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Kinetics of Nitrogen Removal in an Anammox Up-Flow Anaerobic Bioreactor for Treating Petrochemical Industries Wastewater (Ammonia Plant)

NADALI ALAVI[1,2], ROZA AZADI[1], NEMAT JAAFARZADEH[1,2] and ALI-AKBAR BABAEI[1,2*]

[1]Department of Environmental Health, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[2]Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

*Corresponding author: Fax: +98 611 3738282; Tel: +98 611 3738269; E-mail: ababaei52@gmail.com

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The wastewater of a petrochemical industry was treated in an anammox high rate up-flow anaerobic bioreactor (UABR). The UABR was operated under different nitrogen loading rates (NLRs) 450 mg N/L/d to 2083 mg N/L/d and hydraulic retention time (HRT) from 24 to 6 h, in order to determine the substrate removal kinetics of the reactor. As hydraulic retention time was decreased, ammonium removal efficiency decreased from 93.7 % to 83 %, as well as total nitrogen removal efficiency decreased from 92.4 % to 83.6 %. However, nitrite removal efficiency did not change significantly indicating nitrite was the limiting nutrient. Three kinetic models including first-order, Grau second-order and modified Stover-Kincannon, applied to determine the process kinetics of the nitrogen removal in the UABR. The experimental data showed that the kinetics of nitrogen removal by anammox process followed the Grau second-order and modified Stover-Kincannon models for predicting the performance of UABR for treating the petrochemical industrial wastewater.

Key Words: Anammox, Petrochemical wastewater, Kinetics, Nitrogen removal.

INTRODUCTION

One of the most important problems resulting from the activity of petrochemical industries is high environmental pollution. Discharge of wastewater containing ammonia and its compound into the receiving water resource can be considered as water pollution[1]. Among the nitrogen constituents, the most poisonous compounds are ammonia and nitrite causing problems such as environmental destruction and high treatment expenses[2]. Thus, use of biological processes in nitrogen removal has become common due to its cost-effectiveness compared to physical and chemical treatment processes[3,4]. However, biological nitrogen removal process is rarely applied for wastewater containing high ammonium and low carbon[5]. An external carbon source (glucose, methanol, ethanol, acetate, *etc.*) must be added to the wastewater according to shortage of extra carbon in this type of wastewater for the denitrification process, which causes to increase the operation costs[6]. In recent years, ANAMMOX (anaerobic ammonium oxidation) was discovered as a famous, novel, cost-effective process suitable for wastewater containing NH_4^+ and low carbon source in order for biological nitrogen removal. However, the organic loading rate will affect the anammox process performance[7]. Anammox is an autotrophic process which was first detected in a denitrifying fluidized bed reactor treating effluent of a methanogenic reactor[8]. In this process, the anammox bacteria oxidize ammonia to nitrogen gas in the presence of nitrite as an electron acceptor. This process implemented under anoxic conditions[9]. The process use either dissolved carbon dioxide or bicarbonate for cell biosynthesis. Disadvantage of this process is low biomass yield of anammox bacteria with a doubling time of almost 11 days and susceptive in contrast with conditions of environmental changes[10]. The slow growth rate of anammox bacteria makes it hard to use in practice[11]. Although many researchers have survived the performance of the anammox process for treatment of different wastewaters such as landfill leachate in a continuous reactor[12], animal wastewater treatment[13], anaerobic digester supernatant[14], pig manure effluent in UASB reactor[15], *etc*. No studies have investigated the anaerobic treat ability of real petrochemical wastewater using the anammox process for ammonia removal and also not determined the kinetics of anammox process for petrochemical industries wastewater. However, little attention has been paid to substrate removal kinetics of anammox process[16]; only two studies have investigated on the kinetics of nitrogen removal in an anammox non-woven membrane reactor[17] and in anammox up flow filter[16].

Modeling of process is widely applied to control and evaluate the function of biological processes. Kinetics of process create a postulate theorem in order to predict and simulate the process related to utilization rate and it providing optimized performance the optimize reactor performance.

Therefore, the purpose of this investigation was to research the performance of anammox process for treating petrochemical wastewater and also to evaluate kinetic analysis for the anaerobic up-flow bioreactor capability. Thus, first-order substrate removal model, Stover-kincannon model, Grau second-order substrate removal model are used to study the anammox process kinetics in this research.

Kinetic modeling: Kinetic analysis is an accepted method for evaluating the performance of biological process. The process kinetics study can be used for controlling treatment efficiencies of full-scale reactors with the same operational conditions. Therefore, various mathematical models such as monod, contois, first-order model, Grau second-order[18] and Stover-Kincannon model were used successfully to anaerobic treatment using many different types of reactors[19-21].

