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To cite this article: Y Cai et al 2018 IOP Conf. Ser.: Earth Environ. Sci. 108 042117

View the article online for updates and enhancements.
Research on denitrification efficiency of three types of solid carbon source

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Abstract. C/N rates can greatly influence efficiency of denitrification. It is difficult for current treated effluent to reach GB18918-2002 primary effluent standard because of its low C/N rate. To improve the efficiency of denitrification, the quality of effluent, and realize the waste recycling, this article selected magnolia leaves, loofah and degradable meal box as the solid carbon source and set different solid-liquid ratio of magnolia leaves for periodic denitrification stage to study the change of NO₃⁻-N, TN, COD, NO₂⁻-N, NH₄⁺, PO₄³⁻ and color. The results showed that in the condition of influent nitrate concentration of 40 mg/L, carbon dosage of 10 g, the reaction temperature of 25 °C, the nitrate removal rates of magnolia leaves and loofah reached 89.0% and 96.8% respectively, rather higher than degradable meal box (56.3%). The TN removal rates of magnolia leaves (91.7%) and loofah (77.7%) were both higher than degradable meal box (53.9%), and the effluent TN concentration of loofah and degradable meal box reached 25.4 mg/L and 21.1 mg/L respectively, which couldn’t be discharged according to the primary effluent concentration standard of GB18918-2002. The released concentration of ammonia nitrogen and phosphate: loofah> magnolia> degradable meal box. The high solid-liquid ratio of magnolia leaves helped to improve the TN removal rate, which reached 75.0% (1:200) and 91.7% (1:100), but it caused higher released concentration of carbon, ammonia nitrogen and phosphate to effect system heavily. Under the integrated analysis, the low solid-liquid ratio (1:200) of magnolia leaves was more suitable to be the denitrification external carbon source.

1. Introduction

In recent years, China’s environmental problems are increasing, especially the air contamination and water contamination [1-4]. So as to reach the primary effluent standard of “the Pollutant Discharge Standard of the Municipal Wastewater Treatment Plant (GB18918-2002)”, it is necessary to add the external carbon source to improve the efficiency of denitrification because of its low C/N rate. There are higher economic costs or some biological toxicity and other issues in the traditional liquid carbon source like methanol and acetic acid [5], and in the case of large fluctuations in water quality, it is likely to cause the liquid carbon source insufficient or excessive, affecting the quality of effluent heavily [6]. So the relevant researchers have been committed to finding more suitable external carbon sources in recent years. The research on solid carbon source is increasing, especially the organic solid materials with wide range of sources and low economic cost, generally divided into natural organic...
solid materials and synthetic organic solid materials. Currently some natural organic solid materials are used in the study of external carbon source, such as wheat straw [9, 10], corn [11, 12] and cotton [7, 8], and synthetic organic solid materials are mainly biodegradable polymers, such as polycaprolactone (PCL) [15, 16] and poly butylene succinate (PBS) [13, 14]. Yet the existing studies are mostly based on the same type of organic matter [17-19], and cotton, wheat straw, biodegradable polymers have higher economic value [20], which to a certain extent reduces the relevant research value of the practical application.

This experiment selected natural organic solid type of magnolia and loofah and synthetic organic solid class of degradable meal box as the solid carbon source for periodic denitrification stage to study the change of NO$_3^-$-N, TN, COD, NO$_2^-$-N, NH$_4^+$, PO$_4^{3-}$ and color, which was to analysis the effluent quality in three types of solid carbon source systems. And according to the first test results, the different solid-liquid ratios of magnolia were set to study the effects of different solid-liquid ratios on denitrification efficiency and system, so as to find the appropriate carbon source and its solid-liquid ratio.

