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Removal of Ammonium Nitrogen from Petrochemical Wastewater by Anaerobic-Aerobic Process

QING ZHAO[1], XIN CHEN[1,2], MING TONG[1,2], YIN ZHAO[1], YANBO ZHOU[1] and JUN LU[1,*]

[1]Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, Shanghai 200237, P.R. China
[2]SINOPEC Ningbo Engineering Co. Ltd., Ningbo 315103, P.R. China

*Corresponding author: E-mail: lujun@ecust.edu.cn; zhaoqing10061261@126.com

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Pilot equipment was set up to evaluate effectiveness of anaerobic-aerobic (A/O) process on removing ammonia nitrogen (NH_3-N) from petrochemical wastewater. The results showed that the anaerobic-aerobic process had a good biological degradation effect on NH_3-N from petrochemical wastewater. Effluent NH_3-N was below 2 mg/L during steady operation, which can meet the petrochemical wastewater discharge standards in China. The removal rate of NH_3-N was nealy 100 % with the influent NH_3-N from 20-105 mg/L. C/N ratio and pH value were the key factors on removal efficiency of nitrogen in the biosystem. The optimal experiment conditions were determined as follows: C/N ≥ 5, pH value 7-8. The NH_3-N biodegradation process can be described by Monod equation and the kinetics parameters were ν_{max} = 0.12 h^{-1}, K_S = 7.22 mg/L.

Key Words: Petrochemical wastewater, Anaerobic-aerobic process, Ammonia nitrogen, Kinetics.

INTRODUCTION

Petrochemical wastewater is generated from a wide variety of oil refining process and contains different complex components and high concentrations of pollutants. Uncontrolled disposal of these effluents can cause great damage to the environment. Nitrogen discharge to ponds and lakes could contribute to enhance the eutrophication process and damage aquatic life[1,2]. For this reason, Chinese local government has developed restricted regulations. The new industrial wastewater discharge standards require that effluent NH_3-N concentration must be less than 5 mg/L. The new policy makes petrochemical wastewater treatment plants need to regulate their process or processing parameters to improve the denitrification efficiency. Qilu ethylene wastewater treatment plant is a branch of China Petroleum and Chemical Corporation. It undertakes the treatment task of wastewater from more than 40 petrochemical plants and chemical companies in Qilu ethylene area. In order to meet the new emission requirements, anaerobic-aerobic (A/O) process was used for removing organic compounds and nitrogen from the wastewater[3-5]. The aim of this paper was to evaluate the treatment effectiveness of A/O process on petrochemical wastewater and quantify the influence of influent C/N ratio, pH value on removal efficiency of ammonium nitrogen in pilot equipment[6,7], then applied the optimum condition to the wastewater treatment plant. In the meanwhile, set up the kinetics model of degradation of ammonium nitrogen by activated sludge in aerobic tank.

In the last decade, studies on biological removal of nitrogen using synthetic wastewater to simulate industrial discharges have been performed in order to evaluate the potential application of the A/O process in industrial wastewaters treatment[8], but few studies focused on real industrial wastewater have been published in the petrochemical industry. In this study, the performance of pilot equipment fed with real petrochemical wastewater from wastewater treatment plant was measured at different conditions. Based on the experimental results, kinetic coefficients of degradation of ammonium nitrogen were determined, which might provide the basic design criteria required for operating the wastewater treatment plant[9,10].

EXPERIMENTAL

The pilot equipment consists of an anaerobic tank (1.2 m^3), an aerobic tank (2.4 m^3) and a secondary sedimentation tank (0.75 m^3), as shown in Fig. 1. Anaerobic tank and aerobic tank are the main reactors in this study.

During the experiment, these reactors were fed continuously with petrochemical wastewater from the preliminary sedimentation tank in the site, at flow rates of 120 L/h.

The source of inoculation activated sludge was obtained from the sludge mixed liquor in aerobic tank of wastewater treatment plant. The composition of wastewater is given in Table-1. Temperature was controlled to be 20-25 ºC, hydraulic retention time (HRT) of anaerobic and aerobic tank was 9.2 and 19.1 h, respectively. The mixed liquor suspended solid

