Nitrogen balance and transformation in the nitrification process of coking wastewater and the influence on nitrification kinetics

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ABSTRACT

This paper describes the total nitrogen balance, and the direction and degree of nitrogen transformation during the nitrification process of coking wastewater. According to the actual nitrification process, the conventional nitrification kinetic equation was amended. After 48 h of nitrification, the total nitrogen content remained almost the same with error less than 0.6%. The total removal efficiency of NH$_4^+$-N was 91.1%, in which blow-off, producing cells and transforming to nitrate nitrogen accounted for 1.1, 17.8 and 72.2% respectively. Considering the influences of NH$_4^+$-N blow-off and conversion from cyanide, thiocyanide and organic nitrogen, the nitrification kinetic equation was amended as $\mu' = 0.82 \cdot S/(0.48 + S)$.

Key words | nitrification, nitrification kinetics, nitrogen balance, nitrogen transformation

INTRODUCTION

Coking wastewater is generated in the coal coking, coal gas purification and by-product recovery processes in coking factories. Its composition is complicated and varies depending on the quality of raw coal, carbonation temperature and method for by-product recovery. The high ammonium loading and low C/N ratio of coking wastewater make the treatment a big problem both at home and abroad (Maranon et al. 2008; Zhu & Ni 2008; Wang et al. 2012). In recent years, with the frequent occurrence of eutrophication events, nitrogen removal from coking wastewater has received more and more attention. In China, from the ‘Emission standard of pollutants for coking chemical industry’ (GB 16171-2012), emission limits for NH$_4^+$-N, total nitrogen (TN) and CN$^-\, $ were 15, 30 and 0.2 mg/L respectively. In America, there is no uniform standard for nitrogen emissions. The National Pollutant Discharge Elimination System puts forward different emission limits for different polluters. For example, TN emission limits of 3 or 5 mg/L were applied to many polluters. In Australia, some local emission standards showed the probability of TN < 5 mg/L was at least 90%, and meanwhile the probability of TN < 3 mg/L was at least 50%.

The nitrification/denitrification process has been widely used for nitrogen removal. The process consists of two parts: autotrophic nitrification and subsequent heterotrophic denitrification. Ammonium is firstly oxidized to nitrate over nitrite with molecular oxygen as the electron acceptor in aerobic condition. Formed nitrate and nitrite are then reduced to nitrogen gas with hydrogen or organic compounds as electron donors in anoxic condition (Paredes et al. 2007; Van Hulle et al. 2010; Landes et al. 2013). The nitrogenous substances in coking wastewater include organic matter, ammonia, nitrate, nitrite, cyanide, thiocyanate and so on. With the aid of ammonifying and nitrifying bacteria, some nitrogenous substances could be converted to ammonia, and then nitrite and nitrate (Vazquez et al. 2006; Kim et al. 2008; Bai et al. 2011). The rate and degree of nitrification play a vital role on the overall efficiency of nitrogen removal.

Until now, there has been no systematic study about nitrogen balance and transformation in the nitrification process of coking wastewater. This paper studied the total nitrogen balance, and direction and degree of nitrogen transformation during the nitrification process of coking wastewater. The key substances and steps that affect nitrification were found out, which were of great significance in promoting nitrogen removal of coking wastewater. On the basis of the actual nitrification process, the conventional nitrification kinetic equation was amended.

doi: 10.2166/wst.2014.054
MATERIALS AND METHODS

The nitrification process was carried out in a 16 L cylindrical bioreactor made of plexiglass (Figure 1). Air was aerated continuously from the bottom of the bioreactor. Dissolved oxygen (DO) level was maintained at 2.0–2.5 mg/L by adjusting the flow-rate of supplied air. Effluent gas from the top of the bioreactor flowed through three bottles of 2% boric acid solution, which was used for absorbing the escaped ammonia. The bioreactor was operated at room temperature (20–30°C). The initial pH and alkalinity in the bioreactor were 7.3 and 424.6 mg/L. In the process of system operation, NaHCO₃ was added into the bioreactor with dosage of 0.5 g/L to compensate for the alkalinity lost due to nitrification, and the pH value was kept in the range of 7.0–8.0.

