



## Nitrification kinetics of a full-scale anaerobic/anoxic/aerobic wastewater treatment plant

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### ABSTRACT

Nitrification kinetics of a full-scale anaerobic/anoxic/aerobic wastewater treatment plant were investigated by considering the anaerobic ( $\eta_A$ ) and anoxic reduction factors ( $\eta_N$ ) on decay rate of nitrifying biomass ( $b_{AUT}$ ) for estimating minimum sludge age ( $\theta_{mc}$ ). Ammonium nitrogen in the effluent was fluctuating seasonally with low nitrification efficiency from December to June. The measured  $b_{AUT}$  values were 0.175, 0.092, and 0.077 d<sup>-1</sup> under aerobic, anoxic, and anaerobic conditions, respectively. A low maximum specific growth rate at 20°C (0.48 d<sup>-1</sup>) and high temperature correction factor (1.208) were yielded in the range of 10–25°C, indicating that the activity of nitrifying biomass was low and depended more sensitively on lower temperatures. At temperature below 12.1°C, the decay rate of nitrifying biomass exceeded growth rate, and a negative  $\theta_{mc}$  was obtained. The extremely high (12.1–15.0°C) or negative (<12.1°C)  $\theta_{mc}$  indicated that prolonging sludge age was probably malfunctioned at cold temperature.

*Keywords:* Wastewater; Nitrification; Kinetics; Activated sludge; Temperature; Decay

### 1. Introduction

The removal of ammonium nitrogen ( $S_{NH}$ ) from wastewater is extremely important to protect water resources from pollution discharges, as ammonia in water environment consumes dissolved oxygen (DO) and can be toxic to aquatic life. In China,  $S_{NH}$  is a compulsory pollutant indicator in the National 12th Five-Year Plan for Environmental Protection, and the total discharge is planned to be reduced by 10% in

2015 compared with that in 2010. Nitrification is the microbial oxidation of  $S_{NH}$  with oxygen into nitrite-nitrogen ( $NO_2$ -N) followed by the oxidation of  $NO_2$ -N into nitrate-nitrogen ( $NO_3$ -N) by autotrophic nitrifying biomass ( $X_{AUT}$ ). In the activated sludge system which is commonly used for wastewater treatment, nitrification failure can occur easily [1], since  $X_{AUT}$  is extremely high sensitive to several environmental and operating factors, including low temperature, low DO, extreme pH, and a variety of toxic compounds [2–4].

For municipal wastewater treatment plants (WWTPs), temperature is one of the commonest

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influencing factors, while nitrification is known as the most temperature-sensitive step among the biological processes for wastewater treatment [3,5]. Head and Oleszkiewicz [6] found that average nitrification rates were decreased by 58, 71, and 82% for biomass cooled to 10°C when biomass were acclimated to 20, 25, and 30°C, respectively. Hwang and Oleszkiewicz [3] summarized temperature correction factors for maximum specific growth rate of  $X_{\text{AUT}}$  ( $\mu_{\text{AUT}}$ ) ranging from 1.072 to 1.127, and pointed out that 1.072 was widely accepted for designing WWTPs. Several studies also obtained much higher temperature correction factors under rapid temperature change [3,6]. Nevertheless, seasonal variations of nitrification efficiency and kinetic parameters in the biological wastewater treatment process were scarcely reported.

In the activated sludge system,  $\mu_{\text{AUT}}$  and the decay rate of  $X_{\text{AUT}}$  ( $b_{\text{AUT}}$ ) have been considered as the most crucial parameters for reactor design and operation [7,8]. The activity of  $X_{\text{AUT}}$  is easily inhibited by toxic substances in wastewater, and typical values of  $\mu_{\text{AUT}}$  were found to be varied in a wide range [2,6,7]. Previous work has shown that the maximal nitrification rate is achieved at a pH in the range 7.0–8.2 and  $\mu_{\text{AUT}}$  is an increasing function of temperature in the range of practical interest (below 30°C) [2,9]. The values of  $b_{\text{AUT}}$  were usually ranged from 0.15 to 0.21 d<sup>-1</sup> at 20°C in previous studies [6,8,10–13], and were found to be significantly lower under anoxic and anaerobic than under aerobic conditions [7,10,11,13–15]. Some researchers suggested that decreases of  $b_{\text{AUT}}$  under anoxic and anaerobic conditions were probably attributed to the different DO concentrations that strongly affected the predation by protozoa [7,16]. Nevertheless, incorporation of reduction factors of  $b_{\text{AUT}}$  and temperature effects into the calculation of minimum sludge age ( $\theta_{\text{mc}}$ ) has so far received relatively little attention, and therefore it should be elaborated in more detail for the anaerobic/anoxic/aerobic (AAO) process.

