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Optimized operational strategies based on maximum nitritation, stability, and nitrite accumulation potential in a continuous partial nitritation reactor

Hammad Khan, Wookeun Bae*

Department of Civil and Environmental Engineering, Hanyang University, Ansan, Republic of Korea

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ABSTRACT

The relative nitritation rate (q^{*}_{AOB}), nitratation rate (q^{*}_{NOB}), and nitrite accumulation potential (NAP,q^{*}_{AOB}/q^{*}_{NOB}) were investigated to assess the operational conditions for stable and maximized nitritation in a continuous-stirred tank reactor (CSTR) with activated (flocculent) sludge. Novel *stability ridge* and *pH optima* curves were identified on a S_{TAN}-pH plane. The *stability ridge* divides the stable and unstable reaction regions, while the *pH optima* curve identifies optimal pH values for fastest nitritation at any desired S_{TAN}. Thus, the best operational pH for a desired S_{TAN} is found on the *pH optima* curve when it resides in the stable region; otherwise, the *stability ridge* itself indicates the best operational pH value. The locations of the *stability ridge* and *pH optima* are subject to the structure of the kinetic equation and parameter values. While the NAP decreases with an increase in DO, a necessary NAP for sufficient nitrite accumulation (e.g., NAP ≥ 2) is still ensured unless S_{TAN} becomes very low (e.g., ≤ 40 mgN/L). Consequently, desired nitritation performance can be achieved by optimizing both the sludge retention time and pH; a lower pH is essential to generate an anammox-suited feed. Modelling results were verified by treating a semi-synthetic sewage sludge digester effluent having ~600 mgTAN/L at 30 °C and varying pH.

1. Introduction

Shortcut ammonium removal processes that combine nitritation-denitritation or nitritation-anammox have drawn much attention for the treatment of concentrated ammonic streams, as they save a substantial amount of oxygen and have lower electron donor requirements when compared to conventional biological nitrogen removal (BNR) procedures. Efficient and stable nitritation is essential for the successful implementation of a shortcut ammonium removal strategy, since it serves as a bottleneck in the array of such combined processes. Previous reports have shown that the ammonium loading rate (ALR) of nitritation, in most cases (with some exceptions [1,2]) remained less than 5 kgN/m^3 -d in partial nitritation (e.g., 55% ammonium oxidation) and less than 2.5 kgN/m^3 -d in full nitritation (see Tables S1 and S2 of the Supporting material). In contrast, the nitrogen loading rate for anammox or denitritation far exceeds 5 kgN/m^3-d (see Tables S3 and S4 of the Supporting material).

While, the inherent slowness of ammonia oxidizing bacteria (AOB) is partly responsible for the relatively slow nitritation rate, a more important factor is unnecessary suppression of the reaction to limit nitrite oxidizing bacteria (NOB) by inducing free ammonia (FA) and free nitrous acid (FNA) inhibition or dissolved oxygen (DO) limitation [3–5]. Though, both of these approaches offer selective pressure to intensify AOB-NOB differential and produce a high nitrite accumulation ratio (NAR), they also slow down AOB activity significantly [6].

In addition to reduced reaction rates, instability under a fluctuating feed (for instance, in substrate concentration or flow rate) is another factor to consider when evaluating the performance of nitritation systems. When the hydraulic retention time (HRT) in a digester becomes unusually low or high, or when certain industrial wastewater is treated, the composition and concentration in the nitritation feed may fluctuate, resulting in system instability [7]. The situation becomes even more challenging when dealing with high-strength ammonic wastewaters due to the presence of elevated FA or FNA concentrations.

To minimize unnecessary inhibition, limitation, and instability, the optimization of relevant operational conditions is essential. In this study, the effects of ambient conditions on nitritation stability and capacity in a continuous-stirred tank reactor (CSTR) were

* Corresponding author.
E-mail address: wkbae@hanyang.ac.kr (W. Bae).

