Modeling ammonia-nitrogen degradation in a polluted stream with biofilm technique

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Abstract:
The reduction of ammonia-nitrogen fluxes from polluted streams entering the Tai Lake is an important task in areas with limnetic eutrophication. Biofilm technique for the polluted streams has been proposed as one effective method to reduce ammonia-nitrogen fluxes entering the Tai Lake. In this study, ammonia-nitrogen biodegradation in a created biofilm purification engineering was evaluated by a dynamic model of ammonia-nitrogen in a polluted stream (Linzhuanggang) in western Tai Lake of China. The ammonia-nitrogen biodegradation model was described with Monod dynamic equation and hydraulic characteristic of the stream, and modified and evaluated by analyzing biodegradation effect in different periods and at different environmental conditions. Due to temperature dependence and seasonal variation in the stream, decrease in ammonia-nitrogen concentration mainly occurred during summer periods, which affected biodegradation effect of ammonia-nitrogen to some degree. The model showed that the purification engineering reduced the nitrogen transport to the Tai Lake with approximately 5%–40% in the test period.

Keywords: ammonia-nitrogen; model; bionic filler; layout

INTRODUCTION
The Tai Lake of China is suffering from eutrophication, which is mainly or partly caused by increased ammonia-nitrogen (NH₃+NH₄⁺) load. At the western Tai Lake, there are many polluted streams entering the Tai Lake, which are main sources for pollutants of the Tai Lake. In recent decades, there have been many researches on pollutants fluxes from polluted streams to the Tai Lake which elucidated that the values of the chemical oxygen demand (COD), the total phosphorus (TP) and the total nitrogen (TN) had exceeded 90% of the gross load in the Tai Lake (Zheng et al., 2001). Numerous restoration techniques have been developed for polluted streams over the last decade, and restoration of influent streams affects the input of sediment, solutes (including nutrients and contaminants), and water into the lake (Committee on restoration of aquatic ecosystems et al., 1992). But some methods are only suitable for good water quality, for example, restoration of submerge vegetation. So improvement of water quality is an important premise for aquatic ecosystem restoration of polluted streams. And biofilm technique for polluted streams has been proposed as one important method to reduce ammonia-nitrogen fluxes entering lakes. So this study regards ammonia-nitrogen as the index to investigate the model of ammonia-nitrogen biodegradation with biofilm technique.
MATERIALS AND METHODS

Bionic fillers
A new-type bionic filler was designed by imitating *Chara foetida* in streams (Fig. 1). *Chara foetida*, one submerged plant with beautiful appearance, is a common alga in natural streams, and grows in still or slow-flow water bodies. Its existence is an important foundation of hydrobios diversity. On the one hand, it offers abundant foodstuff for aquatic organism directly or indirectly, on the other hand, it offers good living and reproduction places for aquatic organism. A lot of bacteria and protozoa glue on the stems and leaves of *Chara foetida*. In addition, its graceful branches and leaves are unfolded in the streams- and the flexible tough stems can flow and swing with the streams back and forth, which brings weak resistance to the water flow. During designing the filler the flexibility and toughness of the stem and the adhesion of the branch and leaf of *Chara foetida* was emphasized. It was developed with beanpole imitating the stem, central buckle imitating the burl, filler silk imitating the leaf of *Chara foetida*. In this test the diameter of filler slice was 150 millimeter (mm), the interval of slice was 80 mm, and the diameter of beanpole was 4mm.

![Diagram of bionic filler](image)