In recent years, more stringent requirements on urban environment have prompted migration of municipal WWTPs to outer suburbs, and the anaerobic conditions in the pipeline accelerate the generation of high-concentration sulfide [2,17] that usually inhibits the activity of nitrifying biomass and causes low nitrification efficiency [18–20]. Therefore, the objectives of this study are: (1) to analyze seasonal variations of nitrogen pollutants removal performance of a full-scale AAO WWTP fed by long-pipeline transported wastewater based on three-year operational data; (2) to estimate the effect of aerobic, anoxic, and anaerobic conditions on the decay process of  $X_{\text{AUT}}$ ; (3) to investigate the temperature effects on  $\mu_{\text{AUT}}$  of activated

sludge sampled at different temperatures; and (4) to evaluate  $\theta_{\text{mc}}$  based on the measured nitrification kinetic parameters of the full-scale AAO system. It is expected to provide clearer insight to the behavior of  $X_{\text{AUT}}$  in the AAO process.

## 2. Materials and methods

### 2.1. Full-scale WWTP

The evaluation of temperature effects on nitrification performance was carried out for the Bailonggang WWTP in Shanghai. The Bailonggang WWTP is an AAO process with treatment capacity of 2,000,000 m<sup>3</sup>/d fed by combined sewer transported by long pipeline (about 40 km) with domestic and industrial wastewater accounting for approximately 70 and 30% of the total flow, respectively [21]. The hydraulic retention times (HRTs) of the anaerobic, anoxic, and aerobic tank were 1.51, 2.03, and 8.25 h, respectively. The DO in the aerobic stage was controlled at about 2.5 mg/L. Ratios of returned activated sludge and mixed liquor recirculation were both set at 100%, and the sludge age ( $\theta_c$ ) was controlled at 10.0 d. Mixed liquor samples from the Bailonggang WWTP were collected to analyze the growth and decay kinetics of  $X_{\text{AUT}}$ . The operation performance of the Bailonggang WWTP was analyzed over a period of 36 months between January 2009 and December 2011 with monthly average value of influent and effluent calculated according to daily measured data.

Mixed liquor samples from another two WWTPs, Zhuyuan and Quyang, were collected to compare the nitrification kinetics with the Bailonggang WWTP. The Zhuyuan WWTP is an AO process with treatment capacity of 500,000 m<sup>3</sup>/d, and also treats combined sewer with transportation distance slightly shorter than the Bailonggang WWTP. The HRTs of the anoxic and aerobic tank were 4.0 and 9.8 h, respectively, and the  $\theta_c$  was controlled at about 15.0 d. The Quyang WWTP is an AAO process with treatment capacity of 75,000 m<sup>3</sup>/d fed by domestic wastewater originating from adjacent residential areas. The HRTs of the anaerobic, anoxic, and aerobic tank were 1.5, 1.5, and 4.7 h, respectively, and the  $\theta_c$  was maintained at 15.0 d.

### 2.2. Batch experiments

Two different types of batch tests were carried out to assess  $\mu_{\text{AUT}}$  and  $b_{\text{AUT}}$ . The batch test and estimation method for  $\mu_{\text{AUT}}$  is described in detail in Zhou et al. [2]. For the determination of  $\mu_{\text{AUT}}$ , mixed liquor of activated sludge from the aerobic tank of WWTPs was

diluted to 200–400 mg L<sup>-1</sup>, and filled into aerobic batch reactors of 1 L together with 50 mg L<sup>-1</sup> of ammonium nitrogen and 150 mg L<sup>-1</sup> NaHCO<sub>3</sub> as buffer. Homogenized mixed liquor samples were periodically taken, filtered, and analyzed for nitrate- and nitrite-nitrogen. The pH and DO of the mixed liquor were maintained at 4.0 mg L<sup>-1</sup> and 7.0–8.0, respectively.

The  $b_{AUT}$  was evaluated for activated sludge sampled from the aerobic tank of WWTPs. Activated sludge samples were placed in a batch reactor (BR1) that was either continuously aerated (decay under aerobic conditions), stirred (decay under anaerobic conditions), or stirred in the presence of 20–30 mg/L NO<sub>3</sub>-N (decay under anoxic conditions). For the anoxic experiment, NO<sub>3</sub>-N was periodically measured and manually added to maintain anoxic condition. The batch tests were lasted for about 6.0 d. At intervals of one day, 50 mL of activated sludge was withdrawn from the batch reactor, and transferred into another batch reactor (BR2) with 50 mg/L  $S_{NH}$  and 150 mg/L NaHCO<sub>3</sub> for the determination of ammonium uptake rate (AUR). The DO concentration and pH were controlled at 4–5 mg/L and 7.0–8.0, respectively.

Mixed liquor suspended solids (MLSS), suspended solids (SS),  $S_{NH}$ , NO<sub>3</sub>-N, NO<sub>2</sub>-N, total nitrogen (TN), chemical oxygen demand (COD), five-day biological oxygen demand (BOD<sub>5</sub>), and total phosphorus (TP) were analyzed according to Standard Methods [22]. DO and pH were measured by HQ30 Hach Portable DO/pH meter (Hach Co., USA).

