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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 and 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. 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℃, the nitrate removal rates of magnolia leaves and degradable meal box reached 89.0% and 56.3% respectively, and the TN removal rates reached 91.7% and 53.9% respectively. But in the aspect of final treated effluent COD concentration level, magnolia leaves experiment (608 mg/L) was much higher than the degradable meal box (78 mg/L). Besides, the accumulation of nitrite, the released concentration of ammonia nitrogen and phosphate of magnolia leaves experiment were also higher than the degradable meal box. Under the integrated analysis, the magnolia leaves are more suitable than the degradable meal box as the denitrification external carbon source.

1. Introduction

In recent years, China's environmental problems are increasing, especially in aspects of air pollution and water pollution [1-4]. In order to reach the primary effluent standard of "the Pollutant Discharge Standard of the Municipal Wastewater Treatment Plant (GB18918-2002)", it is necessary to use the external carbon source to improve the denitrification efficiency because of its low C/N rate. The traditional liquid carbon source such as methanol and acetic acid, has high economic costs or part of biological toxicity [5], and the carbon dosage is usually insufficient or excessive because of the great fluctuation of the quality of effluent, which influences the quality of effluent greatly [6].So the researchers have been working in which would be more suitable to be the external carbon source in recent years. The research of solid carbon source is increasing, especially the organic solid materials with low cost and wide variety of sources, which are generally divided into natural organic solids and synthetic organic solids. Currently some natural organic solid materials are researched as the external carbon source, such as cotton [7, 8], wheat straw [9, 10] and corn [11, 12], and synthetic organic solid materials are mainly biodegradable polymers, such as poly butylene succinate (PBS) [13, 14] polycaprolactone (PCL) [15, 16]. However, most of the existing research is focused on the same type of

organic [17-19], and cotton, wheat straw, biodegradable polymer has its own higher economic value [20], which reduces the research value of practical application in a certain extent.

This experiment selected natural organic solid type of magnolia leaves 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 efficiency of denitrification and influence on the system and to choose the better external carbon source between magnolia leaves and degradable meal box.

2. Methods and materials

2.1. Materials and instruments

This experiment selected natural organic solid type of magnolia leaves and synthetic organic solid class of degradable meal box as the solid carbon source for periodic denitrification stage. The degradable meal box, cut into 1x1 cm, was purchased from Beiyuan supermarket, and magnolia leaves, washed and dried and cut into 1x1 cm, were picked in the woods behind Wenpei building in Zhongnan University of Economics and Law. The activated sludge was taken from the two sedimentation tank of sewage treatment process in Tangxun sewage treatment plant, in Wuhan. The domestic sewage was taken from the sewage outfall of Wenlan building in Zhongnan University of Economics and Law. The quality indicators of domestic sewage are shown in Table 1.

Table 1. Quality indicatorsof domestic sewage

Indicators	COD/ ($mg\cdot L^{-1}$)	NO_3^--N/ ($mg\cdot L^{-1}$)	NO_2^--N/ ($mg\cdot L^{-1}$)	NH_4^+/ ($mg\cdot L^{-1}$)	TN / ($mg\cdot L^{-1}$)	PO_4^{3-}/ ($mg\cdot L^{-1}$)	Color
Concentration	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. HITACHI U-1900 type ultraviolet spectrophotometer: Xiamen science and 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 Company Limited medical equipment factory; HQ30d portable dissolved oxygen meter: Shandong Qingdao environmental protection technology Co., Ltd. Ming Bo; HJ-4A type multi magnetic heating stirrer: Changzhou Guohua Electric Appliance Co. Ltd.

2.2. *Experiment methods*

The activated sludge was put into the culture container, adding proper amount of domestic sewage for aeration culture. The dissolved oxygen of activated sludge aeration was detected regularly and adjusted appropriately with portable dissolved oxygen meter, 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 quality of effluent was detected regularly to ensure that the concentration of COD is less than 50 mg/L. After cultured for two weeks, the quantity and quality of the activated sludge had grown. Observed by optical microscopy, the number of microbial species changed, and the shaped worms and rotifers appeared.

