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Nutrient Removal by Hybrid Subsurface Flow Constructed Wetlands for High Concentration Ammonia Nitrogen Wastewater

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Abstract

This paper carried on a series of experiments with coupled vertical subsurface flow constructed wetlands(VSSFCWs) and horizontal subsurface flow constructed wetlands(HSSFCWs) for the nitrogen removal of the high concentration nitrogenous domestic sewage. According to the transformation results of inorganic nitrogen in VSSFCWs and HSSFCWs, the paper analyzed the key factors to influence inorganic nitrogen, and discussed the nitrogen removal effects under the conditions of external carbon source addition. The results show that: First point, the VSSFCWs has more powerful nitrification ability, and HSSFCWs has more powerful denitrification ability. Under the condition of excessive high concentration nitrogen in inlet water, not enough carbon source become the restriction of denitrification in HSSFCWs. Second point, in VSSFCWs, when DO is greater than 1.5mg/L, hydraulic retention time is about 2 days, and ammonia nitrogen concentration in inlet water is less than 80mg/L, the ammonia nitrogen concentration in inlet water can be transformed sufficiently into nitrate nitrogen. And so on, in HSSFCWs, adding external carbon source can cause a lower DO level system, and that is helpful to denitrificate successfully. When TOC(Total Organic Carbon)/TN(Total Nitrogen) in inlet water of HSSFCWs is greater than 2.5, the carbon source for denitrification is sufficiently, and the excessive TOC/TN is not constantly advantageous to increase nitrogen removal efficiency.

Keywords:hybrid subsurface flow constructed wetlands; High concentration ammonia nitrogen wastewater, Carbon source, Nitrification and denitrification, TOC/TN

1. Introduction

In the current serious pollution nitrogen situation of global water environment, high efficiency nitrogen removal technology of waster water is a most urgent requirement. The main process of nitrogen removal in the constructed wetlands are nitrification/denitrification, ammonia-volatilizing, adsorption, plants adsorption and so on[1,2,3].

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Nitrification/denitrification is thought to be the main way of removing nitrogen in the constructed wetlands, the other processes have secondary contribution for nitrogen removal because of the limit of adsorption capacity and pH condition. For the difference of the biochemical reaction bacterial flora, the nitrification reaction will take place after completing degradation of carbon BOD, but in this case, the DO for nitrification is obviously inadequate, and after that denitrifying bacteria will be lack of nourishment for the complete oxidization of the carbon source in the wastewater, leading to insufficient denitrification[4]. The amount of the biodegradable carbon source is the key factor to determine the nitrogen removal efficiency for the wastewater with low carbon and high nitrogen[5].

Compare with traditional wastewater treatment, the constructed wetlands have higher nitrogen removal efficiency, and the key reasons are: First point, oxygen inputting of plant root and oxygen-poor of non-root zone make simultaneous nitrification/denitrification processes[6,7]. In fact, the effect of supply of carbon source may exceed that of the DO for the nitrogen removal of high concentration nitrogen containing wastewater. Second point, the ANAMMOX and shortcut nitrification-denitrification may exist in the constructed wetlands, but now their process mechanism and reliable technological condition is uncertain[7]. Now constructed wetland has been widely used to treatment the wastewater of town and countryside, industrial wastewater, agricultural wastewater, landfill leachate and so on[8]. But single Horizontal flow can not ensure efficient nitrification for the limit of oxygen transfer capability, vertical flow system can not ensure efficient denitrification, and single system often can not producing a desired effect[8].

Mixed treatment of the wastewater with different C/N can enhance nitrogen removal efficiency. Some wastewaters, such as discharge of oil refining, chemical fertilizer, food and cultivation industry production have high concentration ammonia nitrogen, and the concentration of ammonia nitrogen is 200～6000mg/L. The other wastewaters, for example, domestic sewage, extract oil, textile industry, paper industry wastewater, have high C/N. We can add high carbon and low nitrogen wastewater as external carbon source to hybrid constructed wetland system, So we can cut down the treatment difficulty of the above two different character wastewaters, and cut down the treatment cost of high concentration nitrogen containing wastewater.

This paper is concentrated on nitrogen transformation in hybrid constructed wetland system, and the relation among nitrogen transformation, DO and carbon source. The aim is to provide acknowledge for constructing high performance hybrid constructed wetlands.