The test stream
The test stream was chosen by considering the density of residential areas along banks, the serious pollution of the stream, concrete banks and few aquatic plants etc.. The test stream lied at Linzhuanggang stream of Dapu town in Yixing city is a typical stream entering the Tai Lake (Fig.2). Its water was classified bad of water environment quality level in the earth's surface of China (GB 3838-2002). The same as other small streams that influence the water quality of the Tai Lake directly, so it was regarded as the test stream in this research, in which the test section length was 120 meter (m), the water face width was 8.6m, and the water depth was 0.7~1.5m, the shape of streambed and bank was unanimous basically in total test stream because of clearing silt and bank slope construction of the "863" project. Its water flows 20 centimeters per second (cm•s⁻¹) or less, the chemical oxygen demand (CODₘₜₙ) ranged from 3 to 12 milligrams per liter (mg•L⁻¹), the total nitrogen (TN) ranged from 2 to 7 mg•L⁻¹, the total phosphorus (TP) ranged from 0.05 to 1.2 mg•L⁻¹, the left bank gradient was 1:1.75, and the right bank was the vertical bank constructed with stone.
Layout of the bionic fillers in the test stream
The test stream section was divided into two parts in the research, the anterior section was the contrast section about 60m long (without fillers) used to examine the natural degradation ability of the test stream for pollutants, the latter was the fillers section with 60m long, its total degradation ability was the sum of the natural degradation and the biofilm degradation on the fillers of the section. The layout of fillers was: the middle part leaved 2.6m wide ‘snakelike channel’, the fillers were decorated on both sides of the snakelike channel (Fig. 3). Assignation interval was $40\text{cm} \times 40\text{cm}$, namely the density of the bionic packing was 9 stems per square meter (stems*$\text{m}^{-2}$). Fillers were different in height to be assigned according to the riverbed form and relative water level: the highest was 1.0m, the lowest was only 0.4m.

Sampling and measuring
(1). Sampling and measuring way: three times a month;
(2). Sampling sections and points: 3 sampling sections were set up in relative 0m (inlet of the contrast section), 60m (outlet of the contrast section, inlet of the fillers section), 120m (outlet of the fillers section) of the test section; 2 sampling points (the distance of sampling points from surface were 30cm and 60cm) were set up on each sampling section;
(3). The analyzed and measured projects included NH$_3$+NH$_4^+$, TN, NO$_3$+2-N, the microorganism’s microscope examining, total amount of bacteria, nitrobacteria counting, alga differentiating and counting, DO, velocity of flow, water level, temperature and pH.

MODELING AMMONIA-NITROGEN BIODEGRADATION
Ammonia-nitrogen degradation in a created biofilm purification system
Monitoring data from the test section created for ammonia-nitrogen biodegradation showed the
concentration of ammonia-nitrogen entering the test section was very low during experimental periods. Except in November and December, the concentrations of the other months was better than II of water environment quality level in the earth's surface of China (GB 3838-2002), which influenced the biodegradation effect of ammonia-nitrogen to some degree. The biodegradation rate was lower than 40% in experimental periods (Fig 4).

![Fig.4 Degradation rate of ammonia-nitrogen in the test section](image)

**Explanation before modeling ammonia-nitrogen degradation**

Assuming conditions

a. The test section was assumed for the ideal section, its shape was uniform and width was very homogeneous. b. It was assumed that there was not any pollutant flowed from two sides of the test section. c. Biofilm adhered to the filler silks was in balancing growth state whenever it was at normal water level and low water level. d. There were no toxic materials existing in the test section.

Flow situation of the test section

Streams are characterized by a one-way flow of water, which tends to transport nutrients, sediments, pollutants, and organisms downstream. And they are open. They can attain oxygen across the boundary between water and air. So flow situation of streams can be regarded as good oxygen and pushed-flow basically.

Transporting course and effect of ammonia-nitrogen in biofilm reacting district

The degradation course of ammonia-nitrogen in biofilm can be divided into four stages:

- Ammonia-nitrogen diffuses to biofilm surface;
- Ammonia-nitrogen spread within biofilm
- Ammonia-nitrogen is oxidized under microorganism's function
- The metabolic product is discharged from the biofilm

Transporting course of ammonia-nitrogen among them can be regarded simply as two: First, the ammonia nitrogen spread from liquid to liquid layer of the biofilm surface; Second, the ammonia nitrogen is oxidized in liquid layer, and continue spreading to the inner biofilm, as Fig. 5 shows.

