

Effective partial nitrification and denitrification via nitrite with inhibitor removal basin for high strength ammonium wastewater treatment

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Abstract—A system consisting of an air stripping unit, an inhibitor removal basin, an aerobic basin, and an anoxic basin was investigated for nitrogen removal from coal gasification plant stripped gas liquor containing high-strength organic, nitrogenous compounds. Nitrite oxidation, followed by the reduction of nitrite to nitrogen gas, was adopted for nitrogen removal. The free ammonia concentration in the coal gasification plant stripped gas liquor was obtained by modified empirical method. The optimum reaction temperature, pH, and ammonia-N concentration in the feeding solutions for the ammonia oxidation to nitrite were 30 °C, pH 8.0, and less than 200 mg/L, respectively. Over 98% of the organic compounds in the wastewater, including phenol, O-cresol, m-cresol, quinoline, and benzene, were removed using the nitrogen removal system by incorporating an inhibitor removal basin. An inhibitor removal basin accelerates ammonia oxidation rate and enhances settleability. This system provides a much faster nitrogen removal rate and less consumption of external carbon sources when compared to conventional nitrogen removal system combined with nitrification and denitrification.

Keywords: Free Ammonia, Nitrification, Denitrification, Nitrogen Removal, Inhibitor Removal Basin, Coal Gasification Wastewater

INTRODUCTION

Nitrogen removal has received increasing attention because of its adverse effects on humans and animals. Since the 1970s, the trend for nitrogen removal has been overwhelmingly in favor of biological processes. There have only been a few instances in which physical/chemical processes such as ion exchange, ammonia stripping, and breakpoint chlorination were implemented. The biological process for nitrogen removal typically employs a basic design coupling the oxidation of ammonia to nitrate and then the reduction of nitrate to nitrogen gas.

Baker et al. [1] reported that ammonium ions and nitrite could have adverse effect on *Nitrobacter* growth. Many researchers [2-4] have also reported that the toxicity to *Nitrobacter* could be caused by pH as well as ammonia concentration. In many cases, nitrite accumulation was observed in biological nitrogen removal systems and considered to be a transitory phenomenon. The accumulation of nitrite in wastewater negatively effects *Nitrobacter* growth and often occurs in high strength ammonium wastewater [5-8].

We attempted to control nitrogenous compounds in coal gasification plant stripped gas liquor through the oxidation of ammonia to nitrite (nitrification) and then the reduction of nitrite to nitrogen gas (denitrification). Several advantages [9-12] for this approach include (1) Minimizes oxygen demand for the ammonia oxidation, resulting in low operating cost; (2) Minimizes reaction time due to rapid ammonia oxidation and reduction to nitrogen gas,

resulting in smaller reactor volume; (3) Reduces the amount of carbon requested for the anoxic process because of shorter reaction pathways; and (4) Reduces toxic effects of nitrite on the *Nitrobacter* growth.

When compared with general wastewater, stripped gas liquor contains various materials that are important factors regarding the removal of nitrogen compounds such as high-strength nitrogen compounds, a variety of toxic materials, and organic materials. Therefore, treatment of the stripped gas liquor is very difficult [1, 13]. The objective of this study is reforming nitrogen removal processes under different operating conditions including optimized nitrogen removal systems for nitrification and denitrification. The results of this study should contribute to the enhancement of conventional biological nitrogen removal systems.

MATERIALS AND METHODS

In the experiment, a system consisting of an air stripping unit, an inhibitor removal basin, an aerobic basin, and an anoxic basin was used to treat the stripped gas liquor product of coal gasification plants. Fig. 1 depicts the experimental setup for nitrogen removal. The air stripping unit had a working volume of 3.2 L, while that of the inhibitor removal basin was 16 L. The aerobic basin, with an effective volume of 48 L, was divided into three chambers. The effective volume of the anoxic basin was 36 L. Feeding solution, which is the ammonia still effluent, was obtained from the coal gasification process waste stream of an iron making company. Feeding rate was kept constant at 20 ml/min with a peristaltic pump. Seed sludge was obtained from return activated sludge of an activated sludge treatment facility.