As mentioned above, three different substrate removal models, including the first-order substrate removal model, the Grau second-order substrate removal model and the modified stover-kincannon model, were applied to evaluate the nitrogen removal kinetics.

Application of substrate removal kinetics

First-order substrate removal model: The change rate of substrate concentration in the system with assuming the first-order model could be expressed as follows:

$$-\frac{dS}{dt} = \frac{QS_i}{V} - \frac{QS_e}{V} - K_1S_e \quad (1)$$

Under steady-state conditions, the change rate in substrate concentration (-dS/dt) is inconsiderable and the equation can be derived as:

$$\frac{S_i - S_e}{HRT} = K_1S_e \quad (2)$$

The value of K_1 can be derived from the slope of the line by plotting (S_i-S_e)/HRT) *versus* S_e in eqn. 2. (HRT = Hydraulic retention time).

Grau second-order substrate removal model: The general equation of a second-order model used by Grau *et al.*[18], is illustrated as bellow:

$$-\frac{dS}{dt} = K_SX\left(\frac{S_e}{S_i}\right)^2 \quad (3)$$

In eqn. 3 the shape of linear can be expressed as follows:

$$\frac{S_iHRT}{S_i - S_e} = HRT + \frac{S_i}{K_SX} \quad (4)$$

If the second term of the right part of eqn. 4 is accepted as a constant, eqn. 5 can be written as follows:

$$\frac{S_iHRT}{S_i - S_e} = a + bHRT \quad (5)$$

$(S_i-S_e)/S_i$ represents the substrate removal efficiency and is symbolized as E. Therefore, eqn. 6 may be written as:

$$\frac{HRT}{E} = a + bHRT \quad (6)$$

Modified Stover-Kincannon model: The Stover-Kincannon model was initially offered to evaluate the attached-growth biomass function in a rotary biological contactor (RBC) by Stover and Kincannon[22]. Though, this model cannot be used for the biological reactors that do not have disc configurations, but later it was proposed that instead of using disc surface area of the rotary biological contactor, the volume of reactor can be applied[23-26]. Therefore, Equation of the modified Stover-Kincannon model is as follows:

$$\frac{dS}{dt} = \frac{Q(S_i - S_e)}{V} = \frac{U_{max}(\frac{QS_i}{V})}{K_B + (\frac{QS_i}{V})} \quad (7)$$

where dS/dt as a function of substrate loading rate at steady-state is defined in eqn. 8:

$$\frac{dS}{dt} = \frac{Q}{V(S_i - S_e)} \quad (8)$$

So, eqn. 9 obtained from linearization of eqn. 8 and it could be expressed as follows:

$$\frac{V}{Q(S_i - S_e)} = \frac{K_B}{U_{max}} \times \frac{V}{QS_i} + \frac{1}{U_{max}} \quad (9)$$

EXPERIMENTAL

Wastewater characteristics: Two different substrates were applied in current research:

Synthetic wastewater: The anaerobic up-flow bioreactor was initially fed with synthetic wastewater. The composition of synthetic wastewater used for the entire process period was (g L^{-1}): $NaHCO_3$ 2.6; KH_2PO_4 0.025; $CaCl_2.2H_2O$ 0.3; $MgSO_4.7H_2O$ 0.2; $FeSO_4.7H_2O$ 0.00625; EDTA 0.00625. Besides, the ammonium and nitrite in the form of $(NH_4)_2SO_4$ and $NaNO_2$ were used in the required amounts as the main influent substrates. The ammonium and nitrite concentrations in influent were 400 and 528 mg/L, respectively. Trace element 1 and 2 (1.25 mL/L) were added similarly explained previously[27].

Petrochemical wastewater: In this research, the effluent was obtained from Razi petrochemical complex. Physical and chemical characteristics of the petrochemical wastewater (ammonia plant) are presented in Table-1. The raw wastewater was collected from the end pipe of the ammonia plant and transferred to the laboratory in 5 butts of 20 L, which were kept at 4 ºC. The samples were filtered (60 mesh) prior to analysis in the laboratory. For each experiment, the concentrations of ammonia and nitrite were adjusted to a selected level by dilution, adding $(NH_4)_2SO_4$ and $NaNO_2$. The ammonia and nitrite was added to the wastewater before feeding the reactor due to lower initial concentrations. The NH_4^+ : NO_2^- ratio was adjusted to 1:1.32 for anammox process. In addition $NaHCO_3$ was added to optimize alkalinity (7.5-8). Concentrations of other parameters were not high to cause any inhabitation effect.