### 2.3. Calculation of decay coefficient by AUR

According to the Activated Sludge Models (ASM) [8], the decay process of  $X_{AUT}$  (in BR1) can be expressed as:

$$dX_{AUT}/dt - b_{AUT}X_{AUT} \quad (1)$$

where  $t$  is time,  $d$ . In the environment rich in  $S_{NH}$  (above 30 mg/L) and DO (above 4.0 mg/L) (BR2), the AUR could reach its maximum level, and the relationship between AUR and  $X_{AUT}$  can be expressed as:

$$AUR = dS_{NO}/dt = \mu_{AUT}X_{AUT}/Y_{AUT} \quad (2)$$

where  $S_{NO}$  is oxidized nitrogen (NO<sub>3</sub>-N+NO<sub>2</sub>-N), mg/L;  $Y_{AUT}$  is yield coefficient of  $X_{AUT}$ , 0.24 gCOD/gN [8]. Substituting the integral solution of Eq. (1) into Eq. (2) gives:

$$AUR = \mu_{AUT}X_{AUT,0}e^{(-b_{AUT}t)}/Y_{AUT} \quad (3)$$

where  $X_{AUT,0}$  is the initial concentration of  $X_{AUT}$  for the decay batch test, mg/L.  $b_{AUT}$  is obtained by the fitting of AUR– $t$  curve.

### 2.4. Temperature correction factor and activation energy of $\mu_{AUT}$

The effect of temperature on  $\mu_{AUT}$  relative to a standard temperature (20°C herein) can be expressed by the simplified Arrhenius equation [23,24].

$$\mu_{AUT,T} = \mu_{AUT,20}\theta^{T-20} \quad (4)$$

where  $\mu_{AUT,T}$  and  $\mu_{AUT,20}$  were, respectively,  $\mu_{AUT}$  values at the temperature  $T$  (in °C) and 20°C, d<sup>-1</sup>;  $\theta$  is the Arrhenius temperature correction factor of  $\mu_{AUT}$ .

The activation energy of nitrification can be determined graphically by taking the natural logarithm of Arrhenius equation, as shown in the following Eq. (5).

$$\ln(\mu_{AUT,T}) = -E_a/[R(273.15 + T)] + \ln A \quad (5)$$

where  $E_a$  is the activation energy, J/mol;  $A$  is the frequency factor for the reaction, d<sup>-1</sup>;  $R$  is the universal gas constant, 8.3145 J/(mol K).

### 2.5. Calculation of minimum sludge age of nitrification

The minimum sludge age represents a sludge age that micro-organisms cannot survive in the biological system since the dilution factor due to solids discharge rate higher than the net growth rate ( $\mu_{AUT} - b_{AUT}$ ). For municipal WWTPs,  $X_{AUT}$  in the influent is negligible with concentration below 1.0 mgCOD/L [8,21]. It should be noted that, in the biological process with anaerobic and anoxic stages for nutrient removal,  $X_{AUT}$  usually grows under aerobic condition, but decays under aerobic, anoxic, and anaerobic conditions. If rate reduction factors of  $X_{AUT}$  decay under anaerobic and anoxic conditions are defined as  $\eta_A$  and  $\eta_N$ , the equivalent volume of  $X_{AUT}$  decay ( $V_D$ ) can be expressed as Eq. (6).

$$V_D = V_O + \eta_N V_N + \eta_A V_A \quad (6)$$

where  $V_O$ ,  $V_N$ , and  $V_A$  are the volume of aerobic, anoxic, and anaerobic stage, respectively, m<sup>3</sup>.

Therefore, the process rate of  $X_{\text{AUT}}$  in the AAO process can be expressed as:

$$V \frac{dX_{\text{AUT}}}{dt} = V_O \mu_{\text{AUT}} \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} X_{\text{AUT}} - V_D b_{\text{AUT}} X_{\text{AUT}} - \frac{M_w}{X} X_{\text{AUT}} \quad (7)$$

where  $V$  is total volume of the AAO system,  $\text{m}^3$ ;  $K_{\text{NH}}$  is the half-saturation coefficient for  $X_{\text{AUT}}$ ,  $1.0 \text{ mgN/L}$  [8];  $M_w$  is the amount of wastage sludge discharged from the system,  $\text{mg/d}$ ;  $X$  is MLSS concentration in the AAO process,  $\text{mg/L}$ . Dividing both sides of Eq. (7) by  $V$ , we obtain Eq. (8).

$$\frac{dX_{\text{AUT}}}{dt} = \frac{V_O}{V} \mu_{\text{AUT}} \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} X_{\text{AUT}} - \frac{V_D}{V} b_{\text{AUT}} X_{\text{AUT}} - \frac{V_O}{V \theta_c} X_{\text{AUT}} \quad (8)$$

In a wastewater treatment process with stable nitrification efficiency,  $dX_{\text{AUT}}/dt \geq 0$ ; therefore, Eq. (8) can be transformed as in Eq. (9).

