Asian Journal of Chemistry; *Vol. 26, No. 11 (2014), 3320-3324*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17520

Biological Contact Oxidation Fluidized Bed in Treatment of Nitrogen Waste Water

QUANMIN BU[1,*] and XING TONG[2]

[1]Center for Social Risk and Public Crisis Management, Nanjing University, Nanjing, P.R. China
[2]School of Government, Nanjing University, Nanjing, P.R. China

*Corresponding author: Fax: +86 25 52881681; Tel: +86 25 52881664; E-mail: qmbu@sina.com

Received: 10 February 2014; *Accepted*: 14 April 2014; *Published online*: 25 May 2014; AJC-15240

In order to ameliorate the treatment of nitrogen waste water using biological contact oxidation fluidized bed, the feasibility, method and effect of simulated wastewater using biological contact oxidation fluidized bed under natural temperature is explored. The experimental results show that: ammonia nitrogen is oxidized to nitrate through catalysis of two independent bacteria; the suitable reaction temperature is 20-35 ºC; nitrite bacteria's optimum pH value is 7.0-8.5, nitrate bacteria's pH value is 6.0-7.5; better nitrification effect can be realized with proportion between nitrite bacteria and nitrate bacteria dissolved oxygen of more than 0.5 mg/L filler particle size should be over 10 mm to enhance removal efficiency of ammonia nitrogen ; Intermittent feeding mode makes activated sludge have good settlement, and can offer good environmental conditions for removal of ammonia nitrogen.

Keywords: Biological contact oxidation, Ammonia nitrogen, Alkalinity, Nitrogen removal, Nitrification.

INTRODUCTION

Discharge of ammonia nitrogen waste water into water can reduce dissolved oxygen in water, which is harmful to fish, shrimp and so on. It can also be absorbed by aquatic plants, algae and others, leading to eutrophic water[1]. Ammonia nitrogen is of the main factors leading to eutrophic water, its harm on the environment has gained more and more attention[2]. Considering that study on treatment of ammonia nitrogen waste water at home and abroad is at an early state, nitrogen removal rate is low and treating effect is not ideal, treatment of ammonia nitrogen wastewater is always a major challenge in the field of engineering and technology[3]. Therefore, carrying out study on treatment of ammonia-nitrogen waste water has important practical significance for improvement of water environment[4]. Therefore, according to nitrogen recycling in biosphere, nitrogen input in the form of ammonia, microorganism goes through assimilation, ammonification, nitrification, dissimilatory nitrate reduction biotransformation and its accompanying migration movement and output in the form of nitrogen through denitrification and removal of ammonia nitrogen is finally realized through microbial nitrogen removal[5,6]. In this experiment, the authors studies on treatment of nitrogen waste water using biological contact oxidation fluidized bed.

EXPERIMENTAL

Experimental wastewater: The waste water is artificially prepared according to certain proportion, glucose is carbon source of microbe, certain nutrients are added and $NaHCO_3$ or KH_2PO_4 are used to adjustment the value of pH. The basic composition of mother liquor nutrient elements is shown as Table-1. Composition of mother liquor of trace elements is shown as Table-2.

TABLE-1
BASIC COMPONENT OF ARTIFICIAL WASTEWATER

Constituent	Concentration (mg/L)	Constituent	Concentration (mg/L)
$C_6H_{12}O_6$	1000	$CaCl_2$	2
$(NH_4)_2CO_3$	50	$MgSO_4$	4
KH_2PO_4	20	$NaHCO_3$	1000
NH_4Cl	50	Yeast extract	50

Experimental progress: The experiment process is shown in Fig. 1. Cylinder column of the reactor used in the experiment is organic glass, water input from the bottom of the reactor and output from the top. Waste water treatment plant's return sludge is used as inoculation sludge and it mixes with filler (PVC suspension particle), after the treatment, the supernatant discharge from outlet pipe, whiles the sludge is discharged

TABLE-2
COMPOSITION OF MOTHER LIQUOR OF TRACE ELEMENTS

Constituent	Conc. (μg/L)	Constituent	Conc. (μg/L)
$FeCl_3·4H_2O$	80	$CoCl_2·6H_2O$	80
$MnCl_4·4H_2O$	20	$InCl_2$	2
$NiCl_2·6H_2O$	2	$CuCl_2·2H_2O$	1.2
EDTA	40	H_3BO_3	2
$(NH_4)_6Mn_7O_{24}·4H_2O$	3.6	36 % HCl	40