The transporting course of ammonia-nitrogen impacts importantly on its oxidized speed, it is expressed with $\xi$, where: $\xi$, a total efficiency factor, and its value lies between 0 and 1. The value is bigger when transporting resistance of ammonia-nitrogen is small and transporting speed is large, inversely the value is smaller. $\xi$ is relevant with such factors as water quality, characteristics of the biofilm, water flow, temperature, pH, etc. mainly (Tang Lii-hua et al, 1995).
Basic dynamic model for ammonia-nitrogen degradation

While utilizing the biofilm technique to deal with the sanitary sewage, the degradation reaction takes place on biofilm’s surface basically because active matters making up biofilm concentrate mostly on biofilm’s surface, therefore the whole biofilm reaction tends towards the mechanism of surface reaction. While utilizing the technique to deal with polluted streams, the formed biofilm is relatively thin because the concentration of pollutants is relatively low in streams. Thus the biofilm is totally in good oxygen state, this is favorable for the growth and reproduction of nitrifying bacteria, and the whole biofilm activation is strengthened, therefore the whole biofilm tends towards the mechanism of surface reaction too. So in the study the nitrifying speed expressed with the degradation amount of ammonia-nitrogen on biofilm’s unit surface area.

The test section in this study was viewed as completely mixed bioreactor (Wang, 1997), where the effect of ammonia-nitrogen transporting course on the biological reaction was leaved out. So the degradation of ammonia-nitrogen over such a reactor is described by:

\[ v'_s = -\frac{v_{\max} C_b}{k'_s + C_b} \]

where \( v'_s \), degradation speed of ammonia-nitrogen (mg m\(^{-2}\) d\(^{-1}\)); \( k'_s \), the greatest ratio degradation speed of ammonia-nitrogen; \( C_b \), concentration of ammonia-nitrogen fitting for biodegradation in water body (mg L\(^{-1}\)); \( k'_s \), semi-saturation constant.

Because the concentration of ammonia-nitrogen is low in the polluted stream, namely, seldom exceeds 2mg L\(^{-1}\), which is very small comparing with \( k'_s \). At the same time considering the effect of ammonia-nitrogen transporting course on the biological reaction, then Eq. (1) can be changed into:

\[ v'_s = -\frac{v_{\max}}{k'_s} \cdot \xi \cdot C_b \]  

Modeling the biodegradation of ammonia-nitrogen in the test section

As Fig. 6 showed, the total length and volume of the fillers section was expressed with L and V. The orientation from upstream to downstream along water axis was regarded as x axis’s positive. Cutting out a small section perpendicular to water axis, its dimensions of section were \( A(x,t) \) and \( A(x + \Delta x, t) \) respectively. The surface area on the filler of unit's length was \( a_c \); the concentration of ammonia-nitrogen fitting for biodegradation in inlet, midst and outlet of the fillers section were expressed with \( C_0 \), \( C_b \) and \( C_e \). The flow was Q and the velocity of flow was \( u_o \). The degradation of ammonia nitrogen because of stream self-purification function was assumed to distribute averagely in every section, and accomplish with nitrifying bacteria, then the balanced equation of ammonia-nitrogen in \( \Delta x \) section was:
\[
Q \cdot \frac{\Delta x}{u_s} \cdot (C_h \mid_{x+\Delta x} - C_h \mid_x) (1 - \frac{\Delta x}{L} q) = v'_s \cdot a_s \cdot \frac{\Delta x}{u_s} \cdot \Delta x
\]  
(3)

where \(\frac{\Delta x}{L} q\) tended towards 0 because \(\Delta x\) was less than \(L\) greatly, thereby the following expression was used instead of Eq. (3):

\[
v'_s = \frac{Q}{a_s} \frac{dC_h}{dx}
\]  
(4)

Combination of Eq. (2) and Eq. (4), and integration between start and end conditions, yielded integral equation:

\[
- \frac{v'_{max}}{k'_s} \cdot \xi \cdot \frac{a_s}{Q} \int dx = \frac{dC_h}{C_h} \quad \left\{ \begin{array}{l}
\text{when } x = 0, \quad C_h = C_0 \\
\text{when } x = L, \quad C_h = C_e
\end{array} \right.
\]  
(5)

Through integral transform Eq. (5) was described by:

\[
C_e = C_0 e^{-K' \frac{a_s L}{A u_s}}
\]  
(6)

The final expression was:

\[
C_e = C_0 e^{-K' \frac{a_s L}{A u_s}}
\]  
(7)

where \(K' = \frac{\xi v'_{max}}{k'_s} \), the total degradation coefficient which generalized the transporting course of ammonia-nitrogen and reaction characteristics in biofilm.