2. Methods and materials

2.1. Materials and instruments

In this study, three kinds of solid materials, such as natural organic solid type of magnolia and loofah and synthetic organic solid class of degradable meal box, were selected to be the solid carbon source for periodic denitrification. Magnolia, picked in the woods in Zhongnan University of Economics and Law, was cut into 1x1 cm after washed and dried. Loofah and degradable meal box, purchased from supermarket, were both cut into 1x1 cm. The activated sludge was taken from the secondary sedimentation tank in the sewage treatment process of Tangxun sewage treatment plant, in Wuhan. The domestic sewage was taken from the sewage outlet in Zhongnan University of Economics and Law. The quality indicators of domestic sewage are shown in Table 1.

| Indicators | COD/ (mg·L$^{-1}$) | NO$_3^-$-N/ (mg·L$^{-1}$) | NO$_2^-$-N/ (mg·L$^{-1}$) | NH$_4^+$/ (mg·L$^{-1}$) | TN/ (mg·L$^{-1}$) | PO$_4^{3-}$/ (mg·L$^{-1}$) | color |
|------------|-------------------|------------------------|------------------------|------------------------|-----------------|------------------------|-------|
| Concentrations | 180~300 | 0.5~0.8 | 0 | 7.2~8.4 | 15.4~17.5 | 14.3~19.6 | 21~31 |
| Average | 250 | 0.65 | 0 | 7.8 | 8.3 | 7.7 | 25 |

The reagents used in the experiment are analytical pure. The instruments used are follows: HJ-4A type multi magnetic heating stirrer (Changzhou Guohua Electric Appliance Co. Ltd), HQ30d portable dissolved oxygen meter (Shandong Qingdao Ming Bo environmental protection technology Co. Ltd), HACH DR2800 digestion instrument (Shanghai Xinsong Industrial Co. Ltd), HACH DRB200 COD analyzer (Shanghai Xinsong Industrial Co. Ltd), BOXUN type vertical pressure steam sterilizer (Shanghai Boxun Industrial Co. Ltd), and HITACHI U-1900 type ultraviolet spectrophotometer (Xiamen science and Technology Co. Ltd).

2.2. Activated sludge culture

The activated sludge was put into the culture vessel, with the proper amount of domestic sewage added for aeration culture. The dissolved oxygen of activated sludge aeration was periodically detected by the portable dissolved oxygen meter, and the aeration amount was adjusted appropriately to ensure that the dissolved oxygen of the activated sludge was maintained at 3~4 mg/L. Replacing the supernatant daily, the amount of domestic sewage was adjusted according to the clear turbidity of effluent. The effluent quality was detected regularly to ensure that the effluent COD concentration was less than 50 mg/L. After two weeks of continuous culture, the quantity and quality of the activated sludge gradually rise. Observed with optical microscopy, the number of microbial species increased, with the shaped worms and rotifers appeared.
2.3. Denitrification experiments
Four copies of activated sludge mixture of 1000 mL (around 4 g/L) were taken, with its supernatant poured out to ensure the sludge volume of 460 mL. The reaction container, Jar of 1000 mL, was put on the magnetic heating stirrer, adjusting temperature of 25 ℃, adding sewage of 500 mL(25 ℃), nitrate solution of 40 mL (1000 mg/L, 25 ℃), solid carbon source of 10 g and activated sludge of 460 mL, to ensure the initial COD/NO3- rate maintained at about 3. A few seconds later, the supernatant of 20 mL was taken as the first sample of 0 h. The sludge and nutrient solution mixed fully in the reaction container after pushing the rotate button, sampling in 0.5 h, 1 h, 2 h, 3 h (20 mL water supplement after each sampling) to be test.

2.4. Analysis method
The water quality index analysis method in the test mainly refers to the standard method in “water and waste water monitoring analysis method (4th edition)” [21]. Nitrate nitrogen was measured by ultraviolet spectrophotometry, and the total nitrogen was oxidized by Potassium persulfate oxidation ultraviolet spectrophotometry, and nitrite nitrogen was detected by N- (1-naphthyl)-ethylene diamine spectrophotometry, and ammonia nitrogen was measured by Nessler reagent photometric method, and phosphate was oxidized by Molybdenum antimony spectrophotometric method, and COD was detected by Potassium dichromate colorimetry, and color was measured by Colorimetric method, and mixed liquid suspended solids (MLSS) was detected by Weight method.