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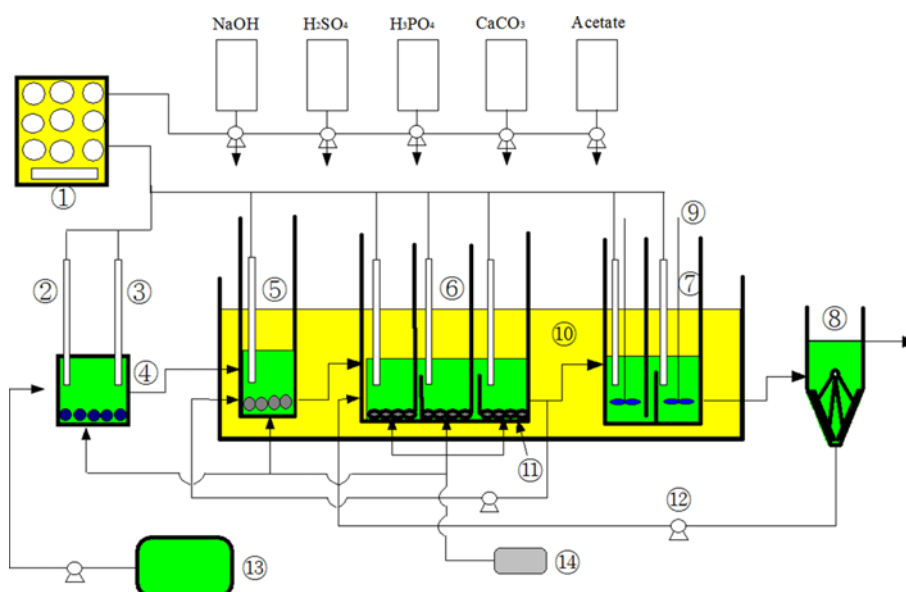


Fig. 1. Schematic diagram of the nitrogen removal system.

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|---------------------------|---------------------------|----------------|-------------------|
| ① Control panel | ⑤ Inhibitor removal basin | ⑨ Agitator | ⑬ Water reservoir |
| ② pH sensor | ⑥ Aerobic basin | ⑩ Water bath | ⑭ Air compressor |
| ③ Temp. sensor | ⑦ Anoxic basin | ⑪ Diffusor | |
| ④ Air stripping apparatus | ⑧ Clarifier | ⑫ Recycle pump | |

The influent of the inhibitor removal basin was a mixture of air stripping unit effluent and part of the effluent from the aerobic basin. The effluent recycle ratio was 300%. The return sludge ratio was 100%. Heaters kept the reaction temperature at $30 \pm 2^\circ\text{C}$. Feeding solution pH was adjusted to 8 ± 1 with 1 w/w% H_2SO_4 or 1 w/w% NaOH . Dissolved oxygen (DO) in the aerobic reaction tank was maintained at 3 mg/l. H_3PO_4 was added to keep BOD/P ratio at 100:1 for the bioreactor influent. The mixed liquor suspended solid (MLSS) was maintained at approximately 2,500 mg/L. Nitrite-type nitrification was defined as $([\text{NO}_2^--\text{N}]_{\text{out}} - [\text{NO}_2^--\text{N}]_{\text{in}})/\text{HRT} [\text{VSS}]$, where, HRT, VSS are the hydraulic retention time, the biomass concentration, respectively.

Coke gasification wastewater composition is listed in Table 1. T-N, $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations were analyzed by colorimetric methods using a C-Max Qvis5000H UV/VIS spectrophotometer, the chromotropic acid method (low range 3.0-25.0 mg/L), the Nessler method (high range 0.2-25.0 mg/L), the ferrous sulfate method (high range 2-250 mg/L), and the cadmium reaction method (high range 0.3-30.0 mg/L), respectively (C-Max CO., Ltd., 2012). The pH and DO were measured immediately after sam-

ple withdrawal using a dissolved oxygen meter (YSI 550A) and a pH meter (Denver Instrument, UB-10). All chemical analyses were performed in accordance with standard methods [14]. The chemical oxygen demand (COD) measurement was based on the potassium dichromate-ferrous ammonium sulfate method. Biomass concentrations were determined as MLSS. The COD measurement was severely affected by the high concentration of nitrite and SCN in the effluent. Therefore, COD and T-N were only monitored periodically.