2. Materials and methods

2.1. Water for experiment

Water for experiment is produced artificially. Materials are natrium aceticum, soluble starch, amylaceum, peptone, sodium nitrate, ammonium chloride, carbamide, and potassium dihydrogen phosphate. The water quality is given in table 1.

Table 1 inlet water quality

Items	CODcr(mg/L)	organic-N(mg/L)	NH_4^+-N(mg/L)	NO_3^--N(mg/L)	TP(mg/L)	BOD_5(mg/L)	pH
range	300～780	6～17	10～120	0～14	4～10	250～650	6.85～7.81

2.2. Test equipment

We design the vertical downstream and horizontal subsurface flow constructed wetlands, the vertical flow constructed wetlands are blank system without plants, and we plant canna in the horizontal flow wetlands. The design size of vertical flow wetlands is: length×width×height=35cm×35cm×120cm, effective depth is 110cm, and the size of horizontal flow wetlands is: length×width×height=180cm×50cm×60cm, effective depth is 55cm. Test equipments are given in the figure 1 and figure 2. In the figures, the position 1-5 means code of sample point.

2.3. Sampling and analysis

We constructed system in November 2006, planted cannas in the horizontal equipment, put in the domestic sewage into the two equipments intermittently. At the beginning, we put in the sludge of Songdong Water Environment purification Ltd. as the breeding sludge, and used the experiment water to tame the system. Equipment initiation period was form March to May in 2007, and follow-up testing was made after May, 2007. The sewage flows into the system continuously, the water from inlet enters vertical flow constructed wetlands, the enters the horizontal flow system, and the flow rate is controlled by constant flow pump. We add carbon source, adjust pH before horizontal flow system from outlet water of vertical flow system. Under different conditions, the concentrations of NO_2^--N, NO_3^--N, NH_4^+-N, TN, DO and TOC of the inlet and outlet flow are measured.

The methods of item analysis is listed. DO: iodometry, BOD_5: Dilution and Inoculation Method, COD_{Cr}: Microwave Digestion Method, TN: Potassium Persulphate Oxidation -ion chromatography ; NH_4^+-N: salicylic acid-hypochlorite photometric Determination; NO_3^--N, NO_2^--N: ion chromatography; TOC: combustion and oxidation -non-dispersed infrared absorbance absorption method. The analysis methods are from the book of METHOD OF SEWAGE AND WASTEWATER MONITORING ANALYSIS(the forth edition)

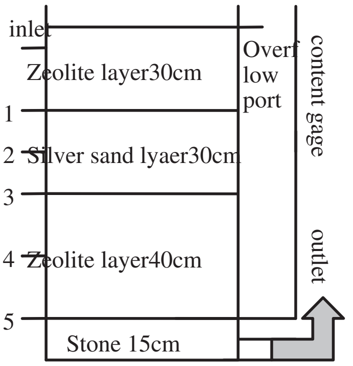

Fig.1.vertical subsurface flow constructed wetlands

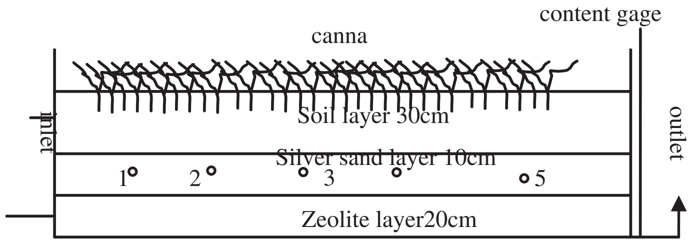

Fig.2.horizontal subsurface flow constructed wetlands

3. Results and discussion

After two months for commissioning operation, the outlet water quality index of the hybrid system tends towards stability. The performance of the hybrid system is: in the certain residence time, the removal efficiency of CODcr, TN, and NH_4^+-N tend toward stability; concentration of NO_2^--N of the outlet water of vertical flow constructed wetlands maintains low condition, the DO value maintains blow 0.5mg/L.We discuss the transformation process of ammonia nitrogen in vertical flow constructed wetlands and the denitrification process in horizontal flow constructed wetlands, and analyze the relation between TN removal efficiency and carbon source addition amount in hybrid system.

3.1. Nitrogen transformation in vertical flow constructed wetlands

(1) The effect of HRT on nitrogen removal: In experimental period, we determine the concentrations of NO2--N, NO3--N, NH4+-N and TN in inlet and outlet water at different hydraulic retention time, the result can be seen in figure 3.