The degradation rate, \(\eta\), could be received by Eq. (7):

\[
\eta = \frac{C_0 - C_e}{C_0} \times 100\% = (1 - e^{-K' \frac{a_s L}{A u_s}}) \times 100\%
\]  
(8)

**CALIBRATION AND CONFIRMATION OF MODELS**

**Influence of stream ecosystem self-cleansing function on models**

The stream was able to cleanse a portion of ammonia-nitrogen through natural processes, so Eq. (7) and Eq. (8) included the degradation not only from biofilm adhering to fillers, but also from streambed and shore. And this study discussed mainly the degradation ability of biofilm adhering to fillers, thus Eq. (7) and Eq. (8) needed to be revised. The natural degradation rate of the stream was assumed as \(q\) (specific value was received by measuring in the contrast section). Finally, the models was described by:

\[
C_e = (1 - q)C_0 e^{-K' \frac{a_s L}{A u_s}} \quad \text{and} \quad \eta = [1 - (1 - q)e^{-K' \frac{a_s L}{A u_s}}] \times 100\%
\]  
(9, 10)

**Models confirmation with actual measuring data of velocity**

In test of 6 months, because factitious factors and natural conditions acted on the stream collectively, the velocity of flow was zero in some months except July, September and December.
And environmental conditions in July and September were favorable to the growth and reproduction of nitrifying bacteria. So the analyzed data were from July and September only, which helped to analyze the influence discipline of the average velocity of flow on biodegradation of ammonia-nitrogen. The velocity of flow in July and September was distributed among 2~4 cm s\(^{-1}\), was not big and belonged to flow-slow water body, accorded with the suitable velocity for stream direct purification. Data measured and derived from models were showed in Fig.7. From it, it was seen that the relation between the degradation rate of ammonia-nitrogen and velocity of flow corresponded with actual measured results basically, the increase of degradation rate accompanied by decrease of velocity of flow.

![Fig.7 Relation of biodegradation rate of ammonia nitrogen to speed of water flow](image)

**Water temperature**

Influence of water temperature on nitrifying velocity was not showed directly in models, but it had important influence in \( K' \), the total degradation coefficient, thus influenced the accuracy of models (Xiao Yu-tang et al, 2002). As Fig.8 showed, except for August and October (the stream being in static state resulted in exception of degradation rate), the rest appeared certain variation tendency with the change of the water temperature. According to proposition of Hultman in 1971, the greatest ratio growth velocity of nitrifying bacteria in the models, namely \(-v'_{\text{max}}\), the semi-saturation constant, \( k'_s \), and water temperature had relation as following:

\[
-v'_{\text{max}} = ( -v'_{\text{max}} )_{20^\circ C} \times 10^{0.033(T-20)} \quad (\text{d}^{-1})
\]

\[
k'_s = 10^{0.0517-1.158} \quad (\text{mg nitrogen L}^{-1})
\]

where \(( -v'_{\text{max}} )_{20^\circ C}\), \(( -v'_{\text{max}} )_{20^\circ C}\), the most ratio degradation velocity when water temperature are T and 20\(^{\circ}\), \text{d}^{-1}.

Combination of Eq. (11) and Eq. (12), finally, the temperature dependence of the total degradation coefficient was described by:

\[
K' = K'_0 \times 10^{(0.36-0.018T)}
\]

where \( K'_0 \),the total degradation coefficient when water temperature is 20.

**pH**

In nitrifying function, pH has a great influence on the growth and reproduction of nitrifying bacteria in the stream, especially subnitrifying bacteria. For subnitrifying bacteria, there is an optimal pH to make them reach the greatest ratio growth speed. Under the optimal pH the nitrifying speed can reach the maximum. The optimal pH is generally around 8.0~8.4. When pH is not in this range, the nitrifying speed will reduce. The greatest ratio growth speed of nitrifying
bacteria when pH is not the optimal, namely the greatest ratio degradation speed of ammonia-nitrogen, and the greatest ratio degradation speed when pH is the optimal have relation as following:

$$(-v'_\text{max}) = (-v'_\text{max})_{\text{pH}^*} \left[1 + 0.04[10^{(\text{pH}^* - \text{pH})} - 1]\right]$$

(14)

where pH*, the optimal pH.