The influent fed into the bioreactor was coking wastewater that had previously been subjected to several pretreatment units. To start up the bioreactor, sludge from a coking wastewater treatment plant was introduced to the system. The mixed liquid suspended solids (MLSS) were around 5 g/L. The start-up period was divided into three phases. In the first phase, a mixture of raw wastewater and tap water with a ratio of 1:2 was added; and then 1:1 in the second phase; in the third phase, raw wastewater was directly used as influent. Each phase lasted about 10 days. After the start-up period, the test period proceeded.

Samples were taken regularly. All samples were a mixture from the three sampling ports. The NH₄⁻N, NO₂⁻N, NO₃⁻N, CN⁻N, SCN⁻N, organic nitrogen, total nitrogen in water, total nitrogen in sludge, mixed liquid volatile suspended solids (MLVSS) and the absorbed NH₄⁻N by boric acid were measured. NH₄⁻N, NO₂⁻N and NO₃⁻N concentrations were determined by spectrophotometric method with Nessler’s reagent, N-(1-naphthyl)-ethylenediamine and phenol disulfonic acid respectively. Cyanide was measured byisonicotinic acid-pyrazolone spectrophotometry. Thiocyanate was analyzed spectrophotometrically using its reaction with ferric nitrate. Organic nitrogen was the difference between Kjeldahl nitrogen and NH₄⁻N, while mixed liquid suspended solid Kjeldahl nitrogen was determined by distillation-Nessler’s reagent spectrophotometry. Total nitrogen was measured by alkaline potassium persulfate digestion UV spectrophotometric method. The NH₄⁺-N absorbed by boric acid was analyzed by Nessler’s reagent spectrophotometry. MLSS analysis was performed by drying at 103–105°C in an evaporating dish, and then MLVSS were determined by roasting the MLSS at 600°C in a muffle. Alkalinity was measured by titration with hydrochloric acid. pH was measured using a BPH-200A pH meter. DO was measured by an Orion Star A213 DO meter.

RESULTS AND DISCUSSION

Nitrogen balance in the nitrification reactor

Nitrogen existed in different forms in the nitrification reactor. The concentration of each form changed as the reaction proceeded. Table 1 gives the concentrations of each nitrogen form in the original solution and after 24 and 48 h reaction.

During calculation, subscript 1 denotes the total nitrogen content that was determined by the sum of the concentrations of different nitrogen forms, while subscript 2 denotes total nitrogen content that was determined by direct measurement. The two methods for determining the total nitrogen content were compared.

Total nitrogen content at the start of nitrification:

\[ N_1 = (72.7 + 37.1 + 73.6 + 0.1 + 6.1 + 16.3) \times 10.64 \times 10^{-3} + 4.08 = 6.27 \text{ g} \]

\[ N_2 = 210 \times 10.64 \times 10^{-3} + 4.08 = 6.31 \text{ g} \]

Total nitrogen content at 48 h of nitrification:

\[ N'_1 = (4.7 + 31.7 + 158.8 + 1.9) \times 10.02 \times 10^{-3} + 4.26 = 6.23 \text{ g} \]

\[ N'_2 = 202.5 \times 10.02 \times 10^{-3} + 4.26 = 6.29 \text{ g} \]


Errors of total nitrogen balance:

\[ \Delta N_1/N_1 = \frac{(6.27 - 6.23) \times 100}{6.27} = 0.6\% \]

\[ \Delta N_2/N_2 = \frac{(6.31 - 6.29) \times 100}{6.31} = 0.3\% \]

Therefore, in the process of nitrification, whether separate or direct measurement, the total nitrogen content in the nitrification reactor remained almost the same; the error was less than 0.6%.

**Nitrogen transformation in the nitrification reactor**

In the nitrification reactor, microorganisms run series of nitrogen transformations between different forms, see Figure 2.