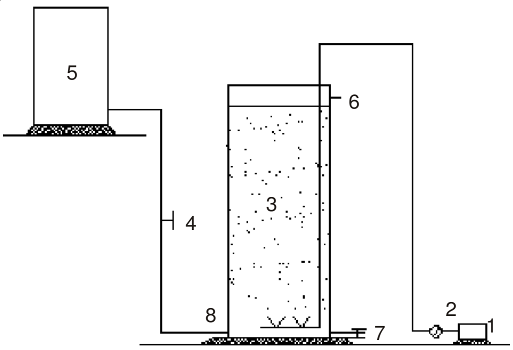

Fig. 1. Experiment progress. 1. Air pump, 2. Flow meter, 3. Suspended packing, 4. Stop valve, 5. Water tank, 6. Water outlet, 7. Discharge port, 8. Inlet

from the bottom. In order to simulate actual situation, it is conducted under natural temperature.

Reactor volume is 3 L, effective volume is 2.5 L. Suspended particle's filling ratio is 50-60 %, intermittent inflow, continuous aeration are adopted. In order to ensure sufficient disturbance of suspended particles and reduce power consumption, aeration quantity is set at 0.4 L/min. In biological contact oxidation reactor, the generated sludge is very little; therefore, frequent discharge of mud is not necessary.

Start-up of reactor: Since the sludge is added into the reactor, appropriate operational method should be adopted, ammonia concentration gradually increase from low level to domesticate nitrifying bacteria, waste water treatment plant's return sludge is used. In the starting period, hydraulic retention time (HRT) is maintained at 24 h, with intermittent inflow and continuous aeration, the aeration quantity is 4 L/min. With the aeration quantity, suspended packing can be fully disturbing, dissolved oxygen concentration is about 3 mg/L, C/N is about 10:1, pH of water is 7-8, then examine whether the reactor's start-up operation data are consistent with those in Table-3.

According to experimental data, ammonia nitrogen concentration of the water is around 5 mg/L, NO_2-N concentration is 6 mg/L, NO_3-N concentration is below 0.1 mg/L, over 50 % of nitrogen in the water exists in the form of nitrite nitrogen, we can see that there is nitrification denitrification reaction and the reaction is great. Because N is a fundamental part of microbial cell, therefore in the process for biological treatment, some of nitrogen in waste water is assimilated into part of biological cell. In the experiment, the removal rate of total nitrogen is 60 %, which indicates that in the biological treatment process, most of nitrogen disappear through nitrification or denitrification action. The proportion of nitrite nitrogen in the water is as high as 50 %, the biological treatment process is mainly shortcut nitrification-denitrification, removal rates of various pollutants in the start-up process are shown as Table-4.

TABLE-3
REACTOR'S START-UP OPERATION DATA

Period (day)	Flow direction	NH_4^+-N	NO_2-N	NO_3-N	TN
1	Water inlet	17.26	7.72	0.057	25.045
	Effluent	1.73	8.27	0.27	10.25
2	Water inlet	20.62	4.12	0.02	24.75
	Effluent	4.66	4.52	0.06	9.19
3	Water inlet	23.86	0.51	0.04	24.45
	Effluent	0.91	0.25	0.05	1.21
4	Water inlet	35.89	0.00	0.00	35.88
	Effluent	0.96	8.22	0.07	9.25
5	Water inlet	46.81	0.00	0.02	46.79
	Effluent	3.59	5.49	0.03	9.18
6	Water inlet	47.91	0.14	0.07	48.08
	Effluent	2.13	4.86	0.03	7.02
7	Water inlet	53.93	0.28	0.04	54.32
	Effluent	16.42	6.12	0.07	22.58
8	Water inlet	56.89	3.93	0.04	60.94
	Effluent	11.93	8.21	0.17	20.38
9	Water inlet	58.08	0.53	0.02	58.67
	Effluent	23.38	0.76	0.09	24.27
10	Water inlet	58.72	6.87	0.074	65.81
	Effluent	0.56	1.96	0.52	3.03