According to $K' = \frac{\xi v'_\text{max}}{K'_1}$ and Eq. (14), the relationship between $K'$ and pH was described by:

$$K' = K'_1 \left/[0.96 + 10^{(6.8 - \text{pH})}\right]$$

(15)

where $K'_1$, $K'$ when pH is 8.2.

**Dissolved oxygen**

During nitrifying Oxygen (O$_2$) is electronic receptor, so its concentration will certainly influence nitrifying speed. In 1969, Nagel and Haworth found while the concentration of dissolved oxygen (DO) exceeded 1mg/L, with DO concentration increasing the oxidizing speed of the ammonia-nitrogen also increased correspondingly. Equally, research of Wild et al.(1971) indicated too, when the concentration of DO was greater than 1mg/L, there was not harmful effect on nitrifying. In the test, the concentration of DO was showed in Tab.1, it was greater than 2mg/L of other all months except for October 25 during testing. Considering the reason that it was low in October was mainly the test stream being in static state and the outburst of alga etc., so the influence of on nitrifying was not considered in the models.

**Tab.1 The relation between the concentration of DO and degradation rate**

<table>
<thead>
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<th>date</th>
<th>7.25</th>
<th>7.26</th>
<th>7.27</th>
<th>8.25</th>
<th>8.26</th>
<th>8.27</th>
<th>9.25</th>
<th>9.26</th>
<th>9.27</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO, mg/L</td>
<td>3.5</td>
<td>3.7</td>
<td>3.6</td>
<td>3.7</td>
<td>3.5</td>
<td>3.3</td>
<td>3.0</td>
<td>2.9</td>
<td>3.1</td>
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<tr>
<th>date</th>
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<th>10.25</th>
<th>10.26</th>
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<th>11.14</th>
<th>12.04</th>
<th>12.05</th>
<th>12.06</th>
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</thead>
<tbody>
<tr>
<td>DO, mg/L</td>
<td>2.6</td>
<td>1.5</td>
<td>2.3</td>
<td>3.2</td>
<td>4.1</td>
<td>4.3</td>
<td>6.5</td>
<td>4.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Biodegradation rate, %</td>
<td>4.66</td>
<td>0.39</td>
<td>4.33</td>
<td>5.91</td>
<td>4.76</td>
<td>6.04</td>
<td>3.93</td>
<td>2.79</td>
<td>-5.17</td>
</tr>
</tbody>
</table>

**Organic pollutants**

The biodegradation of the ammonia-nitrogen depends mainly on the oxidation of nitrifying bacteria, a kind of autotrophic bacteria, whose growth and reproduction are not limited by the organic pollutants, so in the nitrifying of ammonia-nitrogen, the concentration of organic pollutants should not be too high, in general, the value of BOD$_3$ should be less than 20mg/L. If the value of BOD$_3$ is high, heterotrophic bacteria will grow and reproduce rapidly, which will
limit nitrifying bacteria to take advantage, as a result, the nitrifying speed will be reduced. The concentration of organic pollutants was far smaller than this value in this research, it did not influence the biodegradation of ammonia-nitrogen, so it was not considered in the models. Synthesizing the analysis of the above influence factors, the biodegradation models of ammonia-nitrogen were described as follows:

\[
\begin{align*}
C_e &= (1 - q)C_0e^{-\frac{K}{a_L} \frac{a_L}{a_L} - \frac{a_L}{a_L}} \\
\eta &= [1 - (1 - q)e^{-\frac{K}{a_L} \frac{a_L}{a_L}}] \times 100\% \\
K' &= K_0 \times 10^{(0.36 - 0.018T)} /[0.96 + 10^{(6.8 - pH)}]
\end{align*}
\]  

(16)

CONCLUSION
The model of ammonia-nitrogen biodegradation in the stream was described with Monod dynamic equation and hydraulic characteristic of the stream, and modified and evaluated by analyzing biodegradation effect in different periods and environmental conditions. Due to temperature dependence and seasonal variation in the stream, decrease in ammonia-nitrogen concentration mainly occurred during summer periods, which affected biodegradation effect of ammonia-nitrogen to some degree. The model showed that the purification engineering in the stream reduced the nitrogen transport to the Tai Lake with approximately 5%~40%.

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