Cyanide and thiocyanide were oxidized to bicarbonate and ammonium:

\[ \text{CN}^- + 0.5\text{O}_2 \rightarrow \text{CNO}^- \]

\[ \text{SCN}^- + \text{H}_2\text{O} \rightarrow \text{CNO}^- + \text{HS}^- + \text{H}^+ \]

\[ \text{CNO}^- + \text{H}^+ + 2\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{NH}_4^+ \]

Organic nitrogen compounds were decomposed into ammonia by ammonifying bacteria, take amino acid for example:

\[ \text{RCHNH}_2\text{COOH} + \text{O}_2 \rightarrow \text{RCOOH} + \text{CO}_2 + \text{NH}_3 \]

Some of the ammonia was converted with \( C_\alpha \text{H}_\beta \text{O}_\gamma \) to nutrients for microorganisms, promoting the sludge growth:

\[ C_\alpha \text{H}_\beta \text{O}_\gamma + \text{NH}_3 + \text{O}_2 \rightarrow C_5\text{H}_7\text{NO}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

Some of the ammonia was converted to nitrite and nitrate by nitrifying bacteria in aerobic condition:

\[ 2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 4\text{H}^+ + 2\text{H}_2\text{O} \]

\[ 2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^- \]

In addition, part of the free ammonia escaped with aeration and was absorbed by 2% boric acid solution.

The weight of nitrogen in different forms is listed in Table 2.

According to the above reaction equations, cyanide, thiocyanide and organic nitrogen could be converted to ammonia with equal molar concentration. Therefore, the initial weight of \( \text{NH}_4^+\)-N was calculated as follows:

\[ 773.5 + 1.5 + 64.7 + 173.4 = 1013.1 \text{ mg} \]

After 48 h of nitrification, the conditions of \( \text{NH}_4^+\)-N transformation were as listed below and shown in Figure 3:

The percentage of \( \text{NH}_4^+\)-N for producing cells: \( 180/1013.1 \times 100\% = 17.8\% \).

The percentage of \( \text{NH}_4^+\)-N for transforming to nitrate nitrogen: \( (808.1 - 77.1)/1013.1 \times 100\% = 72.2\% \).

The percentage of untransformed organic nitrogen: \( 19.1/1013.1 \times 100\% = 1.9\% \).

The percentage of untransformed \( \text{NH}_4^+\)-N: \( 47.1/1013.1 \times 100\% = 4.6\% \).

**Table 1** | Nitrogen content of different forms in the nitrification reactor

| Time (h) | V (L) | pH | \( \text{NH}_4^+\)-N (mg/L) | \( \text{NO}_2^-\)-N (mg/L) | \( \text{NO}_3^-\)-N (mg/L) | \( \text{CN}^-\)-N (mg/L) | \( \text{SCN}^-\)-N (mg/L) | Organic nitrogen (mg/L) | TN in water (mg/L) | TN in sludge (g) | MLVSS (g/L) | Absorbed \( \text{NH}_4^+\)-N (mg) |
|---------|------|----|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------|----------------|----------------|--------------|------------------|
| 0       | 10.64| 7.3| 72.7                     | 73.6                     | 0.1                      | 6.1                      | 16.3                     | 210.0                    | 4.08                | 3.83            | 0             |                  |
| 24      | 10.64| 7.2| 39.7                     | 124.0                    | -                        | -                        | 5.2                      | 209.8                    | 3.85                | 10.4            | 10.4          |                  |
| 48      | 10.02| 7.5| 4.7                      | 158.8                    | -                        | -                        | 1.9                      | 202.5                    | 4.26                | 4.18            | 10.6          |                  |

**Figure 2** | Schematic of nitrogen transformation in the nitrification process. (1) Oxidation, (2) ammonification, (3) blow-off, (4) production of cells, (5) nitrosification, (6) nitrification.
The percentage of blow-off NH$_4^+$-N: 10.6/1013.1 × 100% = 1.1%.
The total percentage of NH$_4^+$-N transformation: 17.8% + 72.2% + 1.9% + 4.6% + 1.1% = 97.6%.
Error: 100%−97.6% = 2.4%.
The total removal efficiency of NH$_4^+$-N: 17.8% + 72.2% + 1.1% = 91.1%.

Amendment of nitrification kinetics based on the actual nitrification process

The direction and degree of nitrogen transformation between different forms during the nitrification process of coking wastewater were studied. The nitrification rate was represented by the decrease of NH$_4^+$-N concentration. The Monod equation was used to describe the nitrification kinetic equation:

$$\mu = \mu_{\text{max}} \frac{S}{(K_S + S)}.$$ 

In this equation: $\mu$ is the specific degradation rate of NH$_4^+$-N (h$^{-1}$); $\mu_{\text{max}}$ is the maximum specific degradation rate of NH$_4^+$-N (h$^{-1}$); $S$ is the NH$_4^+$-N concentration (mg/L); $K_S$ is saturation constant (mg/L), also known as the NH$_4^+$-N concentration when $\mu$ equaled $\mu_{\text{max}}/2$.