RESULTS AND DISCUSSION

1. Characteristics of the Coke Gasification Wastewater

COD, phenol, fixed $\text{NH}_3\text{-N}$ and temperature of the wastewater from the ammonia still were 1,805 mg/l, 369 mg/l, 598 mg/l and 87°C , respectively. This stream was fed into the activated sludge process after adjusting its temperature. The concentration of COD and phenol in the effluent from the activated sludge process was 75 and 0.1 mg/l, respectively. For the nitrogenous compounds, ammonia concentration in the activated sludge influent and effluent

Table 1. Characteristics of coal gasification wastewater

(unit: mg/l)

Composition	pH	T ($^\circ\text{C}$)	COD	Phenol	$\text{NH}_3\text{-N}$		$\text{NO}_2\text{-N}$	$\text{NO}_3\text{-N}$	SCN	CN
					Fixed	Free				
Raw wastewater	9.28	35	3396	594	1284	6427	ND ^a	ND	295	33.5
Ammonia still effluent	7.09	87	1805	369	598	36	ND	ND	257	4.9
Activated sludge process effluent	7.78	30	75	0.1	506	Tr ^b	2.4	0.21	3.4	1.2

^aND: not detected

^bTr: trace

was 506 and 598 mg/l, respectively. This indicates that the activated sludge system could remove the organics but not the nitrogenous compounds. It has been known that organics such as phenol, cyanide, and sulfur containing compounds in the wastewater inhibit microbial activities in the activated sludge process and reduce ammonia oxidation activities [7,13].

2. Free Ammonia Concentration as a Function of pH and Temperature

When ammonia-nitrogen in wastewater is high, free ammonia concentration increases with the increase of pH and temperature. Free ammonia concentration is obtained by the analytical method or empirical formula suggested by Anthonisen et al. [2] shown in Eq. (1).

$$\text{Free Ammonia (FA)} = \text{NH}_3 \text{ (mg/l)} \\ = \frac{17}{14} \times \frac{(\text{Total Ammonia as N}) \times 10^{pH}}{\frac{K_b}{K_a} + 10^{pH}} \quad (1)$$

where, K_b =ionization constant of the ammonia equilibrium equation
 K_w =ionization constant of water

The value of ionization constant, K_w , depends on the temperature, and K_b and K_w can be expressed as in Eq. (2):

$$\frac{K_b}{K_a} = e^{\left[\frac{6344}{273 + ^\circ\text{C}} \right]} \quad (2)$$

Experimental and empirical values from Anthonisen are summarized in Table 2. Empirical values are very close to the experimental values when pH is above 8; however, there were significant differences when pH values are less than 8. This likely occurs because other nitrogenous compounds such as thiocyanides and cyanide seriously affect free ammonia formation at low pH. This is because free ammonia concentration remains low due to decrease of ionization constant of the ammonia equilibrium equation under low pH. When pH is relatively high, free ammonia concentration is increased in wastewater. In this case, cyanide or thiocyanide should not significantly affect the formation of free ammonia.

To predict free ammonia concentration in the wastewater with high nitrogenous compound concentration and different nitroge-

nous compounds, a modified empirical equation was developed. Fig. 2 shows experimental values and predicted values from Eq. (3). In most cases, experimental values are well fitted with the modified empirical values.

$$\text{FA} = \text{NH}_3 \text{ (mg/l)} \\ = \frac{17}{14} \times \frac{(\text{Total Ammonia as N}) \times 10^{(0.77\text{pH}+1.92)}}{\frac{K_b}{K_a} + 10^{(0.77\text{pH}+1.92)}} \quad (3)$$

Therefore, Eq. (3) may be used to predict FA in coke gasification plant stripped gas liquor. Fig. 2 shows the change in FA concentration with respect to pH and $\text{NH}_4\text{-N}$ concentrations.

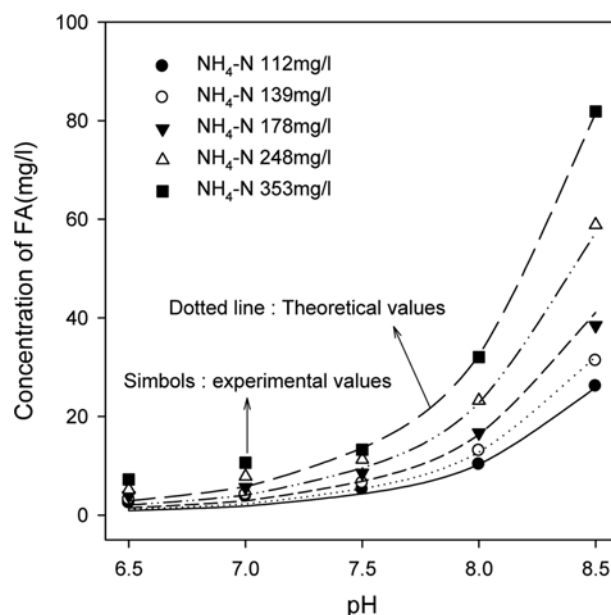


Fig. 2. Change in FA concentration with respect to pH and $\text{NH}_4\text{-N}$ concentrations.