$$\frac{1}{\theta_c} \leq \mu_{\text{AUT}} \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} - \frac{V_D}{V_O} b_{\text{AUT}} = R_g - R_d \quad (9)$$

where  $R_g$  and  $R_d$  are equivalent growth and decay rate of  $X_{\text{AUT}}$  in the AAO process, respectively,  $\text{d}^{-1}$ . The  $\theta_{\text{mc}}$  can be calculated as

$$\frac{1}{\theta_{\text{mc}}} = R_g - R_d = \mu_{\text{AUT}} \frac{S_{\text{NH}}}{K_{\text{NH}} + S_{\text{NH}}} - \frac{V_D}{V_O} b_{\text{AUT}} \quad (10)$$

### 3. Results and discussion

#### 3.1. Pollutants removal performance of the Bailonggang WWTP

The average influent and effluent characteristics of the Bailonggang WWTP during the period from January 2009 to December 2011 are summarized in Table 1. The COD, BOD<sub>5</sub>, and SS concentrations in the effluent were all stable and very low, and the average removal efficiencies of COD, BOD<sub>5</sub>, and SS were 89.9, 94.6, and 90.5%, respectively. The WWTP also showed high efficiency for phosphorus removal (88.1%) with stable and low TP concentrations in the effluent. Nevertheless, the  $S_{\text{NH}}$  and TN concentrations in the effluent were fluctuated widely with coefficients of variation of 0.79 and 0.32, and the low removal efficiencies of 65.4 and 44.2% were observed for  $S_{\text{NH}}$  and TN, respectively.

Table 1

Average influent and effluent characteristics of the Bailonggang WWTP

Pollutants	Influent	Effluent
COD (mg/L)	300.5 ± 45.5	30.3 ± 5.0
BOD <sub>5</sub> (mg/L)	136.4 ± 19.1	7.3 ± 0.9
SS (mg/L)	116.3 ± 20.8	11.1 ± 1.5
TP (mg/L)	3.37 ± 0.50	0.40 ± 0.16
$S_{\text{NH}}$ (mg/L)	29.73 ± 3.14	10.30 ± 8.09
TN (mg/L)	34.17 ± 3.51	19.06 ± 6.09

Fig. 1 shows seasonal variations of  $S_{\text{NH}}$  and TN in the effluent with wastewater temperature in the Bailonggang WWTP. High concentrations of  $S_{\text{NH}}$  ( $15.90 \pm 5.33 \text{ mg/L}$ ) and TN ( $23.29 \pm 4.33 \text{ mg/L}$ ) in the effluent lasted from December to June of the next year, while low concentrations of  $S_{\text{NH}}$  ( $2.82 \pm 2.33 \text{ mg/L}$ ) and TN ( $13.24 \pm 2.16 \text{ mg/L}$ ) were observed between July and November. As shown in Fig. 1, the decrease of temperature results in the increase of  $S_{\text{NH}}$  in the effluent, but the improvement of  $S_{\text{NH}}$  removal shows obvious hysteresis phenomenon with the increase of temperature. In the Bailonggang WWTP, the hysteresis period usually lasted for more than six months, and high concentrations of nitrogen pollutants also observed at temperature above  $20^\circ\text{C}$ . During the period from December to June of the next year, average concentrations of  $S_{\text{NH}}$  in the effluent of the Quyang and Zhuyuan WWTPs were  $7.17 \pm 5.34$  and  $16.65 \pm 5.43 \text{ mg/L}$ , while low concentrations of  $1.15 \pm 0.67$  and  $10.65 \pm 2.97 \text{ mg/L}$  were observed during the other period. The similar trend of  $S_{\text{NH}}$  concentrations of  $S_{\text{NH}}$  in the effluent was observed among the three WWTPs, but the Bailonggang WWTP showed the largest amplitude of variation. It is concluded that the recovery of nitrification performance was very slow, and the low net growth rate of  $X_{\text{AUT}}$  in the Bailonggang WWTP [2] was probably a major reason.

In the effluent of the Bailonggang WWTP, ratios between  $S_{\text{NH}}$  concentration and TN concentration were 68.3 and 21.3% in the period of December to June and July to November, respectively, indicating that higher TN in the effluent were resulted from the low nitrification efficiency. The relationship between  $S_{\text{NH}}$  and TN in the effluent could be expressed as:

$$\text{TN} = 0.7320 S_{\text{NH}} + 11.53 \quad (R^2 = 0.9444) \quad (11)$$

The significant linear correlation between these two variables ( $r = 0.9726$ ,  $p < 0.001$ ) indicated that the

