Kinetic of a monium removal by an ammox rocessusing biomass carrier felibendy

Nguyen Thi My Hanh⁽¹⁾, Tran Thi Hien Hoa⁽²⁾

Abstract 1. In

Ammonium removal from domestic wastewater has attracted increasedattention due to the serious water pollution consequences such as eutrophication ofwater bodies. To remove ammonium from septic tank wastewater of the dormitory,the anammox process was conducted in the fixed bed reactor using Felibendy biomass carrier. In the research, three kinetic models including first order, Grau second order, Stover Kincannon model were studied to describe the process kinetics of the ammonium removal in the AX. Stover Kincaanon proved to be the most suitable for simulating ammonium performance in fixed bed reactor using Felibendy.

Key words: Anammox process, kinetic model, domestic wastewater, biomass carrier Felibendy

 Water Enginerring Department, Hanoi Architectural University, DT: 0919776168, Email: hanhpro77@gmail.com,
 Water Supply & Sanitation Division, Hanoi University of Civil Engineering, DT: 0916511818, Email: hoatth@nuce.edu.vn

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1. Introduction

The domestic wastewater containing nitrogen compounds could be toxic to aquatic life, causing depleting dissolved oxygen levels and theeutrophication in receiving water bodies. To remove nitrogen in the domestic wastewater, themost widely technology was theconventional nitrification-denitrification process. But theconventional process was limited by high operational costs and external additionof organic matter for the denitrification step. In contrast, the Anammoxprocess has recently received more attentionin applied research for domestic wastewater treatmentdue to its more advantages compared withthe conventional technology such asno need the addition of external carbon, less sludgeproduction and low energy consumption.

Nitrogen treatment technology by anammox process is a combination of two partial nitrification processes and anammox process. Firstly, partial nitrification processconvertspartially ammonium to nitrite according to equation (1):

$$NH4^{+} + 0,83O_{2} 0,45NH_{4}^{+} + 0,55NO_{2}^{-} + 0,55H_{2}O + 1,1H^{+}$$
(1)

Secondly, anoxic combination of ammonium and nitrite to form dinitrogen gas by anammox process following equation (2):

$$NH_4^+ + 1,32NO_2^- + 0,066HCO_3^- + 0,13H^+$$

 $\rightarrow 1,02N_2 + 0,26NO_3 + 0,066CH_2O_{0,5}N_{0,15} + 2,03H_2O$ (2)

When studying the application of the Anammox process, an important task is to determine the kinetic model describing the treatment process. In 2012, Ni et al. [4] applied 5 types of kinetic models including Monod, Contois, firstorder, Grau secondorder andStover Kincannon for UASB reactor using granular sludge.In the study of Niu et al [5], the total nitrogen removal efficiency of the UASB model was simulated and predicted bysubstrate removal model of StoverKincannon, Monod, firstorder and Grau second order. The study of Abyar et al. [2] also used four kinetic models including firstorder, secondorder Grau, StoverKincannon and Monod models, the Stover - Kincannon model. The above studies showed that three types of kinetic models that are most suitable to describe the kinetics of Anammox process are first-order kinetic model, Grau second-order kinetic model and Stover-Kincannon model. However, the kinetic parameters of these processes are different for different wastewater types, substrate concentrations and operating conditions of each model [1], [6]. Therefore, this study focuses on whether the model is suitable to decribe the performance of Anammox process using Felibendy biomass carrier to remove nitrogen from domestic wastewater.

2. Kinetic approaches

2.1. First order substrate removal model

The change rate of substrate concentration can be illustrated as:

$$-\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{q.s_o}{v} - \frac{q.s_o}{v} - \mathrm{K}_1.S_o \tag{1}$$

Since the (-dS/dt) is negligible under pseudo steady state to the Eq. (1) can be modified as:

$$\frac{Q.S_0}{V} - \frac{Q.S_e}{V} = \frac{S_0 - S_e}{HRT} = K_1 \cdot S_e$$

$$\frac{S_0 - S_e}{HRT \cdot S_e} = K_1$$
(2)
(3)

where S_0 and S_e express the substrate concentration in the influent and effluent, respectively and K_1 is the first order substrate removal rate constant





Figure 1. Schematic diagram of the experiment

Figure 2. Felibendy cubes

(1/day).The value of K1 can be obtained by plotting (S $_0$ -S $_e$)/ HRT) versus S $_e$, that mean K $_1$ can be obtained from the slope of the line.

2.2. Grau second order substrate removal model

The equation of second order kinetic model is expressed as:

$$-\frac{\mathrm{d}S}{\mathrm{d}t} = \mathrm{K}_2.\mathrm{X}.\left(\frac{\mathrm{S}_{e}}{\mathrm{S}_{0}}\right)^2 \tag{4}$$

where So and Se express the substrate concentration in the influent and effluent, X is the average biomass concentration in the reactor (g/L), and K_2 is the second-order substrate removal rate constant (1/d).