3. Results and discussion

3.1. Nitrate, total nitrogen concentration changes
Nitrate removal rate is an important indicator of denitrification performance. The nitrate concentration of the four groups decreased with time, as shown in Fig. 1 (a). Specifically, the nitrate removal rate of the Magnolia group reached 42.1% within 0.5 h and reached 89.0% in 2 h, then remained stable, with the final effluent nitrate concentration remaining at 3.6 mg/L. Since the COD supply was significantly higher than the control group, which was on account of the fast releasing carbon of early Magnolia, the nitrate removal rate of the Magnolia group was highly faster than the comparison. Initially loofah released a large number of carbon as well as nitrate, resulting in the initial nitrate concentration dramatically increasing to 63 mg/L, but the nitrate removal rate of the loofah group was high, reaching 75.0% within 0.5 h and reaching 96.8% in the end, which was due to the high concentration of COD. The nitrate removal rate of degradable meal box increased overall but slowly, which was similar to the comparison, and even lower than the comparison, on account of the slow releasing carbon and nitrogen of degradable meal box within the 3 h reaction time. Its nitrate removal rate of 20.0% within 0.5 h and 56.3% in the end was a litter lower than the comparison’s nitrate removal rate of 26.9% and 64.3%, respectively. The effluent nitrate concentration was maintained at 13.9 mg/L. Since the initial COD supply was relatively abundant, the nitrate removal rate was significantly higher than that of later stage.

Total nitrogen removal rate is not only an important index of denitrification performance, but also a significant indicator of the effluent quality. TN concentrations in four groups all showed a trend of decline over time in Fig. 1 (b). Specifically, with the TN concentration of magnolia decreasing from 47.4 mg/L to 3.9 mg/L within the 3 h reaction time, the final TN removal rate of magnolia reached 91.7%, which was 26.2% higher than that of the comparison. The TN concentration of loofah decreased from 114.3 mg/L to 25.4 mg/L. The TN removal rate was relatively high, reaching 77.7%, but the remaining amount of TN was still 9.2 mg/L higher than that of the comparison, which was due to the initial fast releasing nitrogen. The TN concentration of degradable meal box reduced from 45.7 mg/L to 21.1 mg/L, of which TN removal rate reached 53.9%, even 11.5%lower than the comparison. The TN concentration of loofah and degradable lunch box were higher than the primary effluent concentration standard of GB18918-2002, so they couldn’t be discharged.
3.2. COD concentration changes

COD is not only a quantitative index of solid material releasing carbon, but also an important indicator of the effluent quality. There are two stages that the releasing carbon of solid materials can be divided into [22]: the first to release are the water-soluble and easy decomposition substances of solid material on the surface, then the internal refractory substances of solid material will be released slowly, after the small molecules are fully released, which are attached to the surface or dissolved slowly from the main body. Therefore, the COD concentration would increase slowly to stability after the first rapid growth.

As shown in Fig. 2, the COD concentration of magnolia was generally on the rise and increased rapidly within 0.5 h, which period was also the fastest denitrification rate. It might because of that the rate of COD increase was much higher than that of the COD consumption of denitrification within 0.5 h, due to the rapid releasing of the small molecules of magnolia on the surface. Subsequently, the rate of carbon releasing was slower, but still higher than that of the COD consumption. The initial COD concentration of loofah increased sharply to 1037 mg/L, and it might be concluded that the small molecular substances on the surface of the loofah was rapidly dissolved in water within a few tens of seconds after adding the loofah. Subsequently, with the denitrification reaction, the carbon source gradually consumed to 772 mg/L within 0.5 h. The COD concentration was stable at about 800 mg/L after 0.5 h, indicating that the rate of releasing carbon was almost equal to that of denitrification consumption. Degradable meal box wasn’t degraded first, after denitrification of 1 h, it released
carbon slowly, resulting in the slow growth of COD concentration. However the denitrification rate didn’t rise, even lower than that of the comparison, which might be concluded that the released substances of degradable meal box couldn’t be utilized by denitrifying bacteria. Then the COD concentration declined over the denitrification reaction.