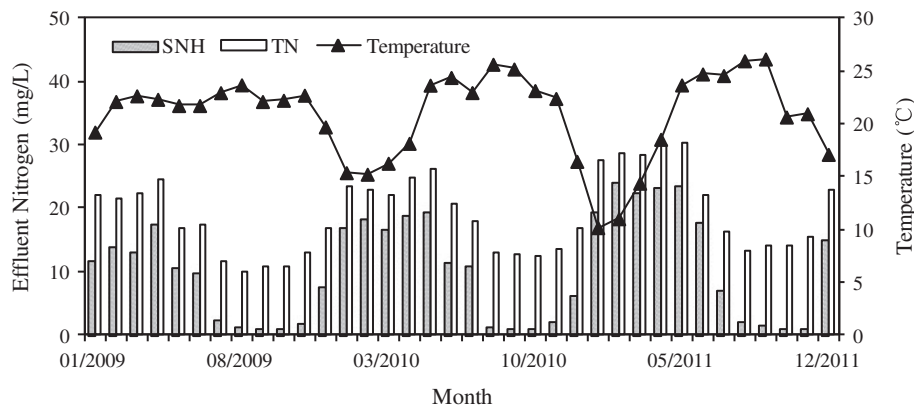


Fig. 1. Variations of  $S_{\text{NH}}$  and TN in the effluent with temperature in the Bailonggang WWTP.

improvement of nitrification efficiency was the crucial step for the removal of both  $S_{\text{NH}}$  and TN.

### 3.2. Comparison on nitrification efficiency at different sludge ages

The sludge ages of two parallel full-scale AAO systems in the Bailonggang WWTP were prolonged from 10.0 d to 12.0 and 19.6 d to improve their nitrification efficiencies at low wastewater temperature ( $10.6 \pm 1.8^\circ\text{C}$ ) in 2011. Fig. 2 shows the variations of  $S_{\text{NH}}$  and  $S_{\text{NO}}$  in the effluent of the two AAO systems. The average concentration of  $S_{\text{NH}}$  in the influent was  $29.05 \pm 0.21$  mg/L during the experimental period.

Before the prolongation of sludge age, average  $S_{\text{NH}}$  and  $S_{\text{NO}}$  concentrations in the effluent of the two AAO systems were  $23.71 \pm 2.89$  and  $2.91 \pm 0.10$  mg/L, respectively. As shown in Fig. 2, the average  $S_{\text{NH}}$  concentrations in the effluent were  $24.78 \pm 2.09$  and

$24.58 \pm 2.81$  mg/L for the AAO systems with  $\theta_c$  of 19.6 and 12.0 d, respectively; the corresponding  $S_{\text{NO}}$  concentrations were  $2.06 \pm 1.36$  and  $2.03 \pm 1.42$  mg/L. Results of analysis of variance demonstrated that no significant improvements of nitrification efficiency were observed after prolonging  $\theta_c$  to 19.6 ( $p = 0.165$ ) and 12.0 d ( $p = 0.357$ ), and no significant differences of  $S_{\text{NH}}$  ( $p = 0.723$ ) and  $S_{\text{NO}}$  ( $p = 0.928$ ) concentrations in the effluent were observed between the two parallel AAO systems with different  $\theta_c$  values. It was probably because sludge ages of the two AAO systems were still lower than the  $\theta_{\text{mc}}$  for nitrification, and the nitrification kinetics should be investigated to determine the value of  $\theta_{\text{mc}}$ .

### 3.3. Decay kinetics of nitrifying biomass

Decrease in the nitrification activity of the Bailonggang WWTP at  $20^\circ\text{C}$  under aerobic, anoxic,

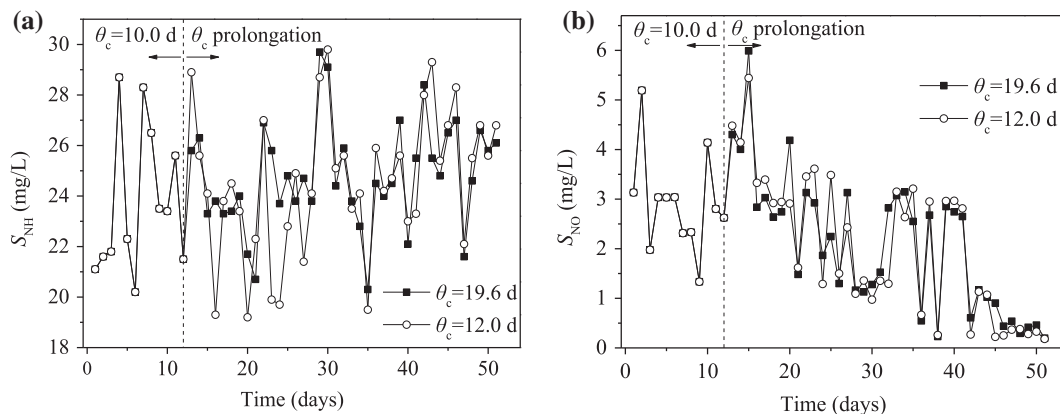


Fig. 2. Variations of  $S_{\text{NH}}$  (a) and  $S_{\text{NO}}$  (b) in the effluent of two parallel AAO systems in the Bailonggang WWTP ( $10.6 \pm 1.8^\circ\text{C}$ ).



and anaerobic conditions is illustrated in Fig. 3. The AUR values were reduced to 62.2, 55.5, and 34.2% of the initial value after 6 d under aerobic, anoxic, and anaerobic conditions, respectively. The  $b_{AUT}$  of the three WWTPs measured in quadruplicate are given in Table 2. As reported in literatures [10,11], the aerobic  $b_{AUT}$  had the highest value, while in the anaerobic condition the lowest  $b_{AUT}$  was observed.