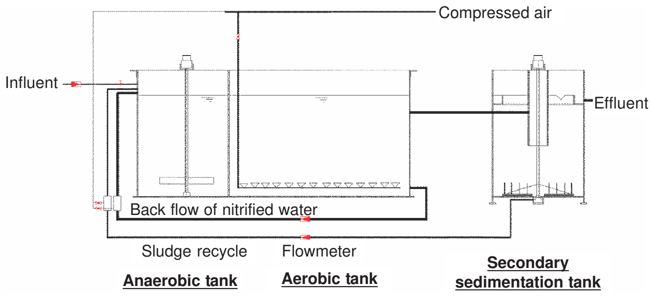


Fig. 1. Schematic diagram of the pilot equipment

TABLE-1
COMPOSITION OF PETROCHEMICAL WASTEWATER

	pH	COD (mg/L)	BOD_5 (mg/L)	SS (mg/L)	NH_3-N (mg/L)
Influent	6-9	170-360	≤290	≤100	20-70
Effluent emission	6-9	≤50	≤20	≤70	≤5

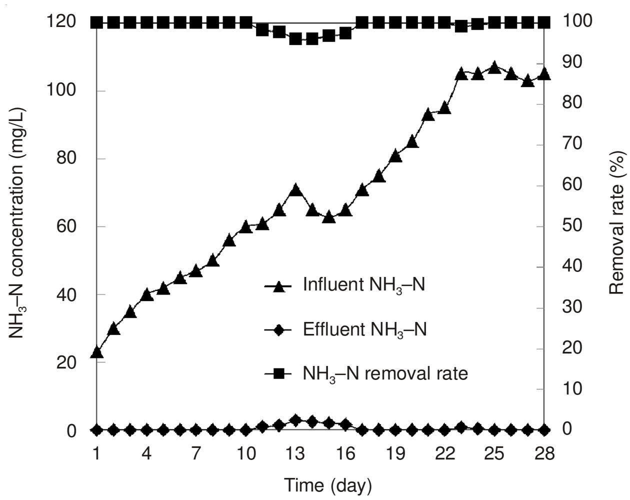


Fig. 2. Removal efficiency of NH_3-N during continuous operation

concentration (MLSS), mixed liquor volatile suspended solids concentration (MLVSS), dissolved oxygen (DO) concentration in aerobic tank were maintained at 7000-8000, 3500-4700 and 4 mg/L.

Experiments were carried out in two phases. In the first stage, the reactors were operated for 10 days until the MLVSS, effluent chemical oxygen demand (COD) concentration and sludge properties reached a steady state. Influent NH_3-N concentration in wastewater treatment plant swings from 20-70 mg/L. Durning the steady continuous operation, ammonium sulfate was added to real petrochemical wastewater to regulate influent NH_3-N concentration from 20-105 mg/L, pilot experiments were designed to evaluate the process behaviour (maximum NH_3-N loading, transient responses, *etc*.) in high influent NH_3-N concentration condition.

In the second stage, experimental conditions were changed in order to determine the optimum operation conditions for denitrification of petrochemical wastewater. At the same time, the kinetics of degradation of NH_3-N by A/O process was studied, which can be a theoretical foundation for optimization and monitoring of A/O process in wastewater treatment plant.

Detection method: Analyses of mixed liquor volatile suspended solids concentration (MLVSS), chemical oxygen demand (COD), ammonia nitrogen (NH_3-N), pH value were conducted as described in standard methods[11]. The concentration of dissolved oxygen was determined by portable dissolved oxygen meter (HQ40d, HACH).