### 3.3. Nitrite and ammonia nitrogen concentration changes

Denitrification process can be simplified to that NO3- is converted to NO2-in the reduction of nitrate reductase, and then the resulting NO2- is converted to N2 in the reduction of nitrite reductase. The nitrite accumulation during the denitrification process is due to the competition for electron acceptor between the nitrate reductase and the nitrite reductase in the absence of organic carbon source, while the nitrite reductase is at a greater disadvantage. [23]. Therefore, as shown in Figure 3(a), the nitrite accumulation of degradable meal box and comparison, which both obviously lack of organic carbon source, reached the maximum amount of 1.0 mg/L at 0.5 h of reaction. However, the nitrite accumulation of magnolia and loofah, of which organic carbon were relatively abundant, were much more severe than that of degradable meal box, that’s because the nitrate could largely affect the activity of the nitrite reductase [24]. The high nitrate concentration seriously inhibit the activity of the nitrite reductase, resulting in the nitrite accumulation of magnolia and loofah rapidly increasing to the maximum amount of 7.3 mg/L and 4.7 mg/L respectively at the first 1 h of reaction. NO2- was more quickly converted to N2 and the nitrite accumulation decreased to 0 mg/L finally, since the inhibition effect of nitrate to nitrite reductase reduced, when the concentration of nitrate decreased to about 13 mg/L over the reaction.

From Fig. 3 (b), it can be seen that the ammonia nitrogen concentration of Magnolia showed a rapid growth trend after 2 h-stability, and the accumulation of ammonia nitrogen was 3.4 times of that of the comparison, finally reaching 18.5 mg/L. The ammonia nitrogen concentration of loofah decreased to stability, and the accumulation concentration of ammonia nitrogen reached 23.4 mg/L, 4.3 times higher than that of the comparison. The concentration trend of ammonia nitrogen between the comparative and degradable meal box were consistent, with no obvious change. The accumulation of ammonia nitrogen was 0.7 times of that of the comparison, finally reaching 3.9 mg/L.

### 3.4. Phosphate concentration and color changes

The phosphate concentration of degradable meal box showed a slow decrease trend, similar to the comparison, but the phosphate concentration of magnolia and loofah presented a slow increase to stability after a slow decline, as shown in Fig. 4 (a). Specifically, in the denitrification process of degradable meal box and comparison, on account of a very small amount of nitrite accumulation and nitrate dominating, phosphorus bacteria began to polyphosphate[26], leading to the concentration of
phosphate decreasing from 7.1 mg/L to 1.3 mg/L. The same to degradable meal box, the phosphate concentration of magnolia and loofah presented a decline trend in the first hour. Subsequently, nitrite accumulated to dominate, and phosphorus bacteria in the system began to release phosphorus, resulting in phosphate concentration of magnolia and loofah increasing to 10.1 mg/L and 13.6 mg/L.

The color of degradable meal box showed a slow decrease trend over the reaction, similar to the comparison, and the color of magnolia presented a trend of rapid increase to stability, and the color of loofah basically remained unchanged, as shown in Fig. 4 (b). Specifically, due to the consumption of organic carbon source in sewage, the initial color of comparison of 22 decreased with the denitrification. Because of the low degradation rate of degradable meal box, the color of its system decreased to stabilize at about 15, similar to the comparison. However, the initial color of magnolia reached 138 due to its rapid releasing pigment. What’s more, magnolia had been releasing pigment over the reaction, causing the color at a high level. However the change range of color decreased in the last hour and the color reached 295 finally, 20 times of that of the degradable meal box, it’s possible that the released pigment was closed to saturation. Similar to magnolia, the initial color of loofah reached 80 due to its rapid releasing pigment. Then it released pigment slowly, while the color of loofah basically remained unchanged because of the consumption of organic carbon source.

3.5. Denitrification indexes of different solid-liquid ratio systems of Magnolia
It could be seen from the above experiments that the magnolia had a higher nitrate removal rate, but at the same time there was also a problem that its releasing concentration of carbon, ammonia and phosphate were too high. In order to further find a suitable dosage for both the removal of nitrate and the decline of the concentration of pollutants in the water, the experiment was carried out with two different solid-liquid ratio systems of 1: 100 (solid carbon source dosage of 10 g) and 1: 200 (solid carbon source dosage of 5 g) to investigate the effect of different carbon source dosage on denitrification efficiency and system.