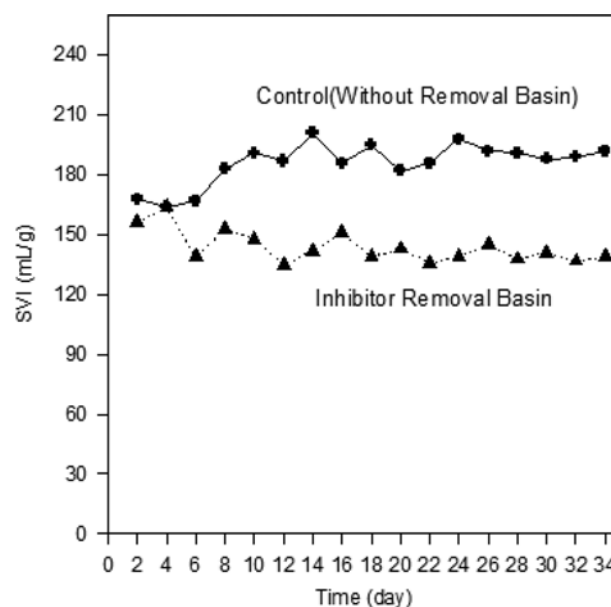


Fig. 3. Effect of inhibitor removal Basin on SVI.

Table 2. Free ammonia concentration as a function of pH and total ammonia concentration at 30 °C

$\text{NH}_4\text{-N}$ (mg/l)	pH	6.5	7.0	7.5	8.0	8.5
112	Exp.	2.51	3.83	5.21	10.30	26.17
	Theo.	0.35	1.09	3.38	10.16	27.66
139	Exp.	3.15	4.16	6.48	13.05	31.32
	Theo.	0.43	1.35	4.33	12.61	34.32
178	Exp.	3.96	5.62	8.53	16.72	38.46
	Theo.	0.55	1.73	5.38	16.14	43.96
248	Exp.	5.14	7.82	11.25	23.24	58.86
	Theo.	0.77	2.42	7.50	22.49	61.24
353	Exp.	7.23	10.62	13.23	32.07	81.87
	Theo.	1.09	3.40	10.58	31.74	86.43

All values, except pH, are given in mg/l

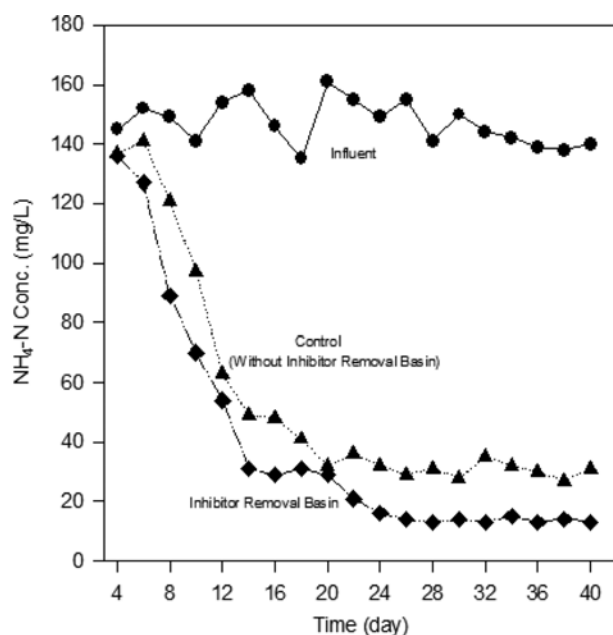


Fig. 4. Effect of inhibitor removal basin on nitrogen removal efficiency.