Taking three parts of activated sludge mixture of 1000 mL (around 4 g/L), the supernatant of the sludge mixture was poured out to ensure the sludge volume in 460 mL. Jar of 1000 mL as the reaction vessel 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 that the initial COD/$NO_3^-$was maintained at around 3. After a few seconds, the supernatant of 20 mL was taken as the first sample of 0 h. The sludge in the reaction unitmixed with

nutrient solution fully 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.

2.3. *Activated sludge culture*

The activated sludge was put into the culture container, adding proper amount of domestic sewage for aeration culture. The dissolved oxygen of activated sludge aeration was detected regularly and adjusted appropriately with portable dissolved oxygen meter, 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 quality of effluent was detected regularly to ensure that the concentration of COD is less than 50 mg/L. After cultured for two weeks, the quantity and quality of the activated sludge had grown. Observed by optical microscopy, the number of microbial species changed, and the shaped worms and rotifers appeared.

2.4. Denitrification experiments

Taking three parts of activated sludge mixture of 1000 mL (around 4 g/L), the supernatant of the sludge mixture was poured out to ensure the sludge volume in 460 mL. Jar of 1000 mL as the reaction vessel 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 that the initial COD/$NO_3^-$was maintained at around 3. After a few seconds, the supernatant of 20 mL was taken as the first sample of 0 h. The sludge in the reaction unit mixed with nutrient solution fully 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.

2.5. Analysis method

Water quality index analysis method was according to the standard method in "water and wastewater monitoring analysis method (4th edition)" [21]. Nitrate nitrogen (UV spectrophotometry), the total nitrogen (Potassium persulfate oxidation ultraviolet spectrophotometry), nitrite nitrogen (N- (1-naphthyl)-ethylene diamine spectrophotometry), ammonia nitrogen (Nessler reagent photometric method), phosphate (Molybdenum antimony spectrophotometric method), COD (Potassium dichromate colorimetry), Chromaticity (Colorimetric method) and MLSS (Weight method) were detected.

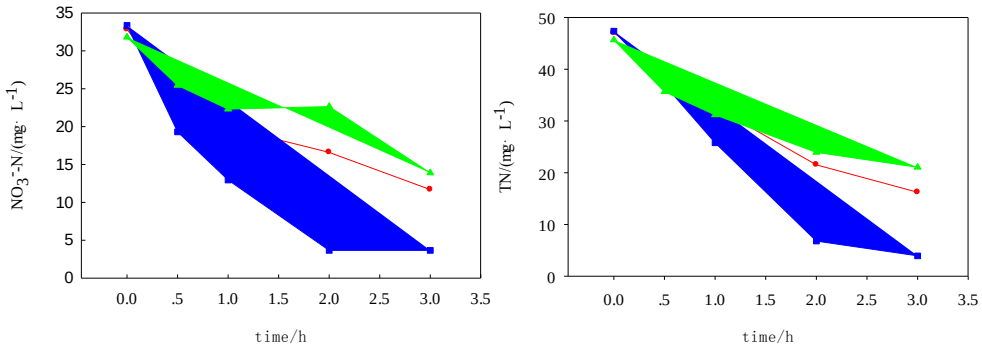
3. Results and discussion

3.1. *Nitrate, total nitrogen concentration changes*

Nitrate removal rate is an important index to measure the performance of denitrifying.Nitrate concentrations in three groups all showed a trend of decline over time in Fig. 1 (a). Specifically, nitrate removal rate of magnolia leaves reached 42.1%within 0.5 h and reached 89.0% in 2 h,then it was basically stable, while the finaleffluent nitrate concentration maintainiedat 3.6 mg/L.Because COD supply was significantly higher than the comparison, which was due tothe fast releasing carbon of early magnolia leaves,the nitrate removal rate ofmagnolia leaves washighly faster than the comparison. Due to the slow releasing carbon and nitrogen ofdegradable meal box within 3 h, itsnitrate removal rate was similar to the comparison, and even lower than the comparison. The nitrate removal rate ofdegradable meal box increased overall but slowly. Its nitrate removal rate (20.0%) was a litter lower than the comparison (26.9%) within 0.5 h, what's even worse was that its nitrate removal rate (56.3%) was also lower than the comparison (64.3%) in the end. The effluent nitrate concentration was maintained at 13.9 mg/L, in the mean time, the nitrate removal rate early was much higher than the late period, which was due to the initialabundant COD supply.