RESULTS AND DISCUSSION

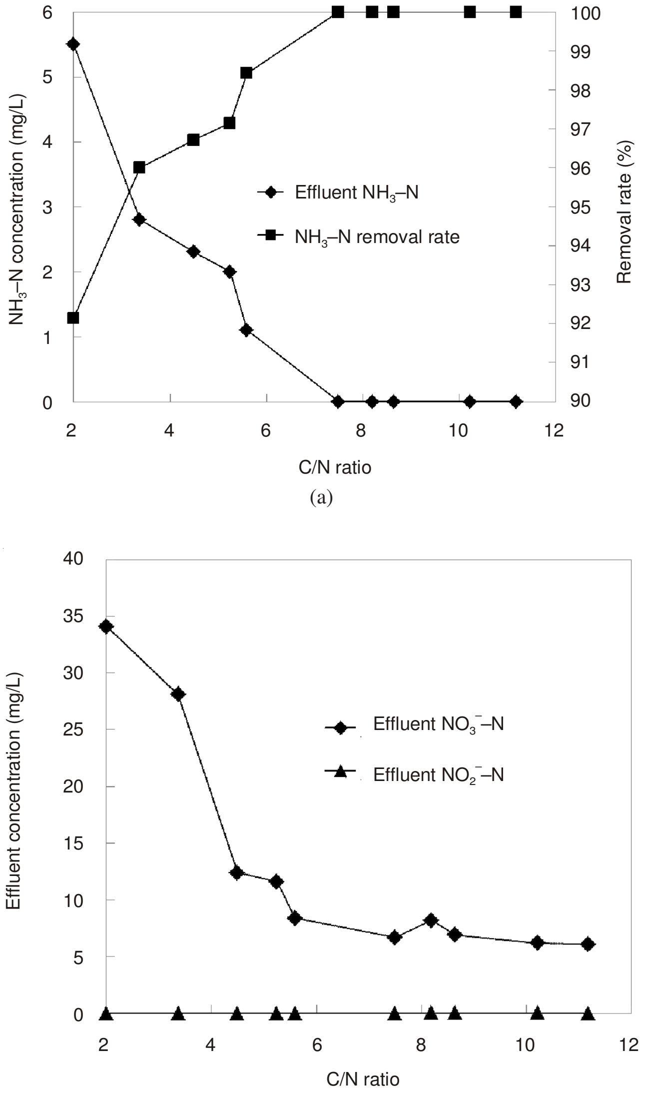
Removal of NH_3-N during continuous operation: The average influent NH_3-N concentration was less than 50 mg/L during normal operating stage. In this study, the effectiveness of high concentration NH_3-N degradation by A/O process was evaluated. Ammonium sulfate was added to real petrochemical wastewater to increase the influent NH_3-N concentration, the effect of sludge loading on removal of NH_3-N was studied by changing the influent NH_3-N concentration step by step from 20-105 mg/L. The removal rate of NH_3-N during continuous operation is shown in Fig. 2.

Fig. 2 shows that the effluent NH_3-N concentration was under 2 mg/L throughout the experiment, removal rate of NH_3-N was nearly 100 % steadily, even when influent NH_3-N concentration was up to 105 mg/L. The NH_3-N loading was low for the first 4 days, only about 0.002 kgNH_3-N/(m^3 d), then gradually increased to maximum 0.010 kgNH_3-N/(kgMLSS d), compared with the design value of wastewater treatment plant (0.0029 kg NH_3-N/(kgMLSS d)), the experimental value increased by 245 %. The pilot experiment results indicated that the biosystem had a large load capacity, experimental data was the basis for overload operation of the wastewater treatment plant in the future.

Effect of C/N ratio: Operational parameters affecting denitrification rate are diverse, such as C/N ratio and pH value. In order to study the influence of C/N ratio on removal rate of nitrogen in aerobic tank, pH value and DO concentration were maintained at 7.0-8.0 and 4 mg/L, respectively. The original wastewater from the wastewater treatment plant was variable, influent COD and NH_3-N were 198-350 mg/L, 35-70 mg/L, respectively. The influent COD/N ratio was modified by adding sucrose and ammonium sulfate to the original influent. Effulent NH_3-N, NO_3^--N, NO_2^--N concentrations at different C/N ratio condition in the pilot equipment are shown in Fig. 3(a-b).

As C/N ratio increased from 2 to 5, effulent NH_3-N decreased from 5.5 mg/L to lower than 2 mg/L, NH_3-N removal rate was up to 97.2 %. In the meanwhile, effluent NO_3^--N decreased from 34.1 to 11.6 mg/L. When C/N ratio was higher than 7, NH_3-N removal rate was almost 100 %, effluent NH_3-N was below the detection limit, NO_3^--N was around 5, NO_2^--N was only 0.01 mg/L. The results indicated that C/N ratio is one of the most critical parameters of the nitrification process, low C/N ratio was inadequate for establishing an efficient A/O process, because it directly influences the growth competition between autotrophic and heterotrophic microorganism populations[12]. In order to achieve good nitrogen removal effect in A/O system, C/N ratio should be higher than 5, in case the nitrogen removal may be limited by the lack of available organic carbon.

Effect of pH value: The influent COD and NH_3-N concentration was 300 mg/L, 30-70 mg/L during steady operation in the wastewater treatment plant. In order to investigate the effect of influent pH value on removal rate of COD and NH_3-N with different initial influent concentrations, influent pH value was



(a) (b)

Fig. 3. Effect of C/N ratio on effulent NH_3-N, NO_3^--N and NO_2^--N

controlled at 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, respectively, influent COD was 300 mg/L, influent NH_3-N were 30, 60 and 70 mg/L.

