve nitrification;
2. Secondly, sludge biochar is rich in \( \text{K}^+ \), \( \text{Na}^+ \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) and other heavy metal ions. Its negative charge attracting ability is weakened, and its cation exchange ability is weakened.

3. Structural optimization test

3.1. Experiment design
The addition of sludge biochar is effective in the interaction between NH$_4^+$ filler in bioretention and Rain Water, but the performance of removing NH$_4^+$ in the operation of the plant has not been improved or even decreased, which may be due to the problem of the height of submerged area and the NH$_4^+$ of leaching and release of modified packed soil. Therefore, two kinds of fillers were combined, one group with the upper half of the modified filler soil and the lower half with the standard filler soil; the other group with the upper half with the standard filler soil and the lower half with the modified filler soil. And Wtp, Xrt. Simulated rainfall infiltration tests were carried out on two new filler structures, the height of the submerged area was set to 300mm, and the water sampling time was 4h. The rainfall water distribution concentration is shown in Table 2.

| Rainfall | COD  | TN   | NH$_4^+$-N | NO$_3^-$-N | TP   | Niacin |
|----------|------|------|------------|------------|------|--------|
| 1        | 200.0| 9.0  | 3.0        | 4.5        | 1.5  | 1.5    |
| 2        | 350.0| 12.5 | 4.5        | 5.0        | 2.0  | 3.0    |
| 3        | 400.0| 15.0 | 6.0        | 6.0        | 3.0  | 3.0    |

3.2. Results and analysis

After the structural optimization shown in Fig.5, both Wtp and Xrt achieve better removal of NH$_4^+$ ions in water. The highest removal rate of Wtp to NH$_4^+$ reached 97.52% in three rainfall periods, while the highest removal rate of NH$_4^+$ reached 90.58%. The main reasons may be that: (1) the submerged zone height of both groups of bioretentions is set to 300 mm, compared with the test at 1.4, which reduces the submerged area of sludge biochar in water; (2) The submerged zone decreases and the seepage zone increases, which makes it have more time for nitrification to achieve the effect of removal of the NH$_4^+$; (3) The submerged area is reduced and the flow rate is accelerated, which makes the nitrogen source in the submerged area decrease, the oxygen content increases, and the nitrate nitrogen in Rain Water is not easy to occur the reduction process (DNR). Hence, the packing modified bioretention after optimizing the structure greatly improves the removal of NH$_4^+$.

Meanwhile, placing the modified packed soil above and below the structure has a better effect on the removal of NH$_4^+$, and its lifting range is 5.39%~10.43%. Possible reasons are: (1) After the modified packed soil is placed above, it is mainly in the seepage zone, not the submerged zone, and the adsorbed NH$_4^+$ is not easily eluted out; (2) During the rainfall interval, the modified packed soil in the seepage zone is in better contact with the air, and the subsequent retained NH$_4^+$ ions are better nitrified. After the modified structure, the removal effect of the NH$_4^+$ by the bioretention was higher than that of the standard packed soil, and the maximum removal rate of the standard group was only 74.99%. As a result, structural adjustment is of great significance for sludge biochar to strengthen the removal NH$_4^+$ of bioretention.
4. Conclusions
1) Application of sludge biochar in soil helps to enhance its adsorption of NH$_4^+$.
2) The single modified filler soil can not improve the ability of bioretention to remove NH$_4^+$. Applying only sludge biochar above the submerged area in the tank is important in strengthening the removal of NH$_4^+$. The removal rate reaches 88.62%–94.48%.

References
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