Total nitrogen removal rate is not only an important index to measure the performance of denitrifying, but also an important index to judge the quality of effluent. TN concentrations in three groups all showed a trend of decline over time in Fig. 1 (b). Specifically, TN concentrationof magnolia leaves reduced fromthe original 47.4 mg/L to the final 3.9 mg/L,and its final TNremoval rate reached 91.8%, even 45.6%

within 1 h. However,TN concentrationof degradable meal box reduced fromthe original45.7 mg/L to the final 21.1 mg/L, of which TNremoval rate reached53.9%, even lower than the comparison (65.5%).



(a) (b)

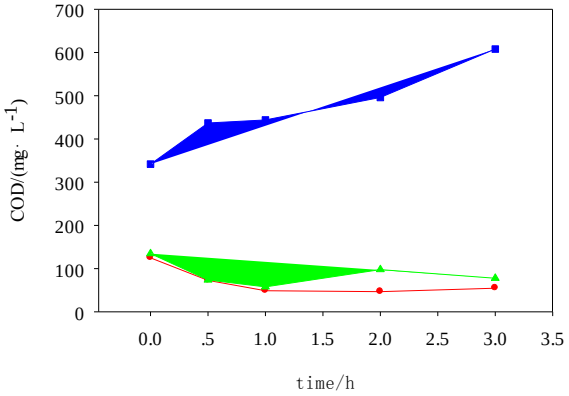
● Comparison; ■Magnolia leaves; ▲Degradable meal box

Fig. 1 NO_3^--N and TN changes of different carbon sources

3.2. COD concentration changes

COD is not only a quantitative index of solid material releasing carbon, but also a important index to judge the quality of the effluent.That solid material release carboncan be divided into two stages[22]: firstlythe water-soluble and easy decomposition substances of solid material on the surface are released, then internal refractory substancesof solid material will be releasedslowly, after the small molecules, on the surface and dissolved slowly from the main body, are released in full. Therefore, the COD concentration increase rapidly first and then slowly to stable.

As shown in Fig. 2, the COD concentration ofmagnolia leaves presented a slow increase trendover the reaction, ultimately much higher than GB18918-2002 primary effluent standard, but the COD concentration ofdegradable meal box changed in the trend of slow to decrease, similar to the comparison.Specifically, the COD concentration of magnolia leavesincreased quicklywithin 0.5 h,which period was also the fastest rate of denitrification. Analysised that the small molecules of magnolia leaves on the surface were released rapidly to cause the fast increase of COD concentrationwithin 0.5 h, and the rate of COD increase was much higher than theCOD consumption of denitrification, subsequently, the rate of carbon releasing was more slow, but still higher than the COD consumption. Degradable meal boxwasn't degraded first, after 1 h of reaction, it released carbonslowly, which causedtheslow riseof COD concentration, but thedenitrification rate didn't rise, even lower than that of thecomparison. Analysised that the released substances ofdegradable meal box couldn't be used by denitrifying bacteria, then the COD concentration declined over denitrification reaction.