3. Removal of Organic Carbon in an Inhibitor Removal Basin

Organic carbon in wastewater streams could inhibit nitrogenous compound removal and hinder sludge settling in a secondary clarifier. In this experiment, an inhibitor removal basin was installed to avoid inhibition of organic carbon to ammonia oxidation and to improve sludge sedimentation.

As shown in Fig. 3, sludge volume index (SVI) was 167–201 mg/L without the inhibitor removal basin and 132–156 mg/L with the inhibitor removal basin. This indicates that the inhibitor removal basin can improve sludge sedimentation.

Ammonia oxidation with and without an inhibitor removal basin was also monitored (Fig. 4). The oxidation of ammonia with an inhibitor removal basin was 12% faster than without it, leaving 13–28 mg/L of ammonia in the effluent, when 148–168 mg/L of ammonia was initially fed into the reaction tank. The organic carbon in the feeding solution was analyzed for phenol, cresol, quinoline, benzene, and other compounds (Table 3).

Organic carbon concentration in the effluent of the inhibitor removal basin was also analyzed. The removal efficiency of organic carbons after the inhibitor removal basin was more than 98% for organics such as phenol, cresol, quinoline, and benzene, and 85% for 1,1-biphenyl. The faster oxidation of ammonia in aerobic reaction tank in Fig. 4 is caused by the removal of the organics in the inhibitor removal basin. Abeling and Seyfried Gross [9] reported that over 15 mg/L of cresol or 5.6 mg/L phenol in aqueous solution could seriously inhibit the nitrification process.

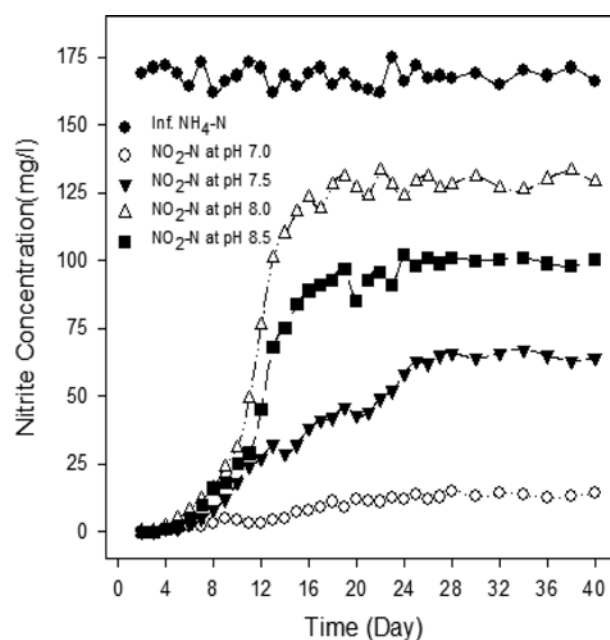


Fig. 5. Effect of pH on nitrite nitrification rate.

4. Oxidation of Ammonia to Nitrite (Nitrification)

The optimum conditions for the oxidation of ammonia to nitrite were investigated by feeding about 600 mg/L of ammonia. The ammonia stripping process pretreated feeding solution. Stripping reduced the concentration of ammonia by stripping about 200 mg/L from the process. Temperature and pH for the stripping process were $70 \pm 2^\circ\text{C}$, and 10.5, respectively [13]. The effluent from the stripping process was fed into the nitrogen removal system. To investigate the effect of pH on nitrite accumulation, feeding solution pH was adjusted between 7.0 and 8.5 with increments of 0.5.

The result of nitrite formation at various pHs was derived from continuous operations in the whole system and is shown in Fig. 5. Nitrite formation in the aerobic reaction tank was initiated after five days, but the concentration did not exceed 20 mg/L after 30 days operation at pH 7.0. Nitrite formation was a little higher at pH 7.5 than at pH 7.0, resulting in about 50 mg/L after 30 days. At pH 8.0, the formation of nitrite in the effluent was about 130 mg/L. When pH was kept at 8.5, the concentration of nitrite in the effluent was lower than at pH 8.0. This result indicates that free ammonia is dominant at pH 8.5 in aqueous solution and is toxic to the *Nitrosomonas*.