We can see that as HRT prolonging the concentration of NH_4^+-N of outlet water decreases gradually, the concentration of NO_2^--N keeps constantly, the concentration of NO_3^--N is ascend in first and descend at last, and the concentration of TN increases drastically in first and then decreases obviously. When HRT is more than 4 days, concentrations of NO_2^--N, NO_3^--N, NH_4^+-N and TN change little.

The experiment results show that when HRT is 1day, the removal rate of NH_4^+-N is higher than 80%, the concentration of NH^+_4-N of outlet water is lower than 6mg/L. From figure 3, we can see when HRT is 1 day, the outlet water concentrations of NH_4^+-N and TN decrease drastically, and the outlet wate concentration of NO_3^--N increase obviously. When HRT is 2 days, the concentration of TN in outlet water increases, and NO_3^--N constitute a high proportion of TN. The reason may be when HRT is 1 day, the NH_4^+-N removal depends on absorption and interception of substance. The bottom and surface layer of the system are filled 40cm and 30cm zeolite, so, the medium absorption may be an important process for nitrogen removal. In most mediums, zeolite has special tetrahedron crystal lattice structure with negative charge, so the surface of zeolite has polarity (it can absorb small polar molecular simply), and there is large internal surface square in the framework, zeolite can adsorb and store numerous molecules, and has good ammonia nitrogen choice adsorption capacity[9]. After commissioning operation period, the biofilm is formed on the surface of substance, and a large number nitrifying bacteria has bred in biofilm.

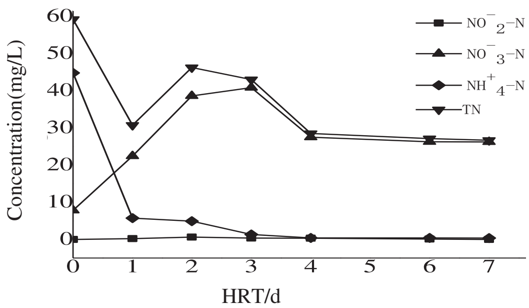

Fig.3.NO_2^--N, NO_3^--N, NH_4^+-N, TN concentration in outlet water with different HRT

Firstly, NH_4^+-N is trapped in the vertical flow system by substance adsorption, then, when HRT is 2 days, the NH_4^+-N adsorbed by substance is transformed to NO_3^--N by nitrobacteria, so, the concentration of TN in outlet water increases again. When HRT is between 3 and 4 days, because of the limit of carbon source, DO and pH et al., the nitrification and denitrification are limited basically, now in the system the TN removal efficiency reaches maximum, and TN removal efficiency is more than 50%, NH_4^+-N trapped by substance adsorption also is transformed to NO_3^--N completely, so, the proportion of NO^-_3-N in the TN of outlet water is 96.5%. Furthermore, from the figure 3, we can see the concentration of NO_2^--N in outlet water maintains at a very low level, and it proves vertical flow constructed wetlands have good DO supplying ability, the high concentration of DO value restrains the production of NO_2^--N.

(2)The effect of do on the transformation of ammonia nitrogen: Because the 2nd sample point is located in the central wetland, so we use DO of outlet water of vertical flow in the 2nd sample point to represent DO level of system, we analyze the relation between DO and nitrogen of vertical flow outlet water, the result can be seen in the fig 4. The inlet water quality is stable, the concentration of TN maintains around 50mg/L. The pH value of inlet water is between 6.5 and 7.5.

The results show that the DO value maintains 0.9mg/L level in the vertical flow wetlands under the condition of no aeration. The reason is that the surface zeolite layer has good air permeability, and its supplying oxygen is sufficient. Under the condition of aeration, when DO value is less than 1.2mg/L, NH^{+}_{4}-N concentration is high, the proportion that NH^{+}_{4}-N is transformation into NO_3^--N is low, when DO is 1.5mg/L level, the NO_3^--N concentration in outlet water reaches maximum basically , and the almost NH_4^+-N has transformed into NO_3^--N(figure 4)

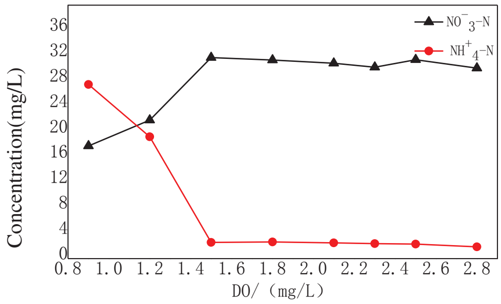

Fig.4 The relation between DO in system and NO_3^--N、NH_4^+-N concentration in outlet water

The above results show that almost NH_4^+-N can be transformed into NO_3^--N under the condition of DO value exceeding 1.5mg/L, that is to say, the high NO_3^--N concentration can be achieved though the vertical flow constructed wetlands.