● Comparison; ■Magnolia leaves; ▲Degradable meal box

Fig. 2 COD changes of different carbon sources

3.3. Nitrite and ammonia nitrogen concentration changes

Denitrification process can be simplified to that NO_3^- is converted to NO_2^- under the reduction of nitrate reductase, and thenNO_2^- is converted to N_2 under the reduction of nitrite reductase. Nitrogen removal process will produce nitrite accumulation, which is due to the competition for electron acceptor between nitrate reductase and nitrite reductase under the situation of lack of organic carbon source, and nitrite reductase at a disadvantage [23]. Therefore, as shown in Figure 3(a), the nitrite accumulation of degradable meal box, which obviously lack oforganic carbon source, reached the maximum amountof 1.0 mg/Lat 0.5 h of reaction, similar to the comparison.However, the nitrite accumulation of magnolia leaves,which full of organic carbon source, was much more than degradable meal box, that's because the activity of nitrite reductase was influenced largely by nitrate [24]. The nitrite accumulation of magnolia leaves rapidly increased to themaximum amount of 7.3 mg/Lat the first 1 h of reaction, which was due to the high concentration of nitrate to seriously inhibit the activity of nitrite reductase. When the concentration of nitrate decreased to about 13 mg/L over the reaction, the inhibition of nitrate to nitrite reductase reduced, which caused that $NO_2^-$was more quickly converted to $N_2$and the nitrite accumulation decreased to 0 mg/L finally.

The ammonia nitrogen concentration of degradable meal box had no significant change, similar to the comparison, asshown in Fig. 3 (b), but the ammonia nitrogen concentration of magnolia leaves showed a trend of rapid growth after 2 h initial stable. Specifically, the ammonia nitrogen concentration of magnolia leaves had been stable at around 7.0 mg/L during the first 2 h, but increased to 18.5 mg/L in the last hour. Analysised thatammonia nitrogen could be released in the leaching process, and ammonia and nitrite might occur in reaction of anaerobic ammonia oxidation under hypoxic conditions [25] because of the presence of nitrite in the reaction system within 2 h, resulting in the consumption of the released ammonia nitrogen. Two hours later, nitrite was exhausted, and the released ammonia nitrogen was accumulated to 18.5 mg/L. Degradable meal box released a bit of ammonia nitrogen in a short time, resulting in the concentration of ammonia nitrogen changing from 3.8 mg/L to 6.9 mg/L in the first 1 h. In the last hour, the released ammonia nitrogen and a small amount accumulation of nitrite occurred in reaction of anaerobic ammonia oxidation, resulting in the concentration of ammonia nitrogen slowly decreasing to 3.9 mg/L.