Reactor start-up and operation period: The Anammox culture used in this study was obtained from an anammox lab-scale reactor. In this research, bioreactor was at first continuously fed with synthetic wastewater and the effect of high ammonium load (0.45 g/L N-NH_4) was survived with mentioned wastewater. After 9 month of reactor operation, synthetic wastewater was changed by petrochemical wastewater, obtained from effluent of the ammonia unit in the Razi Petrochemical Complex, as reactor feed.

TABLE-1
PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE PETROCHEMICAL WASTEWATER

Parameters	Average value
pH	7.9
EC	3258 µs/cm
COD	95 mg/L
TSS	149 mg/L
PO_4	9.8 mg/L
Oil	30 mg/L
N-NH_3	450 mg/L
N-NO_2	594 mg/L
N-NO_3	55 mg/L

The lab-scale bioreactor with the effective volume of 1.8 L consisted of a double wall plexiglass cylindrical column (25 cm high and 11 cm internal diagonal), was operated at 35 ± 1 ºC. The initial ammonium and nitrite concentrations were 400 and 528 mg/L, respectively. With gradual increasing of nitrogen concentration, the hydraulic retention time decreased from 24 to 6 h step by step. The reactor was filled with immobilized biofilm supports which were bee-cell 2000. This type of media was used as biofilm support material due to its large surface area (650 m^2/m^3) and cost-effective when compared with other packing media and also because of its high porosity (pore volumes up to 87 %). Other characteristics of this media include: media size 10-15 mm, density 1030 kg/m^3, 361000 media per m^3 and specific area of any media was 18 cm^2. The volume filled with media supports in an empty reactor was about 50 %.

Analytical techniques: The influent and effluent samples were collected and analyzed immediately. NO_3^--N, NO_2^--N, NH_4^+-N, COD, pH, SS and VSS were measured according to the standard methods[28]. 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. The soluble COD was measured colorimetrically by closed reflux methods. The suspended solids and volatile suspended solids were measured by gravimetric method. The pH was adjusted *via* a digital portable pH meter. Each examination was run in triplicate.

RESULTS AND DISCUSSION

Reactor performance: Bioreactor performance during entire run time is illustrated in Fig. 1. The performance results of the bioreactor under various HRTs and concentrations indicated high nitrogen removal efficiencies at NLR more than 2 g/L/d. Also in order to gain the kinetics constants form three kinetic models, the anaerobic up-flow bioreactor was operated by petrochemical wastewater at different HRTs from 24 to 6 h, through 63 days of the operation period. The ammonium and nitrite concentrations were increased gradually to 550 and 700 mg N/L, respectively. Initially, the NLR (QSi/V) was 450 mg N/L/d and during the operation period, it was increased to 2083 mg N/L/d with decreasing of HRT. As HRT was decreased, ammonium removal efficiencies decreased from 93.7 % to 83 %, as well as total nitrogen removal efficiencies decreased from 92.4 % to 83.6 %. However, nitrite removal efficiencies did not change significantly that indicated that the nitrite was the limiting nutrient. This result is in agreement with the Liang and Liu[12] and Molinuevo *et al.*[15].

Substrate removal kinetics

First-order substrate removal model: Fig. 2. shows the first-order substrate removal kinetics of the UABR treating petrochemical wastewater. The first-order kinetic constant k_1 was calculated as 24.015 d^{-1} from the model line by plotting (Si-Se)/HRT *versus* Se (R^2= 0.923).

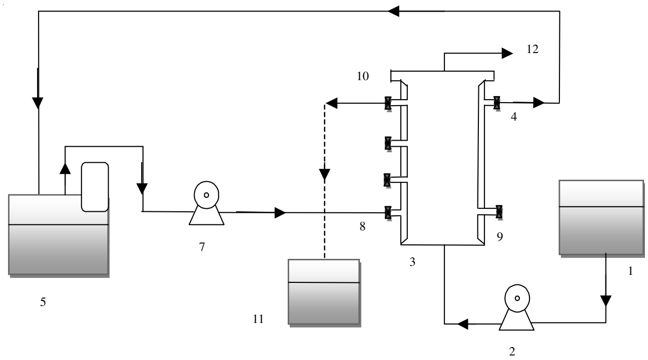

Fig. 1. Schematic diagram of the up-flow anaerobic biofilm reactor. (1. Feed tank, 2. Peristaltic pump, 3. Reactor, 4. Effluent hot water, 5. Water tank, 6. Thermostat, 7. Recycle pump, 8. Influent hot water, 9. Sampling port, 10. Effluent wastewater and sampling point, 11. Effluent collection tank 12. Gas out)