The average aerobic  $b_{AUT}$  of the Bailonggang, Quyang, and Zhuyuan WWTP were 0.175, 0.176, and 0.176  $d^{-1}$ , respectively (Table 2). The measured data of the three WWTPs are very close and correspond to the literature data in the range of 0.15–0.21  $d^{-1}$  [8,10–13,15,16]. The  $\eta_N$  of the Bailonggang, Quyang, and Zhuyuan WWTP were 0.52, 0.53, and 0.55, respectively. This relates well to the trends reported by Siegrist et al. [10], Martinage and Paul [14], Lee and Oleszkiewicz [13], and Salm et al. [11] who found  $\eta_N$  were 0.48, 0.50, 0.63, and 0.50, respectively. The  $\eta_A$  of the Bailonggang, Quyang, and Zhuyuan WWTP were 0.44, 0.44, and 0.43, respectively. The results is higher than the reported values in the range of 0.12–0.30 [10,11]. Nevertheless, the average anaerobic  $b_{AUT}$  values of this study were compared with reported values (0.06–0.10  $d^{-1}$ ) by Salm et al. [11].

### 3.4. Growth kinetics of nitrifying biomass

In the batch test for  $\mu_{AUT}$  determination, only the net specific growth rate could be calculated by nonlinear curve fitting [2]. With the measured values and Arrhenius coefficient of aerobic  $b_{AUT}$ , the  $\mu_{AUT}$  at different temperatures could be obtained. The relationship between the measured  $\mu_{AUT}$  values and

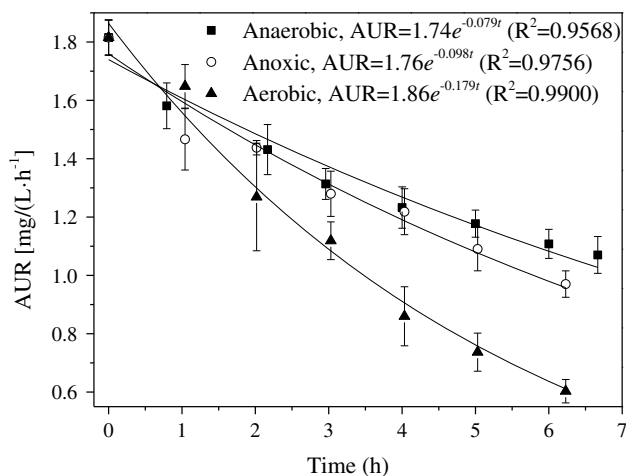


Fig. 3.  $b_{AUT}$  of the Bailonggang WWTP under aerobic, anoxic, and anaerobic conditions (20°C).

Table 2

Measured  $b_{AUT}$  values (with standard errors) at 20°C for the three WWTPs

WWTP	$b_{AUT}$ ( $d^{-1}$ )		
	Aerobic	Anoxic	Anaerobic
Bailonggang	0.175 ± 0.002	0.092 ± 0.005	0.077 ± 0.003
Quyang	0.176 ± 0.006	0.093 ± 0.002	0.078 ± 0.004
Zhuyuan	0.176 ± 0.008	0.097 ± 0.006	0.076 ± 0.002

temperature of the Bailonggang and Quyang WWTP are illustrated in Fig. 4(a). The comparison in details of  $\mu_{AUT,20}$ , Arrhenius coefficients and activation energies reported in different studies is listed in Table 3.

As shown in Table 3,  $\mu_{AUT,20}$  of the Bailonggang WWTP is significantly lower than the Quyang WWTP and other systems for municipal WWTPs, demonstrating the lower activity of  $X_{AUT}$  in the Bailonggang WWTP. ( $n = 6$ ). Sulfide in Bailonggang WWTP ( $13.95 \pm 2.40$  mg/L) was significantly higher than that in Quyang WWTP ( $3.56 \pm 1.86$  mg/L). As reported in our previous studies, the nitrification activity of activated sludge was reduced by 75.9% after un-aerated exposure to 6.2 mg/L sulfide for 0.5 h [2]; therefore, low value of  $\mu_{AUT,20}$  of the Bailonggang WWTP was probably attributed to the inhibitory effects of sulfide or other toxic compounds. The relatively lower  $\mu_{AUT,20}$  of the Zhuyuan WWTP, which is also fed by long-pipeline transported wastewater, could validate the deduction to a certain extent. Compared to the  $b_{AUT}$  value, the  $\mu_{AUT}$  in each WWTP were significantly different (Table 3) and more sensitive to the toxic compounds. This is because metals such as copper and iron, the cofactor of ammonium monooxygenase in nitrifying biomass that related to ammonium oxidation, are easily to be bound with toxic substances [18,19]. The temperature correction factor of the Bailonggang WWTP was higher than the Quyang WWTP, which indicates that AUR in the Bailonggang WWTP was influenced by temperature more sensitively. The temperature correction factor of the Bailonggang WWTP is significantly higher than the published data, which were normally quoted in the range of 1.05–1.12 [8,9,23–25]. Nevertheless, a higher  $\theta$  value of 1.17 was also observed by Guo et al. [23] at a lower temperature interval (5–20°C).