(3)The effect of ammonia nitrogen load on the nitrogen transformation in vertical flow constructed wetlands:

Under the condition of 2 days HRT, when the concentration of DO is higher than 1.5mg/L in the system and the concentration of NH_4^+-N of inlet water is between 10mg/L and 120mg/L in continuity inlet flow, the outlet water quality of vertical flow constructed wetlands is determined(figure 5).

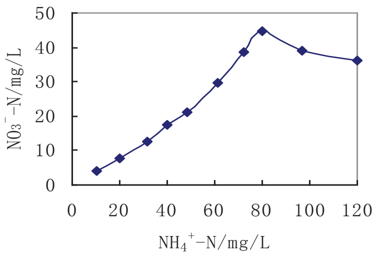

Fig.5. the influence of NH^{+}_{4}-N concentration on nitrogen transformation

when the concentration of NH_4^+-N in inlet water is below 80mg/L, the concentration of NO_3^--N in the outlet water of the vertical constructed wetlands increases gradually, the proportion of NH_4^+-N conversion to NO^-_3-N increases gradually (the maximum conversion proportion reaches 56%). When the concentration of NH_4^+-N in inlet water is higher than 80mg/L, the proportion of ammonia nitrogen conversion to nitrate decreases fastly. The reason may be that the too high accumulated concentration of NO_3^--N in the system effects on the chemical reaction kinetics of the ammonia nitrogen transformation into nitrate nitrogen.

3.2. Nitrogen transformation in horizontal flow constructed wetlands

In this experiment, the horizontal flow constructed wetlands is mainly used for the denitrification of outlet water of vertical flow. The effect factors on the denitrifacation mainly conclude carbon source, pH value, DO, temperature and so on, and the factors influence each other. We choose methanol as external addition carbon source in this experiment, and methanol is decomposed into carbon dioxide and water molecule completely. We adjust pH value of the outlet water of vertical flow system before entering into the horizontal flow system, and the pH value of inlet water of horizontal flow constructed wetlands is controlled between 6.5 to 7.5, which is the most favorable condition for denitrifying bacteria. During the trials, the air temperature maintains between 22 and 34 centigrade degrees basically, we do not apply any temperature control measure. According to the measuring results, the temperatures of outlet water of each sample point are between 10 and 28 centigrade degrees, which is basically suitable for denitrification reaction.

(1)The effect of external addition carbon source on do of horizontal flow system: We maintains the 3 days HRT for vertical flow constructed wetlands, and 2 days HRT for horizontal constructed wetlands, the DO values of each sample point are determined under the condition of on addition carbon source and addition carbon source, respectively. The results can be seen in figure 6.

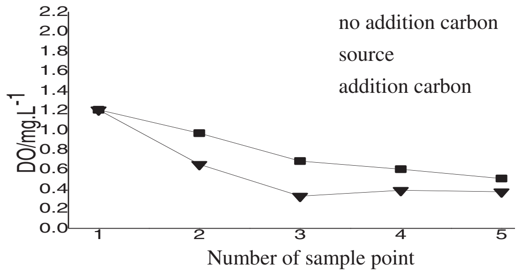

Fig.6 DO change along length of horizontal subsurface flow constructed wetlands

We can see that the DO value is below 1.0mg/L before the water passing through the 3rd sample point without addition carbon source. This proves the DO value in the horizontal flow constructed wetlands is low and suitable for denitrification. After adding carbon source, the DO value of horizontal flow constructed wetlands decreases obviously, the DO value decreases blow 0.5mg/L basically after the water passing through the 2nd sample point. The additive carbon source depletes DO in the water fastly. Addition carbon source not only supplies the nutrition for denitrifying bacterium, but also supplies good environmental conditions for the metabolism and reproduction. The denitrification reaction takes place more easily and the efficiency of nitrogen removal increase obviously.