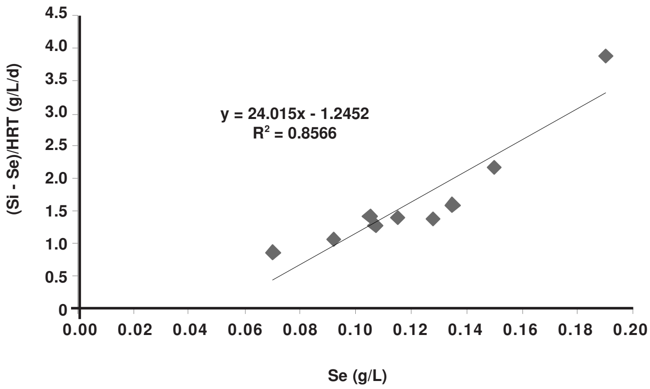

Fig. 2. Model plot of first-order kinetic

Grau second-order substrate removal model: In order to obtain the Grau second-order model coefficients, Eqn. 6 was plotted in Fig. 3. The values of a and b, were determined by the intercept and slope of the line on the graph. These values were calculated as 0.0523 and 1.0391 (R^2 = 0.9986). The Grau second-order substrate removal rate constant (K_2) was then calculated from the equation $\alpha = Si/(K_2X)$.

Modified Stover-Kincannon model: A plot of the V/Q(Si-Se) against (V/QSi) showed a satisfactory linear correlation (R^2 = 0.9983) (Fig. 4). Saturation value constant (K_B) and maximum utilization rate (U_{max}) were determined as 21.61 $kg/m^3/d$ and 20.70 $kg/m^3/d$, respectively. Therefore, the maximum total nitrogen removal rate in the Anammox reactor was *ca.* 21 kg/m^3/d.

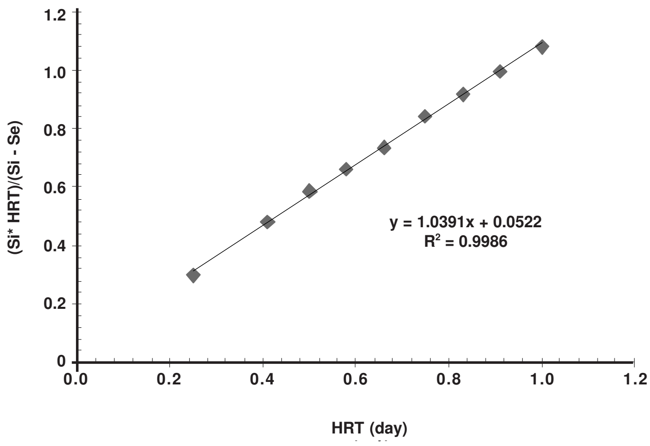

Fig. 3. Grau second-order kinetic model

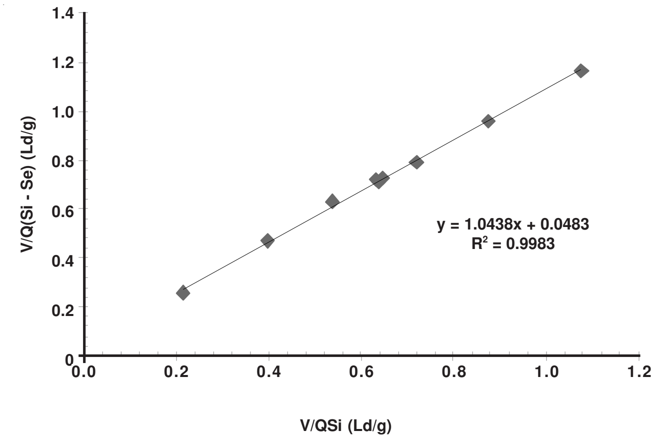

Fig. 4. Modified Stover-Kincannon nitrogen removal model plant

Evaluation of the kinetic models: The substrate removal kinetic constants for treating petrochemical wastewater obtained from different models were showed in Table-2. Comparison between regression coefficients and kintetic coefficients showed that Stover-Kincannon and Grau second-order models were more suitable than the first-order model to predict the performance of nitrogen removal from petrochemical wastewater in anaerobic up-flow bioreactor. Other researches indicated that these models were appropriate for anaerobic reactors[23,25,29]. As illustrated in Fig. 3, the regression coefficient (0.9986) and small intercept of straight line supported the credibility of the Grau second-order model. Thus, this model is capable of predicting the performance of the anaerobic up-flow bioreactor used in this research. Table-3 indicates the U_{max} obtained value in this study (20.7 kg/m^3/L) was higher than the U_{max} value found by Ni *et al.*[17] and Jin and Zheng[16]. In addition a, b values were lower than the values found by Ni *et al.*[17]. The most likely reasons for the differences in values are the substantial variations in type of wastewater and sludge used and reactor configurations. The values of K_B and U_{max} obtained from the graph, indicates that the anaerobic up-flow bioreactor has higher potential in treatment of high strength wastewater. Thus, it could be concluded the Grau second-order model is capable of describing substrate removal at any loading conditions[17]. As illustrated in Table-2, Grau second-order kinetic model and the modified Stover-Kincannon kinetic model have similar correlation coefficient. Therefore, due to similarity of the two models, by replacing eqn. 4 in eqn. 9 from dividing S_i to each part the equation, it can be followed as:

$$V/Q(Si-Se) = V/QSi+1/KsX \quad (10)$$

The following eqn. 10 can be obtained:

$$K_B = U_{max} \quad (11)$$

Thus, it could be concluded that the kinetic coefficients obtained from petrochemical wastewater treatment by Anammox process, agree with the modified Stover-Kincannon and Grau second-order kinetic models.

TABLE-2
KINETIC CONSTANTS OF ANAMMOX REACTOR TREATING PETROCHEMICAL INDUSTRIES WASTEWATER (AMMONIA PLANT)

Kinetic models	Kinetic constants	Values	R^2
First-order	K_1 (L/d)	24.015	0.8566
Grau second-order	a (L/d)	0.0522	0.9986
	b	1.0391	0.9986
Modified Stover-Kincannon	K_B (kg/m^3/d)	21.61	0.9983
	U_{max} (kg/m^3/d)	20.70	0.9983

Conclusion

The results of this research demonstrated that biological nitrogen removal from petrochemical wastewater could be implemented effectively in an anaerobic up-flow bioreactor by Anammox process. After a satisfactory steady-state conditions, were prevailed, the bioreactor was tested under nitrogen loading rate of 0.45-2.083 (g/L d) and hydraulic retention times of 24 h to 6 h, stepwise. Based on calculations, total nitrogen removal efficiencies decreased from 92.4 % to 83.6 % by gradually decreasing hydraulic retention times (Fig. 5). Consequently, the kinetics of this reactor was investigated using different

TABLE-3
COMPARISON OF KINETIC PARAMETERS IN DIFFERENT SUBSTRATES

Anammox reactor	Substrate	NLR (g/L d)	HRT (h)	First-order	Modified Stover-Kincannon			Grau second-order		Reference
				K_1	K_B	U_{max}	R^2	a	b	
Up-flow filter	Synthetic medium	7.3	10-2	0.4395	12	12.4	0.979	1.397	0.9641	[30]
Non-woven membrane reactor	Synthetic medium	0.107-0.746	43-20	5.305	8.98	7.89	0.9986	0.1054	1.1101	[12]
Up-flow anaerobic biofilm reactor	Petrochemical wastewater	0.45-2.083	24-6	24.015	21.61	20.7	0.9983	0.0522	1.0391	Present work

biokinetic models such as first-order, Grau second-order and Stover-Kincannon model. Grau second-order and modified Stover-Kincannon kinetic models with correlation coefficients of 0.998 were found to be more suitable than the other applied models for nitrogen removal in UABR. However, the Grau second-order model was slightly more appropriate as compared to modified Stover-Kincannon model. The result of kinetic studies obtained from the lab scale, showed that UABR can be used to predict the treatment performance of full-scale up-flow anaerobic bioreactors if the petrochemical wastewater was treated at similar loading conditions and wastewater composition.

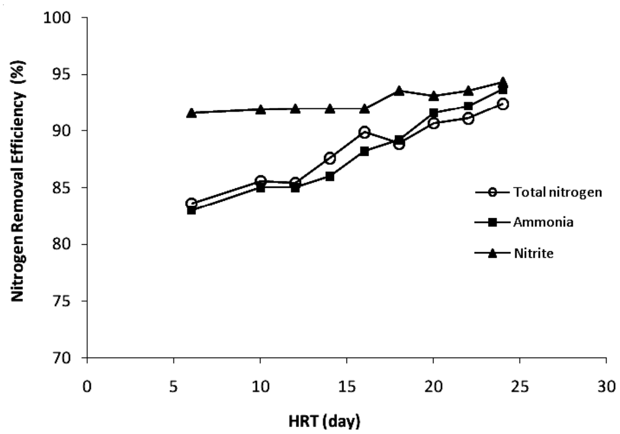

Fig. 5. Effect of different hydraulic retention times (HRT) on nitrogen removal efficiency during the parameters study operation

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