TABLE-4
REMOVAL RATES OF VARIOUS POLLUTANTS IN START-UP PROCESS

Period (day)	Removal rate of ammonia (∂)	Removal rate of TN	Proportion of NO_2 in the water
1	0.900456	0.590913	0.806168
2	0.775805	0.628694	0.492034
3	0.910899	0.690689	0.703895
4	0.905967	0.709429	0.677048
5	0.880588	0.694957	0.627601
6	0.860978	0.658768	0.580541
7	0.695425	0.583905	0.271647
8	0.761188	0.656938	0.302963
9	0.789387	0.664902	0.403674
10	0.597146	0.585829	0.032121

Table-4 shows that after two weeks of operation, the reactor is basically stable, ammonia nitrogen achieves good treatment effect and therefore, biological contact oxidation using fluidized bed is highly feasible and efficient in the treatment of ammonia nitrogen pollutants.

After 2 weeks, the filler is observed the start-up of the whole system, biofilm appears on the filler, the effluent's quality becomes stable, removal rate of pollutants also gradually become stable. Based on this, we can see that the start-up of the system has been completed and the treatment effect is best when the influent's concentration is 40 mg/L. So, 40 mg/L is used as starting concentration for studying impacts of various factors on the reactor's treatment effect.

Impact of alkalinity on removal of ammonia nitrogen: The experimental system adopts intermittent inflow and continuous aeration, hydraulic retention time is 24 h, COD concentration of the influent is about 600 mg/L, C/N is about 10:1, the aeration quantity is 4 L/min, the dissolved oxygen concentration is 3 mg/L, the influent's pH value is 6.5-8.0, starting concentration of N is 40 mg/L, the initial mol ratio between $NaHCO_3$ and ammonia nitrogen is 2:1 and then declines gradually. Values of various indexes at different alkalinities

TABLE-5
OPERATION DATA ON EFFECT OF ALKALINITY

Period (day)	$NaHCO_3$: NH_4-N (mol)	Flow direction	NH_4	NO_2	NO_3	TN	Alkalinity	pH value
1	2:1	Water inlet	46.47	0.96	0.062	47.551	393.39	7.34
		Effluent	1.29	1.79	0.108	3.23	367.61	8.23
2	1:1.5	Water inlet	23.02	0	0	23.02	365.65	7.06
		Effluent	1.31	1.82	0.11	3.23	367.65	8.25
3	1:1	Water inlet	47.37	0	0	47.34	323.5	7.21
		Effluent	1.97	3.61	0.0032	5.5792	245.1	7.75
4	0.8:1	Water inlet	51.29	0.84	0.015	52.163	341.85	7.48
		Effluent	1.07	1.24	0.15	2.46	225.75	7.94
5	0.5:1	Water inlet	35.71	0.076	0	35.761	264.45	7.01
		Effluent	0.61	1.95	0.089	2.671	180.6	7.7
6	0.4:1	Water inlet	59.97	0.53	0.069	60.609	219.3	6.99
		Effluent	1.43	0.51	0.25	2.18	116.1	7.75
7	0.4:1	Water inlet	65.66	0.51	0.09	66.28	174.15	6.6
		Effluent	5.68	5.93	0.091	11.714	45.15	6.8
8	0.3:1	Water inlet	81.61	1.137	0.057	82.765	219.3	7.3
		Effluent	16.34	5.77	0.0078	22.1481	96.75	7.22
9	0.3:1	Water inlet	82.85	1.87	0.056	84.786	193.5	7.45
		Effluent	8.74	5.26	0.025	14.015	58.05	6.96
10	0.5:1	Water inlet	89.38	0.74	0.037	90.177	212.85	7.52
		Effluent	0.91	2.39	0.031	3.342	58.05	6.95

are measured to examine the impact of alkalinity; corresponding data are shown as Table-5.

The experiment of alkalinity effect is conducted for 10 days, 7 mol values are selected. From the table we can see that alkalinity need not be as high as theoretical value, the effluent's treatment effect can certainly reach requirement, when mol is above 0.5:1 and COD, ammonia nitrogen and total nitrogen all have very good treatment effect. If mol is less than 0.5:1, the effluent's ammonia nitrogen concentration increases significantly.