(2)The effect of external carbon source on tn removal of horizontal flow system: We add carbon source to the outlet water of vertical flow constructed wetlands and adjust the pH value to 7.0, and treat the water added carbon source as inlet water of horizontal flow constructed wetlands. The carbon source of experimental water is organic carbon, so the quantity of carbon source added is determined by TOC. Under the condition of different TOC/TN rate and TN of different inlet water, the TN removal efficiency is determined. According to the quantity of addition carbon source in inlet water of horizontal flow constructed wetlands, we carry out 4 batches tests, test number is 1#, 2#, 3# and 4#, respectively (Table 2). When all the HRT is 2 days, we test TOC, BOD_5, COD_{Cr} and TN concentration in outlet water of horizontal flow constructed wetlands (Table 2).

Table 2 The relation between carbon source quantity and removal efficiency of TOC, BOD_5, COD_{Cr}, TN

Test project	Test No.	Vertical flow outlet	Horizontal flow intlet	Horizontal flow outlet	Removal rate
TOC/mg/L	1#	8.323	107.453	10.814	89.94%
	2#	7.562	158.683	14.193	91.06%
	3#	6.709	128.775	9.279	92.79%
	4#	4.838	107.575	9.742	90.94%
BOD_5/mg/L	1#	18.74	139.69	9.78	93.00%
	2#	15.35	212.64	12.85	93.96%
	3#	9.89	164.19	8.40	94.88%
	4#	4.93	144.15	7.89	94.53%
CODCr/mg/L (B/C)	1#	25.42(0.74)	265.62(0.53)	15.60(0.63)	94.13%
	2#	21.96(0.70)	393.53(0.54)	22.81(0.56)	94.20%
	3#	18.79(0.53)	318.85(0.51)	15.95(0.53)	95.00%
	4#	15.50(0.32)	259.90(0.55)	15.07(0.52)	94.20%
TN/mg/L (TOC/TN)	1#	42.981(0.19)	42.981(2.50)	3.441(3.14)	92.00%
	2#	45.338(0.17)	45.338(3.50)	2.675(5.31)	94.10%
	3#	32.194(0.21)	32.194(4.00)	1.313(7.07)	95.92%
	4#	21.325(0.23)	21.325(5.04)	1.372(7.10)	93.56%

We can see that the TOC/TN ratio in inlet water of horizontal flow constructed wetlands is between 2.5 and 5.0, and the TN concentration (composing mainly NO^-_3-N) is between 20 and 45 mg/L, when HRT is 2 days, the TN removal efficiency of horizontal flow constructed wetlands is more than 90%, and this demonstrates that the carbon source is sufficient when TOC/TN ratio is more than 2.5. On the contrary, when TOC/TN ratio is more than 5.0, the removal efficiency of TN has a decreasing trend though the concentration of TN, CODcr and BOD_5 are not high.

The possible reason is that excessive TOC/TN ratio destroyed primary nourishment balance between C and N for adaptive denitrifying bacterium, so, when HRT is short, denitrifying bacterium will be not adaptive, and this situation results in decreasing removal efficiency of TN. Furthermore, under the condition of low nutrient concentration(testing 4), excessive organic carbon lead the heterotrophic bacterium will compete living space with the denitrifying bacterium. The heterotrophic bacterium do not take NO_3^--N as a electron acceptor, so the results in a decreasing removal efficiency of TN. The above research conclusion is in accordance with other research basically that denitrification can take place sufficiently and high nitrogen removal efficiency can be achieved if the C/N ratio is between 3 and 6[10].

4. Conclusion

In the vertical flow constructed wetlands(VFCW), nitrification is higher ,and in horizontal flow constructed wetlands(HFCW), the denitrification is higher. The combination of VFCW and HFCW can enhance the nitrogen removal efficiency obviously, but insufficient carbon source in HFCW will be restriction factor for enhancing the nitrogen removal efficiency. In the vertical flow constructed wetlands, when DO is more than 1.5mg/L, HRT is 2 days, and ammonia nitrogen is less than 80mg/L, then, ammonia nitrogen are transformed into nitrate nitrogen more completely. If the ammonia nitrogen concentration in inlet water of vertical flow constructed wetlands is too high, the nitrification can not take place completely. addition carbon source in inlet water of horizontal flow constructed wetlands can decrease DO of HFCW to 0.5mg/L or less, and which creates a good condition for denitrification reaction.

we added carbon source in the VFCW outlet water that TN is between 20mg/L and 45mg/L(composing mainly NO^-_3-N), and took it as a inlet water of HFCW. When TOC/TN ratio is between 2.5 and 5.0, the carbon source is sufficient and the TN removal efficiency is higher than 92%. On the contrary, if TOC/TN ratio increases continually, the TN removal efficiency will decrease to a certain extent.

Acknowledgements

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