Fig. 4 shows the changes of COD and removal rate of NH_3-N at different pH condition. As shown in Fig. 4, removal rate of COD was fluctuant with the increase of pH value. In pH range of 5-6 and 8-10, removal rate of COD decreased with the increase of pH value. When pH value was between 7-8, the A/O system achieved the best COD removal performance. By contrast, removal rate of NH_3-N was improved with the increase of pH value. Fig. 5 shows the effluent NH_3-N and removal rate of NH_3-N at pH value from 5-12.

In general, pH has a significant impact on nitrification efficiency[13]. As shown in Fig. 5, when pH value exceeded this range, nitrifiers activity decreased greatly after pH value was higher than 10, because they were sensitive to variety of pH, denitrification was restrained intensively and nitrate was accumulated at high pH condition. Therefore, appropriate pH can stimulate the denitrification process and keep high organic pollutant removal rate, the optimal pH value should be 7-8.

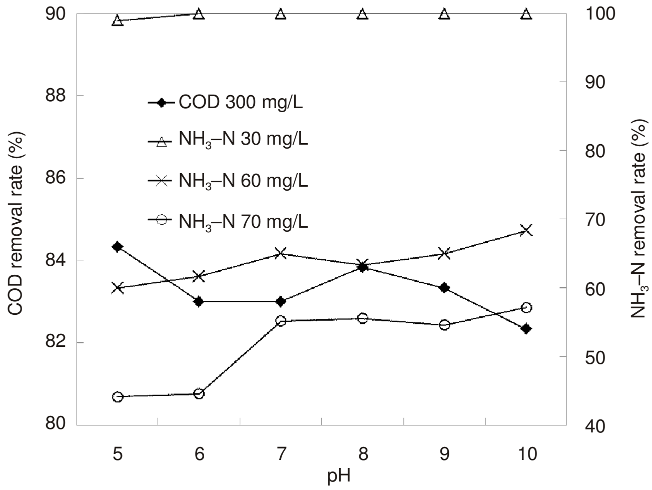


Fig. 4. Effect of pH on removal rate of COD and NH_3-N

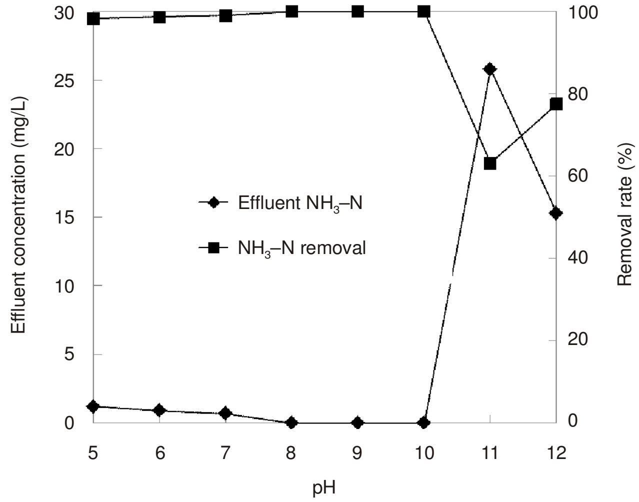


Fig. 5. Effluent NH_3-N and removal rate at different pH condition

Denitrification kinetics: Study on substrate degradation and microbial proliferation kinetics of biosystem is meaningful to control and optimize the process of wastewater treatment. Biodegradation kinetics of wastewater is often expressed by the Monod equation[14]. A simplified model development was used to simulate the experimental results. The sludge denitrification kinetics could be described by Monod model:

$$\nu = \frac{\nu_{max} S}{K_S + S} \quad (1)$$

where S is the nitrate concentration; ν is the denitrification rate; ν_{max} is the maximum denitrification rate; K_S is the Monod or half-saturation constant.

According to the physical meaning of the substrate degradation, the denitrification rate can be expressed as follows:

$$\nu = -\frac{1}{X}\frac{dS}{dt} \quad (2)$$

where $-\frac{dS}{dt}$ is the denitrification rate; X is the mixed liquor suspended solid concentration(MLSS).

Denitrification kinetics equation can be expressed according to eqns. 1 and 2:

$$-\frac{dS}{dt} = \nu_{max}\frac{XS}{K_S + S} \quad (3)$$

Monod equation can be simplified depending on different substrate concentrations. When $10K_S > S > K_S$, simplified and linearized Monod equation can be used for describing the degradation kinetics of ammonia nitrogen by activated sludge. The fitting equation can be expressed as follows[15]:

$$\frac{1}{\nu} = \frac{1}{\nu_{max}} + \frac{K_S}{\nu_{max}}\frac{1}{S} \quad (4)$$

Drawing the relation curve of $1/\nu$ and $1/S$ can obtain the numerical value of ν_{max} and K_S.