Removal rates of various pollutants at different alkalinities are shown as Table-6.

TABLE-6
REMOVAL RATES OF VARIOUS POLLUTANTS AT DIFFERENT ALKALINITIES

Period (day)	Removal rate of NH_4^+	Removal rate of TN	Nitrosation rate	Alkalinity consumption rate
1	0.971593	0.931594	0.942005	0.065474
2	0.942559	0.857818	0.942005	0.077217
3	0.957412	0.872136	0.991114	0.235
4	0.978146	0.948842	0.891886	0.337623
5	0.982604	0.924357	0.954775	0.316073
6	0.975321	0.963788	0.670973	0.470498
7	0.91292	0.82281	0.984511	0.740141
8	0.798959	0.732001	0.998595	0.558774
9	0.894229	0.834301	0.99467	0.68
10	0.988732	0.958951	0.9753	0.721273

From Tables 5 and 6, we can find that alkalinity has direct influence on pH values of water, thus affecting nitrification rate of biological response and type of denitrifying in the reactor correspondingly changes.

The relationship between ammonia nitrogen, the effluent's concentration and time is as shown in Fig. 2.

According to Fig. 2, as long as alkalinity is maintained at certain level, increase of ammonia nitrogen concentration in the inlet water does not affect the quality of effluent.

The relationship between inlet water's alkalinity and effluent's water, time is shown as Fig. 3.

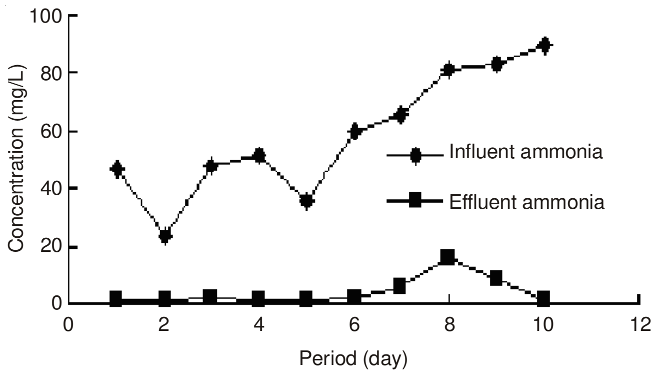

Fig. 2. Relationship between ammonia mitrogen, effluent's concentration and time

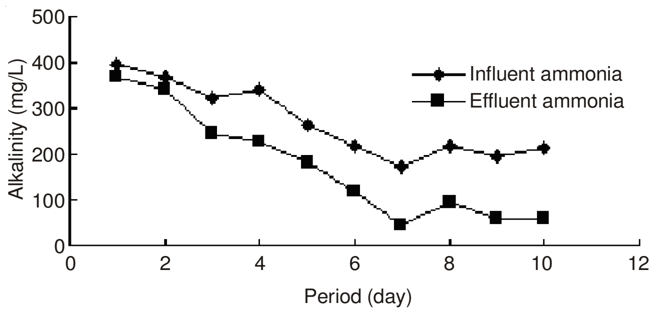

Fig. 3. Relationship between inlet water's alkalinity and effluent's water, time

Fig. 3 indicates that the alkalinity consumption is positively correlated to concentration of ammonia nitrogen, the increase of the concentration leads to higher alkalinity consumption. As long as the inlet water's alkalinity is not lower than the consumption, the biological response can be normal, but Ph value is relatively low, especially that of effluent. When the pH value is below 7, it will affect nitrite bacteria's activity, when the pH value is below 6, it will inhibit the digestion reaction.

RESULTS AND DISCUSSION

Shortcut nitrification-denitrification: For a long time, in both theory and practice of engineering, it is believed that, biological denitrogenation of waste water can be fully realized only through typical nitrification and denitrification process[7,8] with NH_4^+, but according to ammonia nitrogen's microbial transformation process, ammonia nitrogen is oxidized to nitrate through response of two types of independent bacteria with catalysis. As for denitrifying bacteria, either NO_2^- or NO_3^- can be used as final hydrogen accepter, thus the whole process of biological nitrogen removal can be realized through the method: $NH_4^+ \rightarrow HNO_2 \rightarrow N_2$.