The denitrification and TN removal rate of 1: 100 solid-liquid ratio system were obviously higher than those of 1: 200 solid-liquid ratio system, as shown in Fig. 5 (a) and Fig. 5 (b). The TN removal rate of two systems were 75.0% (1: 200) and 89.7% (1: 100) respectively, while the final nitrate removal rate of the two systems were similar, reaching 94.9% (1: 200) and 89.0% (1: 100) respectively. The effluent nitrate concentration reached 1.6 mg/L and 3.7 mg/L respectively. It could be seen that the increase of solid-liquid ratio is beneficial to improve the TN removal rate, but not the nitrate removal rate.
Fig. 5 Denitrification indicators analysis of different solid-liquid ratio

- 1: 100 solid-liquid ratio system; □ 1: 200 solid-liquid ratio system
The increase of solid-liquid ratio significantly increased the COD concentration in the system, as shown in Fig. 5 (c). After 3 h of denitrification, the COD concentration of the 1: 200 solid-liquid ratio system increased from 163 mg/L to 354 mg/L, and the COD concentration of the 1: 100 solid-liquid ratio system rose from 342 mg/L to 608 mg/L, which was almost twice as much as the former. The high effluent COD concentration might increase the burden of subsequent aerobic treatment.

As shown in Fig. 5 (d), the accumulation of nitrite occurred in both systems, indicating that there will be nitrite accumulation once the magnolia as denitrifying carbon source. However the pre-accumulation nitrite of 1: 100 solid-liquid ratio system was consumed completely at the end of the reaction.

As shown in Fig. 5 (e) and 5 (f), the ammonia nitrogen and phosphate concentrations of the 1: 100 solid-liquid ratio system were both higher than those of the 1: 200 solid-liquid ratio system during the whole reaction, indicating that the greater the amount of magnolia, the more pollutants introduced. The ammonia nitrogen concentration of 1: 100 solid-liquid ratio system presented a decline trend after a rise, while that of 1: 100 solid-liquid ratio system showing a slight rise and a sharp increase in the last one hour. What’s more, the phosphate concentration of 1: 200 solid-liquid ratio system decreased over the reaction, while that of 1: 100 solid-liquid ratio system presenting a rise trend after a decline.

During the reaction, the color of the two systems were slowly increased, and the color of the 1: 100 solid-liquid ratio system was significantly higher than that of the 1: 200 solid-liquid ratio system, as shown in Fig. 5 (g).

As for Magnolia, the increase of solid-liquid ratio was beneficial to improve the TN removal rate. The denitrification and TN removal rate of 1: 100 solid-liquid ratio system were obviously higher than those of 1: 200 solid-liquid ratio system, and the TN removal rate of two systems were 75.0% (1: 200) and 89.7% (1: 100) respectively, of which TN concentration both lower than the primary effluent concentration standard of GB18918-2002 to be discharged. The final nitrate removal rate of the two systems was similar, reaching 94.9% (1: 200) and 89.0% (1: 100) respectively. The effluent COD concentrations were both high and the nitrite accumulation occurred, and the releasing concentration of ammonia nitrogen and phosphate in 1: 100 solid-liquid ratio system were both higher than those in 1: 200 solid-liquid ratio system. Therefore, taking the denitrification rate and other influencing factors to the system into account, it was more suitable for the low solid-liquid ratio (1:200) of magnolia to be the denitrification external carbon source, under the condition of influent nitrate concentration of 40 mg/L, carbon dosage of 10 g, the reaction temperature of 25 ℃.

4. Conclusion
Under conditions of influent nitrate concentration of 40 mg / L, carbon source dosage of 10 g and reaction temperature of 25 ℃, the nitrate removal rates of magnolia (89.0%) and loofah (96.8%) were both higher than that of degradable meal box (56.3%). The TN removal rates of magnolia and loofah reached 91.7% and 77.7% respectively, rather higher than 53.9% of degradable meal box. And the effluent TN concentration of loofah and degradable meal box reached 25.4 mg/L and 21.1 mg/L respectively, which couldn’t be discharged according to the primary effluent concentration standard of GB18918-2002. At the same time, the releasing concentration of carbon, ammonia nitrogen and phosphate of magnolia and loofah were much higher those of degradable meal box, which would have a greater impact. On the whole, magnolia was more suitable as the additional carbon source for the stage denitrification among the three kinds of solid carbon sources.

The increase of solid-liquid ratio was beneficial to improve the TN removal rate, but also exacerbated the problem of excessive release of carbon source, ammonia nitrogen and phosphate, which had a greater impact on the system. Therefore, Nitrification efficiency and the impact of the system test can be seen, 1: 200 solid-liquid ratio of the system is more suitable as a denitrification of the extra-carbonated carbon source. Under the integrated analysis, the low solid-liquid ratio (1:200) of magnolia was more suitable to be the denitrification external carbon source.
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