In this study, denitrification were investigated in aerobic tank of the pilot equipment. MLSS, pH and DO concentration in aerobic tank were maintained at 7000 mg/L, 7.0-8.0 and 4 mg/L, respectively. The initial NH_3-N concentration was 10 mg/L. Determined NH_3-N concentration in aerobic tank every 2 h, the curve of NH_3-N degradation was shown as Fig. 6.

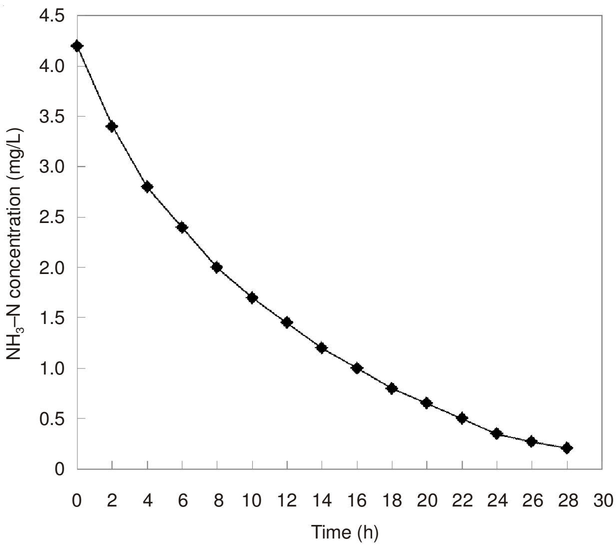


Fig. 6. Curve of NH_3-N degradation

As shown in Fig. 6, NH_3-N concentration was under 0.2 mg/L after 28 h, which means the degradation of NH_3-N in aerobic tank was almost finished. Drawing the relation curve of $1/\nu$ and $1/S$, the fitting curve was shown in Fig. 7.

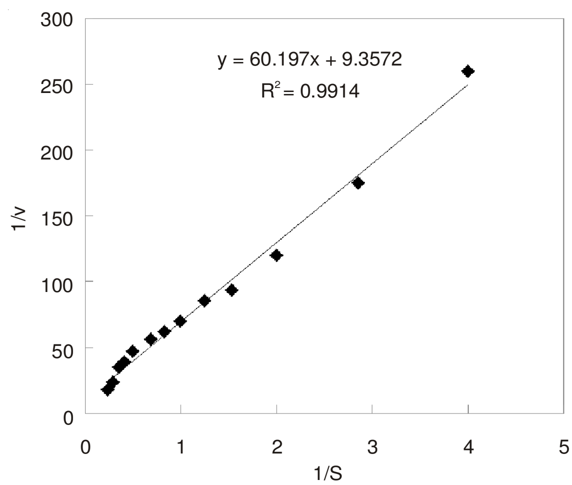


Fig. 7. Monod equation fitting curve

Correlation coefficient of Monod equation fitting curve was 0.9914, according to the fitting equation, kinetics parameters of Monod equation can be calculated as: $\nu_{max} = 0.12\ h^{-1}$, $K_S = 7.22$ mg/L. The kinetic equation of NH_3-N degradation by activated sludge can be expressed as:

$$\nu = \nu_{max}\frac{S}{K_S + S} = 0.12 \times \frac{S}{7.22 + S} \quad (5)$$

Conclusion

Pilot experiment showed that anaerobic-aerobic (A/O) process was effictive to remove NH_3-N from petrochemical wastewater. With the influent NH_3-N concentration from 20-105 mg/L, effluent NH_3-N was less than 2 mg/L, NH_3-N removal rate was almost 100 %. The maximum NH_3-N loading was 0.010 $kgNH_3$-N/(kgMLSS d). The experimental value increased by 245 % compared with the design value of wastewater treatment plant.

C/N ratio and pH value were the key factors on nitrogen removal effect in the biosystem. The optimal experiment conditions in pilot equipment were determined as follows: C/N = 5, pH value 7.0-8.0. NH_3-N biodegradation kinetics of wastewater can be expressed by the Monod equation. The kinetic parameters of NH_3-N degradation were determined, where the maximum degradation rate was 0.12 h^{-1}, half-saturation constant was 7.22 mg/L.

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