Nitrite accumulation: The conventional process of nitrification is completed with synergistic reaction of nitrite bacteria and nitrate bacteria, because these two types of bacteria form relatively close symbiotic relationship in open ecosystem[9], complete nitration is impossible. How to control nitration reaction and make it stop at HNO_2 phase and obtain stable and high volume of HNO_2 (nitration rate NO_2-N/(NO_2-N+NO_2-N) should at least be more than 50 %) is the key to realizing shortcut biological nitrogen removal[10,11]. Factors affecting nitrite accumulation are mainly pH value, temperature, concentration of ammonia, nitrogen load, DO and sludge age.

Temperature: Biological nitrification reaction can occur at about 45 ºC, the proper temperature is 20-35 ºC, its nitrification action rate slows down when the temperature is below 15 ºC[12,13]. At the same time, effect of low temperature on nitration products and activity of two types' nitrifying bacteria, at 12-14 ºC, activity of nitrate bacteria in activated sludge is subject to severe inhibition, resulting to HNO_2 accumulation. At 15-30 ºC, nitrite resulting from nitrification process is completely oxidized into nitrate, HNO_2 accumulation occurs again when the temperature is above 30 ºC.

pH value: With nitration reaction, acid generated in nitrification process make pH value of waste water drops continually. Nitrite bacteria's optimum pH value is 7-8.5 and that of nitrate bacteria is 6-7.5[14]. When pH value is below 7, the nitration reaction can be suppressed. When the pH value increase to above 8, HNO_2 concentration of the effluent increase, namely, the proportion of nitrite in nitration product rises, HNO_2 accumulates.

NH_3 concentration and nitrogen load: Ammonia nitrogen in waste water, respectively in molecular and ionic forms, free ammonia (FA) of molecular form has obvious effect on nitrification, nitrifying bacteria are more susceptible to the inhibition of free ammonia compared to nitrosomonas species, free ammonia with concentration of 0.6 mg/L can inhibit the activity of nitrifying bacteria, stop HNO_2 oxidation, resulting in HNO_2 accumulation[15]. Only when free ammonia's concentration is over 5 mg/L, can it affect nitrite bacteria's activity, when free ammonia's concentration reaches 40 mg/L, the formation of nitrite will be severely inhibited.

With the increase of pH value, concentration of free ammonia also rises and it is easy to cause the accumulation of HNO_2[16]. Similarly, when ammonia nitrogen load is too high, since nitrite bacteria grow quickly and the amount of nitrite generated exceeds the oxidation amount at the beginning of system operation, nitrite accumulates.

Dissolved oxygen: Nitrite bacteria and nitrate bacteria are aerobic bacteria, in experiment, only when dissolved oxygen is above 0.5 mg/L, can nitrification reaction occur, otherwise, nitrification reaction will be supressed. Reduction of dissolved oxygen has little impact on oxidation of nitrite, but great impact is found in oxidation of nitrite and it is easy to cause the accumulation of HNO_2.

Sludge age: In suspended processing system, if sludge age is between nitrate and nitrite bacteria's minimum residence time, nitrate bacteria in the system will gradually be washed away, making nitrite bacteria become advantageous nitrobacteria, nitrifying product is mainly HNO_2, thus HNO_2 easily accumulates.

Effects of fillers: Carrier fillers used in the reactor are PVC suspension particles whose particle size is about 10 mm, their specific surface area is large and a lot of living things are there, leading to large microbial biomass[17,18]. As collision of fillers occur during the operation, the carriers' surface biological film is relatively thin and their biological activity is relatively high. At the same time, due to large specific surface area, clear hierarchical distribution is found in the fillers, from outside to inside, they are, respectively facultative bacteria, anaerobic bacteria and anaerobic bacteria and the diversity of bacteria is conductive to improvement of removal efficiency of ammonia nitrogen[19]. Fillers have cutting, preventing and adsorption effect on bubbles, leading to increase of bubbles' staying time and contact surface area with gas and liquid, thus accelerating oxygen's transfer rate, improving effect of mass transfer and oxygen absorption capacity, thereby reducing aeration demand, saving energy and equipment capacity.