Suppose the specific degradation rate $\mu = V/X$. $V = -dS/dt$ is the NH$_4^+$-N degradation rate (mg/(L·h)). During the experiment, NH$_4^+$-N concentration (S, mg/L) was measured once an hour, and then the $S$ against $t$ curve was plotted (Figure 4), whose slope indicates the NH$_4^+$-N degradation rate. $X$ is the MLVSS (mg/L); the MLVSS changed little and could be regarded as constant; the value was 3.95 g/L (average of 3.83, 3.85 and 4.18 g/L).

![Figure 4](image-url)

The reciprocal of the above equation is $X/V = K_S/(\mu_{\text{max}} \cdot S) + 1/\mu_{\text{max}}$. Based on the experimental results, the $X/V$ against $1/S$ curve was plotted and is shown in Figure 5. From Figure 5, $1/\mu_{\text{max}} = 1.36, K_S/\mu_{\text{max}} = 0.72$, $\mu_{\text{max}} = 0.74, K_S = 0.53$. So the nitrification kinetic equation was: $\mu = 0.74 \cdot S/(0.55 + S)$.

However, as previously mentioned, part of NH$_4^+$-N escaped from the solution without nitrification; the cyanide, thiocyanide and organic nitrogen in coking wastewater were converted to ammonia, which was equivalent to increasing the initial NH$_4^+$-N concentration. Both the blow-off and increased NH$_4^+$-N are not considered in the conventional nitrification kinetic equation (Machon et al. 2007; He et al. 2009; Liu et al. 2012). Then, the conventional nitrification kinetic equation would be amended so as to more accurately reflect the actual nitrification process.

<table>
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<th>Time (h)</th>
<th>NH$_2$-N (mg)</th>
<th>NO$_2$-N (mg)</th>
<th>NO$_3$-N (mg)</th>
<th>CN -N (mg)</th>
<th>SCN -N (mg)</th>
<th>Organic nitrogen (mg)</th>
<th>TN in sludge (mg)</th>
<th>Absorbed NH$_2$-N (mg)</th>
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<tr>
<td>0</td>
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<td>783.1</td>
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<td>173.4</td>
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<td>0</td>
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<td>0</td>
<td>19.1</td>
<td>4,260</td>
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<td>-77.1</td>
<td>808.1</td>
<td>-1.5</td>
<td>-64.7</td>
<td>-154.3</td>
<td>180</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 2 | Nitrogen weight of different forms in the nitrification reactor
The blow-off NH$_4^+$-N accounted for 1.4% of the apparently removed NH$_4^+$-N; meanwhile, the NH$_4^+$-N converted from cyanide, thiocyanate and organic nitrogen accounted for 30.4%. Therefore, the nitrification rate could be amended as:

$$V' = (1 - 1.4\% + 30.4\%)V = 1.29V$$

The $X/V$ against $1/S$ curve was plotted (figure not shown), then $\mu'_{\max}$ and $K_S'$ were obtained as 0.82 and 0.48. The nitrification kinetic equation was amended as

$$\mu' = 0.82 \cdot S/(0.48 + S).$$

**CONCLUSION**

The total nitrogen balance, and direction and degree of nitrogen transformation were studied during the nitrification process of coking wastewater. After 48 h of nitrification, the total nitrogen content remained almost the same, with error less than 0.6%. Microorganisms run series of nitrogen transformations between different forms. Cyanide, thiocyanate and organic nitrogen could be converted to ammonia with equal molar concentration. The removal of NH$_4^+$-N included producing cells (17.8%), converting to nitrate (72.2%) and escaping with aeration (1.1%). The sum of 91.1% was the total removal efficiency of NH$_4^+$-N. Considering the NH$_4^+$-N blow-off and conversion from cyanide, thiocyanate and organic nitrogen, the nitrification kinetic equation was amended as

$$\mu' = 0.82 \cdot S/(0.48 + S).$$

**REFERENCES**