By linearization of Eq (4), the following equation can be obtained:

$$\frac{\mathbf{s}_0 + \mathbf{RT}}{\mathbf{s}_0 - \mathbf{s}_0} = \mathbf{HRT} - \frac{\mathbf{s}_0}{\mathbf{k}_2 \cdot \mathbf{X}}$$
(5)

When $(S_0-S_e)/S_0$ express the substrate removal efficiency and is symbolized as E, HRT is the hydraulic retention times (days), E_q (5) can be modified as follows:

$$\frac{\mathbf{H}\mathbf{R}\mathbf{T}}{\mathbf{E}} = \mathbf{a}.\,\mathbf{H}\mathbf{R}\mathbf{T} + \mathbf{b} \tag{6}$$

where $a=S_0/(K_2X)$ and b is a constant. a, b can be obtained by plotting HRT/E versus HRT in Eq.(6).

2.3. Stover Kincannon model

The Stover Kincannon model is used for determining the change rate of substrate concentration at steady state which can be expressed by Eq (7):

$$-\frac{dS}{dt} = \frac{Q.(S_0 - S_0)}{V} = \frac{U_{max}\left(\frac{Q.S_0}{V}\right)}{\kappa_B + \left(\frac{Q.S_0}{V}\right)}$$
(7)

where dS/dt, substrate removal rate (g/L day); S₀ and S_e are the influent and effluent substrate concentration (g/l); V, the reactor volume (L); Q, the flow rate (L/day); U_{max}, the maximum utilization rate constant (g/L day) and K_B is the saturation value constant (g/L day).

If $(dS/dt)^{-1}$ is taken as V/[Q(S₀ – S_e)], which is the inverse of the loading removal rate and achieved Eq. (8):

$$\left(-\frac{dS}{dt}\right)^{-1} = \frac{\kappa_B}{U_{max}} \cdot \frac{HRT}{S_0} + \frac{1}{U_{max}}$$
(8)

The maximum utilization rate constant Umax and the saturation value constant K_B can be obtained by plotting HRT/(S₀-S_e) verus HRT/S₀ in Eq. (8).

3. Materials and methods

3.1. Reactor configuration

The schematic diagram of Anammox reactor (AX) was shown in Fig.1. The AX reactor is plastic cylindrical column which had an inner diameter of 7.1 cm and total height of 41 cm.The AX reactor contains biomass carrier called Felibendy, a product of Kuraray company, has porous structure with resin of EVOH and core of PET (polyethylene terephthalate). In this study, Felibendy cubes with numbers of poreswill support for attached Planctomycetes bacteria

The AXreactor was enclosed with a thermostatateto maintain a constant temperature of 33-35°C, and also was covered with black cloth to avoid growth of phototropic bacteria. Daily purging by nitrogen gas was used to reduce dissolved oxygen (DO) levels in the influent medium to below 0.5 mg/L.

3.2. Domestic wastewater and operationphases

Generally, the raw wastewater from dormitory's septic tankcontains nitrogen compounds, most of which exits in form of ammonium.So, this experiment used synthetic wastewater (simulating domestic wastewater) with ammonium as the main nitrogen component.The wastewater used for the AX reactor is the effluent of the PN reactor, which has nitrite to ammonium ratio of aprociately 1:1.

Withaiming to investigate the nitrogen removal performance of the anammox reactor, the NLR was increased stepwise through raising influent concentrations of ammonium and nitrite or by shortening HRT. So that, the study was conducted in 4 phases: Phase 1 has an HRT of 9 hours and an ammonium/nitrite concentration of 19.5±0.58 mgN/L; Phase 2 and phase 3 had ammonium/nitrite concentration of 39.55±0,64mgN/L and HRT decreased from 9h to 6h. Stage 4 kept HRT at 6h and increased ammonium/ nitrite concentration to 56.55±0,44mgN/L.



Figure 3. First order kinetic model plot



Figure 5. Stover Kincannon kinetic model plot

3.4. Analysis

The influent and effluent samples were analyzed immediately or stored in a refrigerator at 4°C until the analyses were carried out. Measurements of ammonium, nitrite, and nitrate were performed according to the Standard methods. Ammonium and nitrite were measured by using colorimetric method; nitrate was analyzed by using ultraviolet spectrophotometric method. Total nitrogen concentration was determined by the sum of ammonium nitrogen, nitrite nitrogen and nitrate nitrogen concentration. Data based on arithmetic means of three or more measurements obtained at pseudosteadystate were adopted for kinetic study.