Conclusion

Through the experiment on treatment of nitrogen waste water using biological contact oxidation fluidized bed, the following conclusions are summarized:

• Fillers with particle size of about 10 mm not only have good hanging membrane and membrane's biological activity is relatively high, which is conducive to the improvement of ammonia nitrogen's removal efficiency. Intermittent inflow is conductive to flocculation bacteria's growth, inhibition of bulking sludge formation, it makes activated sludge have good settlement and can offer good environmental conditions for nitrification.

• The distribution aerobic bacteria, facultative bacteria and anaerobic bacteria in carrier fillers help realize better layered structure and higher biological activity; It has great processing capacity and good treatment effect on high load caused by increase of inlet water concentration and shortening of hydraulic retention time (HRT). In the field of waste water treatment, removal of ammonia nitrogen is the most serious issue which urgently needs to be solved after resolving the issue of organic pollution. In this experiment, it is found that nitrogen removal effect of the whole biological nitrogen removal system is always in good condition, the quality of effluent and handling capacity in condition of high load are great, so the experimental results have important guidance and reference significance on the development of new technology of ammonia nitrogen waste water treatment.

ACKNOWLEDGEMENTS

This work was supported by Jiangsu Science and Technology Support Program (BE2010738); Jiangsu Province Post-Doctoral Fund Projects (Grant No. 1201054C); Outstanding Young Teachers of Jiangsu Higher Education Overseas Training Scheme Funded; Qing Lan Project; Public Security Technical Discipline and PAPD.

REFERENCES

1. G.W. Chen and Z.C. Wu, *Chin. J. Environ. Eng*., **4**, 540 (2010).
2. K. Czerwionka, J. Makinia, K.R. Pagilla and H.D. Stensel, *Water Res*., **46**, 2057 (2012).
3. L.E. McQuade and S.J. Lippard, *Curr. Opin. Chem. Biol.*, **14**, 43 (2010).
4. C. Wu, Y. Peng, S. Wang, X. Li and R. Wang, *Chin. J. Chem. Eng*., **19**, 512 (2011).
5. F. Cui, S. Lee and M. Kim, *Water Res*., **45**, 5279 (2011).
6. S. Duda, J.E. Stout and R. Vidic, *HVAC&R Res*., **17**, 872 (2011).
7. L.M. Gieg, T.R. Jack and J.M. Foght, *Appl. Microbiol. Biotechnol*., **92**, 263 (2011).
8. L. Ding, J.C. Tang, Z.Z. Ying, Y.X. Zhao, M. Xu and Z.X. Liu, *Chin. Water Wastes Water*, **26**, 116 (2010).
9. D.C. Botia, M.S. Rodríguez and V.M. Sarria, *Chemosphere*, **89**, 732 (2012).
10. X.M. Han. J.W. Martin, T. Barri, X. Han, P.M. Fedorak, M.G. El-Din, L. Perez, A.C. Scott and J.T. Jiang, *Environ. Sci. Technol*., **44**, 8350 (2010).
11. Y.S. Wong, M.O.A.B. Kadir and T.T. Teng, *Bioresour. Technol.*, **100**, 4969 (2010).
12. B. Farizoglu and S. Uzuner, *Biochem. Eng. J.*, **57**, 46 (2011).
13. M. Neifar, A. Jaouani, M.J. Martinez and M.J. Penninckx, *J. Microbiol*., **50**, 746 (2012).
14. S. Harvey and M. Dixon, *Int. J. Hydrogen Energy*, **35**, 9611 (2010).
15. S. Munzi, T. Pisani and S. Loppi, *Ecotoxicol. Environ. Saf*., **72**, 2009 (2009).
16. P. Bogino, F. Nievas, E. Banchio and W. Giordano, *Eur. J. Soil Biol*., **47**, 188 (2011).
17. J. Desloover, S.E. Vlaeminck, P. Clauwaert, W. Verstraete and N. Boon, *Curr. Opin. Biotechnol*., **23**, 474 (2012).
18. D. Austin and J. Nivala, *Ecol. Eng*., **35**, 184 (2009).
19. S.G. Won and C.S. Ra, *Water. Res*, **45**, 171 (2011).