The activation energy of  $\mu_{AUT}$  can be determined graphically by taking the natural logarithm of Arrhenius equation, as shown in Fig. 4(b). The activation energy of  $\mu_{AUT}$  in the Bailonggang WWTP (10–25°C) was about 1.8 times of the Quyang WWTP, and also higher than the reported values [23,26].

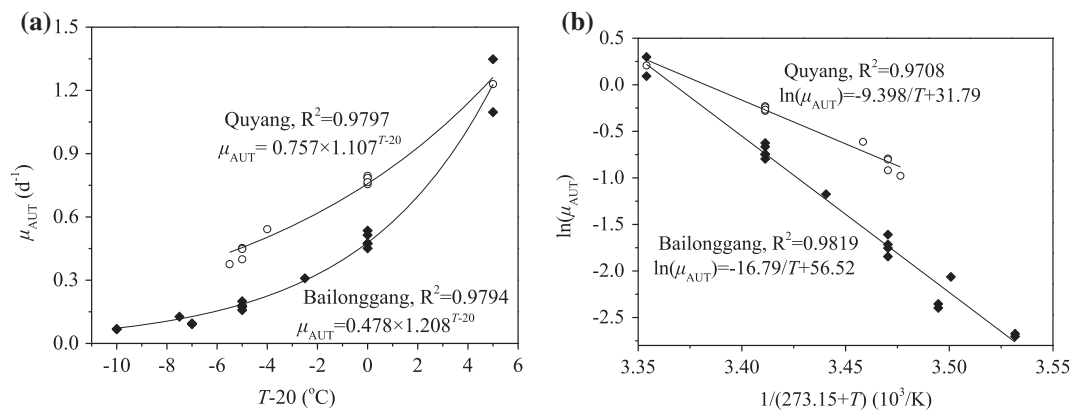


Fig. 4. Effects of temperature on  $\mu_{AUT}$  of the Quyang (a) and Bailonggang (b) WWTP.

Table 3

Comparison of Arrhenius coefficients,  $\mu_{AUT,20}$  and activation energies in activated sludge process reported in literatures and in this study

Source and process	T (°C)	$\theta$	$\mu_{AUT,20}$ (d <sup>-1</sup> )	$E_a$ (kJ/mol)	Reference
AAO, Bailonggang WWTP	10–25	1.208	0.48	139.6	This study
AAO, Quyang WWTP	14–25	1.107	0.76	78.1	
AO, Zhuyuan WWTP	20	–	0.65	–	
ASM	15–25	1.105	0.80	73.4	[8]
Kanapaha WWTP	15–25	1.120	0.73	80.3	[9]
Istanbul domestic wastewater	15–20	1.098	0.58	–	[27]
Activated sludge, leather industry	20–35	1.045	0.17	–	[25]
US EPA	10–30	1.103	0.74	–	[28]
Lab-scale sequencing batch reactor	5–20	1.172	–	111.5	[23]
	20–35	1.062	–	42.0	
Membrane bioreactor	10–20	–	–	87.1	[26]
	20–30	–	–	38.6	

The higher activation energy indicates the lower catalytic activity of  $X_{AUT}$  in the Bailonggang WWTP, which might be owing to the binding of sulfide from the influent and such metals as copper and iron [2], which are cofactor of ammonium monooxygenase in  $X_{AUT}$  [18,19].

### 3.5. Analysis of minimum sludge age for nitrification

The limit of  $S_{NH}$  concentration (8 mg/L) in Class B Grade A level of Chinese Discharge Standard of Pollutants for Municipal WWTP was adopted for the calculation of  $\theta_{mc}$ . The measured kinetic parameters of the Bailonggang WWTP were employed for the calculation, and the equivalent HRT for  $X_{AUT}$  decay was 9.97 h according to Eq. (6). The recommended Arrhenius coefficient of  $b_{AUT}$  (1.105) by ASM [8] is used here. Therefore, the  $\theta_{mc}$  for the Bailonggang WWTP was calculated as Eq. (12).

$$1/\theta_{mc} = 0.48 \times 1.208^{t-20} \times 8/9 - 9.97/8.25 \times 0.175 \times 1.105^{t-20} \quad (12)$$

The  $\theta_{mc}$  based on recommended kinetic parameters by ASM [8] can also be obtained according to Eq. (10). Besides  $\theta_{mc}$ ,  $R_g$  and  $R_d$  values were calculated from Eq. (12). Influences of temperature on  $\theta_{mc}$ ,  $R_g$ ,  $R_d$ , are shown in Fig. 5.