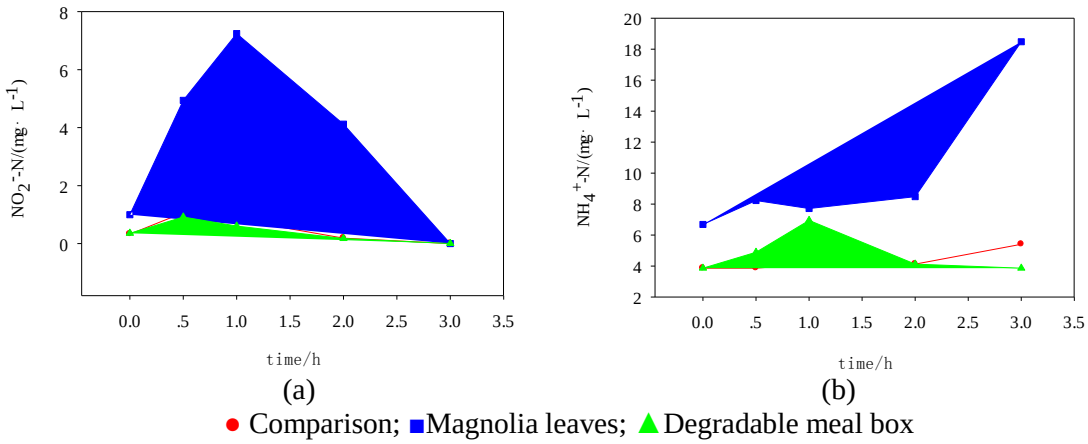


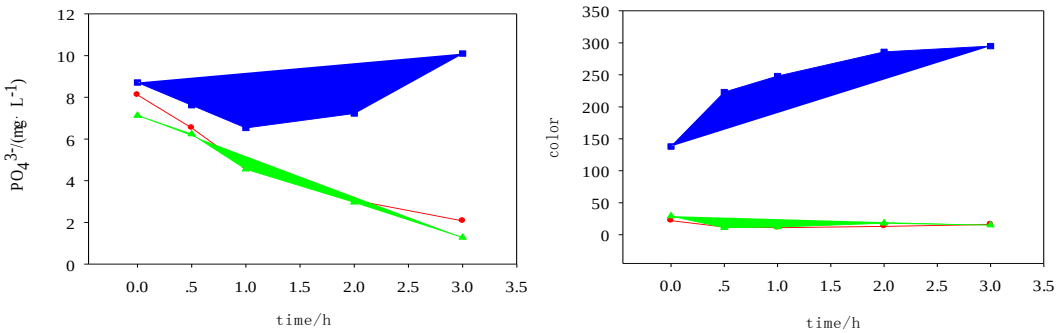
Fig. 3 NO_2^--N and NH_4^+ changes of different carbon sources

3.4. Phosphate concentration and colorchanges

The phosphate concentration of degradable meal box changed in the trend of slow to decrease, similar to the comparison, but the phosphate concentration of magnolia leaves presented a slow increase after a slow decrease trend, as shown in Fig. 4 (a).Specifically, in the denitrification process of degradable meal box and comparison, phosphorus bacteria began to polyphosphate[26], due to a very small amount of

nitrite accumulation and nitrate dominating, which caused the concentration of phosphate decreased from 7.1 mg/L to 1.3 mg/L. The same to degradable meal box, the phosphate concentration of magnolia leaves decreased from 8.7 mg/L to 6.5 mg/L in the first hour. Subsequently, nitrite accumulated to dominate, and phosphorus bacteria in the system began to release phosphorus, resulting in phosphate concentration increasing to 10.1 mg/L.

the color of degradable meal box changed in the trend of slow to decrease, similar to the comparison, but thecolor of magnolia leaves presented a rapidincreaseto a stable trend, as shown in Fig. 4 (b). Specifically, with the denitrification, the color of comparisondecreasedfrom initial 22because of the consumption of organic carbon source in sewage. The color of degradable meal boxdecreased and eventually stabilized at about 15,similar to the comparison, due to the low degradation rate of degradable meal box. However, magnolia leaveshad been releasing pigment fast to the maximum of 138 at 0 h, resulting in the color at a high level. Because of the released pigment closing to saturation, the change rang of color decreased in the last hour, finally the color reached 295, 20 times that of the degradable meal box.



(a) (b)

● Comparison; ■Magnolia leaves; ▲Degradable meal box

Fig. 4 PO_4^{3-} and colour changes of different carbon sources

4. Conclusion

In the condition of influent nitrate concentration of 40 mg/L, carbon dosage of 10 g, the reaction temperature of 25℃, periodic denitrification time within 3 h, the nitrite maximum accumulation of magnolia leaves and degradable meal box reached 7.3 mg/L and 1.0 mg/L, respectively, but eventually entirely consumed with no nitrite accumulation. At the same time, the final release of ammonia nitrogen and phosphate of magnolia leaves were 18.5 mg/L and 10.1 mg/L, respectively, and the final release of ammonia nitrogen and phosphate of degradable meal box were 3.9 mg/L and 1.3 mg/L, respectively. Magnolia leaves released a large amount of pigment within 3 h, resulting in the color reaching 295, 20 times that of the degradable meal box.

In the condition of influent nitrate concentration of 40 mg/L, carbon dosage of 10 g, the reaction temperature of 25℃, periodic denitrification time within 3 h, the release carbon amount of magnolia leaves was much higher than degradable meal box, which provided sufficient carbon source for denitrification, but caused the high effluent COD concentration. The nitrate and total nitrogen removal rates of magnolia leaves reached 89.0% and 91.7%, respectively, significantly higher than 56.3% and 53.9% of the degradable meal box. Under the integrated analysis, the magnolia leaves are more suitable than the degradable meal box as the denitrification external carbon source.

Acknowledgments

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