4. Results and discussion

From the data analyzed in the experiment such as influent substrate concentration (S₀), effluent substrate concentration (S_e), hydraulic retention time (HRT), reaction model volume (V), inflow rate (Q), process efficiency (E) establishes a correlation relationship between the parameters of the kinetic equation. Using Microsoft Excel software, set up linear equations to describe the kinetic process.

4.1. First order substrate removal model

First-order substrate removal model was applied to the AX reactor at pseudo-steady-state (Fig.3). The value of K₁ was obtained from the slope of the line by plotting $(S_0 - S_e)/$ HRT versus S_e as 14,001d⁻¹ and the determination coefficient (R²) was 0.911.



Figure 4. Second order Grau kinetic model plot

The ammonium concentration in effluent (Se) is predicted from the approximate curve in Fig.3 as follows:

$$S_{e} = \frac{S_{0}}{14.001HRT + 1}$$
(9)

4.2. Grau second order model

The values of a and b in Eq. 6 were calculated to be 1.4498 and 0.0509 from the intercept and slope of the approximate curve shown in Fig. 4. The determination coefficient (R^2) of this model was 0.9925, indicating that Grau second-order substrate removal model was suitable for simulation of nitrogen removal performance in the AX reactor.

The formula for predicting effluent substrate concentration for the ammonx process is given by:

$$S_e = S_0 \left(1 - \frac{HRT}{1.449 BHRT - 0.0509}\right)$$
(10)

4.3. Stover Kincannon model

The Stover Kincannon model plot is shown in Fig. 5. Saturation value constant (K_B) and maximum utilization rate (U_{max}) were determined as 1.241 g/L/d and 1.738 g/L/d, respectively. A plot of the V/Q(S_i-S_e) against (V/QS_i) showed a satisfactory linear correlation ($R^2 = 0.999$).

The ammonium concentration in effluent (Se) is predicted by Stover Kincannon as follows:

$$S_e = S_0 - \frac{1.738}{1.241 + \frac{S_0}{HRT}} \tag{11}$$

4.4. Evaluation of the kinetic model

Three kinetic models were applied to simulate the ammonium removal performance in the fixed bed reactor using Felibendy biomass carrier. The linear regression lines set up with each kinetic model have a coefficient of determination R^2 and summarized in Table 1.

A low R^2 value means a high dispersion of the data, which means that the accuracy of the established equation is not high. Therefore, it is necessary to choose a kinetic model with the highest R^2 coefficient to describe the performance of biological treatment. In this research, the StoverKincannon model has the highest R^2 , that means the Stover-Kincannon model is the most suitable and applicable for predicting the effluent substrate concentration and efficiecncy of process.

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Models	Reactor	NLR (g/L/d)	HRT (d)	Constant		R ²	Ref.
First order				K ₁			
	Fixed bed	0.015-0.226	0.25-0.5	14.001		0.9111	This study
	MBBR	0.43-0.72	0.2-0.3	11.64		0.8043	[4]
	UASB	1.5-12	0.93-7.34	0.458		0.43	[5]
	Column	0.08-1.94	0.25-1.0	7.44		0.756	[3]
Second order Grau				а	b		
	Fixed bed	0.015-0.226	0.25-0.5	0.0509	1.4498	0.992	This study
	MBBR	0.43-0.72	0.2-0.3	1.0287	0.0936	0.998	[4]
	UASB	1.5-12	0.93-7.34	1.13	0.087	0.93	[5]
	Column	0.08-1.94	0.25-1.0	1.136	0.0554	0.991	[3]
Stover Kincannon				U _{max}	K _B		
	Fixed bed	0.015-0.226	0.25-0.5	1.738	1.241	0.999	This study
	MBBR	0.43-0.72	0.2-0.3	12.1	11.4	0.999	[4]
	UASB	1.5-12	0.93-7.34	0.892	1.019	0.94	[5]
	Column	0.08-1.94	0.25-1.0	6.41	7.37	0.993	[3]

Table 1. Comparison of kinetic models applied to anammox process

The results of this study are similarity to the results of several other studies. However, the difference between these kinetic coefficients suggests that the rate of substrate removal is mainly dependent on the nature of the substrate, the reactor structure, the metabolism and the microorganisms in the reactor rather than concentration of that substrate [7].

5. Conclusions

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Biokinetic models such as first-order, Grausecondorder and StoverKincannon models were applied for the anammox process in fixed bed reactor using Felibendy carrier. StoverKincannon model for ammonium removalgave thehighestcorrelation coefficients of 99.9%. Therefore, StoverKincannon model may be used in the design of the anammox process to remove nitrogen in domestic wastewater./.

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