Variations of the calculated  $R_g$  and  $R_d$  values of the Bailonggang WWTP with temperature are illustrated in Fig. 5(a). Compared to the curve simulated by recommended parameters of ASM in Fig. 5(b), the  $R_g$  curve falls faster, and there is an intersection point between  $R_g$  and  $R_d$  curves in Fig. 5(a). At this point,  $1/\theta_{mc}$  is equal to 0, and the solution of Eq. (12) is 12.1°C. It is concluded that 12.1°C is a critical temperature for the growth and decay rates of  $X_{AUT}$  in the

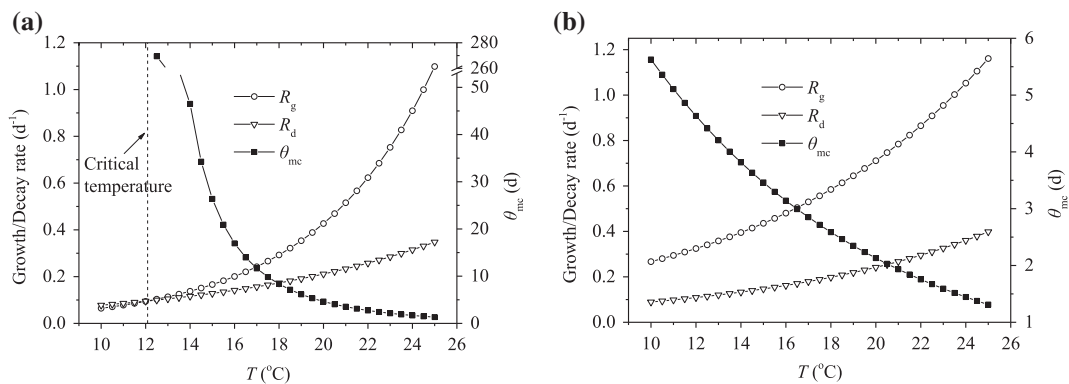


Fig. 5. Calculated growth and decay rate of nitrifying biomass, and  $\theta_{mc}$  at different temperatures based on parameters of the Bailonggang WWTP (a) and ASM (b).

AAO system. When  $T < 12.1^\circ\text{C}$ , the decay rate will exceed growth rate, and  $X_{AUT}$  will be washed out even  $\theta_c$  approaches infinity.

Fig. 5 also demonstrates the relationship of  $\theta_{mc}$  and temperature in the AAO process. At  $15^\circ\text{C}$ , the  $\theta_{mc}$  calculated by parameters measured in the Bailonggang WWTP and recommended by ASM are 26.4 and 3.5 d, respectively. Unfortunately, in the Bailonggang WWTP, the  $\theta_{mc}$  value reaches 269.4 d at  $12.5^\circ\text{C}$ , and negative  $\theta_{mc}$  occurs at temperature below  $12.1^\circ\text{C}$ . Therefore, the efficiency of  $S_{NH}$  removal was not improved by  $\theta_c$  prolonged from 10.0 to 19.6 d at  $10.6^\circ\text{C}$  in Fig. 2. It is concluded that prolonging sludge age was not an effective measure in this case, and the negative  $\theta_{mc}$  suggested that external  $X_{AUT}$  should be supplemented to the AAO system to maintain stable nitrification efficiency [6].

#### 4. Conclusions

$S_{NH}$  and TN in the effluent of a full-scale AAO WWTP were fluctuated seasonally, and low nitrification efficiency lasted from December to June. Prolonging aerobic sludge age from 10.0 to 19.6 d at  $10.6 \pm 1.8^\circ\text{C}$  had insignificant effect on the improvement of nitrification. The measured  $b_{AUT}$  values of the WWTP were 0.175, 0.092, and  $0.077\text{ d}^{-1}$  under aerobic, anoxic, and anaerobic conditions, respectively. A low  $\mu_{AUT,20}$  at  $20^\circ\text{C}$  ( $0.48\text{ d}^{-1}$ ) and high temperature correction factor (1.208) were obtained in the temperature range of  $10\text{--}25^\circ\text{C}$ . According to the calculation of mathematical model, at temperature below  $12.1^\circ\text{C}$ , the decay rate of  $X_{AUT}$  exceeded growth rate, and the extreme high ( $12.1\text{--}15^\circ\text{C}$ ) or negative ( $<12.1^\circ\text{C}$ )  $\theta_{mc}$  indicated that prolonging sludge age was probably malfunctioned at cold temperature.

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