When pH is increased, the NH_3 portion of the feeding solution is increased and has adverse effects on *Nitrobacter* activities, resulting in lower transformation of nitrite to nitrate. The lower transformation of nitrite to nitrate at pH 8.5 than at pH 8.0 should be the effect of nitrite accumulation in the aerobic reaction tank. Accumulation of nitrite in the solution is also toxic to *Nitrobacter*,

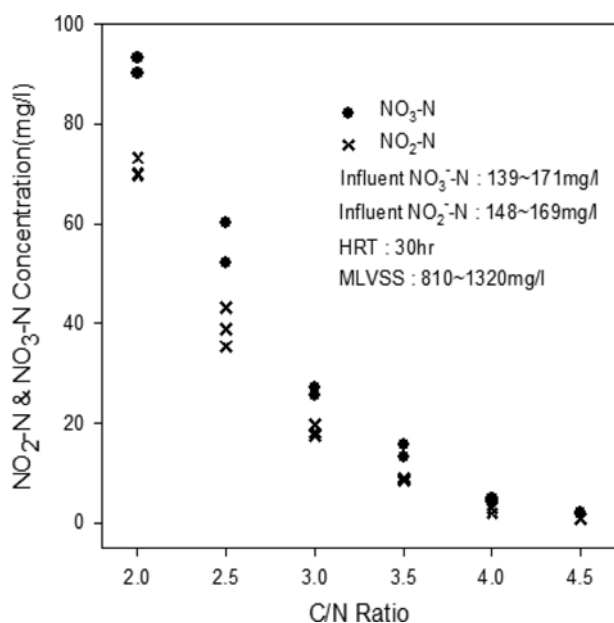
Table 3. Concentration of organic carbons in influent and effluent of the inhibitor removal basin

(unit: mg/L)

Organics	Phenol	O-cresol	M-resol	Quinoline	Benzene	1,1-Biphenyl
Influent	384	30.1	48.2	16.3	15.8	19.6
Effluent	0.18	0.54	0.69	Tr	Tr	2.89

Table 4. Concentration of nitrite to COD (unit: mg/L)

NO ₂ -N	5	10	15	20
COD _{cr}	5.81	11.85	17.10	23.47

**Fig. 6. Effect of influent COD to NO₂-N ratio on the removal of nitrite and nitrate.**

resulting in lower transformation of nitrite to nitrate. This result is consistent with previous reports [1,2].

5. Reduction of Nitrite to Nitrogen (Denitrification)

The formation of nitrite in the effluent of the aerobic basin inhibits the *Nitrobacter* activities and also increases COD concentration. The nitrite contribution to COD is listed in Table 4. Theoretical contribution of nitrite to COD is 1.17 mg/NO₂⁻-N and the experimental contribution was 1.14 mg/mg NO₂⁻-N. Since the organics are removed in the inhibitor removal basin, the addition of a carbon source (in this case, acetate) was required for the reduction of nitrite to nitrogen gas [15]. Nitrite and nitrate reduction experiments were conducted to compare transformation rates in each case. The results are shown in Fig. 6.

When COD to NO₂⁻-N ratio was kept at 2.5, the concentration of nitrite in the effluent was less than 50 mg/L. To keep the concentration of nitrite below 10 mg/L, the ratio should be increased to 3.5. Nitrate reduction requires 17% more carbon source than nitrite reduction.

CONCLUSIONS

Ammonia oxidation to nitrite followed by nitrite reduction to nitrogen gas was conducted for nitrogen removal from coal gasification plants stripped gas liquor containing high strength organic, nitrogenous compounds. Based on the results, the following con-

clusions are appropriate:

a. Free ammonia concentration in coke gasification plant stripped gas liquor may be predicted by the modified empirical equation.

$$FA = NH_3 \text{ (mg/l)} = \frac{17}{14} \times \frac{(\text{Total Ammonia as N}) \times 10^{(0.77pH+1.92)}}{\frac{K_b}{K_a} + 10^{(0.77pH+1.92)}}$$

b. The addition of an inhibitor removal basin to the treatment facility can improve the transformation of ammonia and sludge sedimentation by removing organic carbons in raw wastewater.

c. Transformation of about 200mg/L of ammonia to nitrite was completed at pH 8.0, leaving 138 mg NO₂⁻-N and 5.17 mg NO₃⁻-N after 18 days operation.

d. The reduction of nitrite to nitrogen gas in an aerobic basin requires the addition of 17% less acetate. When COD to NO₂⁻-N ratio was kept at 3.5, the concentration of nitrite in the effluent was less than 10 mg/L.

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