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Nomenclature

ALR	Ammonium loading rate (kgN/m^3 -d)
AOB	Ammonium oxidizing bacteria
AOR	Ammonium oxidation rate (%)
a, *c*	Characteristic parameters for temperature
b	Decay coefficient (day^{-1})
DO	Dissolved oxygen (mg/L)
FA	Free ammonia (mg NH_3-N/L)
FNA	Free nitrous acid (mg HNO_2-N/L)
I_{FA}	Concentrations of FA as the inhibitor (mg NH_3-N/L)
I_{FNA}	Concentrations of FNA as the inhibitor (mg HNO_2-N/L)
K_{EA}	Half-maximum-rate concentration for electron accepter (mg/L)
K_{ED}	Half-maximum-rate concentration for electron donor (mg/L)
K_I	Inhibition constant for FA or FNA (mg/L)
K_{pH}	pH dependency parameter
$K_{S,TAN/TNN}$	Half-maximum-rate concentration for AOB/NOB when substrate is TAN/TNN (mg/L)
$K_{S,FA}$	Half-maximum-rate concentration for AOB when substrate is FA ($mgNH_3$/L)
NAP	Nitrite accumulation potential
$NAP^{S\&M}$	NAP at any $q^*_{AOB,S\&M}$
NAR	Nitrite accumulation ratio (%)
NOB	Nitrite oxidizing bacteria
pH_{opt}	Intrinsic pH optimum
$pH^{thres}{}_{AOB}$	Threshold pH above which unstable region starts at given S_{TAN}
Q	Flow rate (L/d)
q^*_{AOB}	Relative nitritation rate
$q^*_{AOB,S\&M}$	Maximum and stable relative nitritation rate at a given S_{TAN}
q^*_{NOB}	Relative nitratation rate
$\hat{q}_{max}$	Theoretical maximum specific substrate utilization rate at optimal pH and temperature under saturated DO and inorganic carbon
SACR	Specific ammonium conversion rate (kgN/kgVSS-d)
S_C	Critical substrate concentration at which maximum reaction rate attained (mg/L)
S_{EA}/S_{DO}	Substrate concentration for electron accepter (i.e., DO) (mg/L)
S_{ED}	Substrate concentration for electron donor (mg/L)
S_{FA}	Concentration of FA as substrate for AOB (mg/L)
S_{IC}	Substrate concentration for inorganic carbon (mg/L)
S_{TAN}	Effluent total ammonium nitrogen (mg/L)
S_{TNN}	Effluent total nitrite nitrogen (mg/L)
S°	Influent total ammonium concentration (mg/L)
S_{opt}	Residual TAN at which the grand maximum and stable nitritation rate is achieved at given DO and temperature (mg/L)
θ_x	Sludge retention time (SRT) day
T_{max}	Maximum temperature at which growth is feasible
T_{min}	Minimum temperature at which growth is feasible
w	pH range within which the maximum specific substrate utilization rate is larger than a half of the maximum
Y	Yield coefficient (mgVSS/mg-TAN)

investigated at various pH and DO levels. Kinetic models integrating simultaneous inhibition by FA and FNA, direct and indirect effects of pH, and DO limitation [8,9] were utilized to (1) assess nitritation rates and nitrite accumulation at various operating conditions, (2) ascertain stable working boundaries, and (3) achieve desired nitritation performance under various pH and DO conditions by selecting a correct sludge retention time (SRT, θ_x). Modelling results were verified by treating a semi-synthetic sewage sludge digester effluent having ~600 mgTAN/L at 30 °C and varying pH with an elevated NAR of >97% and an ALR of ~6 kgN/m^3 -d.

2. Materials and methods

2.1. Defining system stability

When a CSTR is operating at a steady state, the substrate concentration (***S***) in the reactor remains constant. Even in the case of accidental fluctuations in substrate concentration or flow rate, ***S*** tends to quickly recover to its original steady state value, as the specific substrate utilization rate (***q***) increases with a rise in ***S*** (or decreases with a reduction in ***S***), when conventional Monod kinetics hold. This behavior is defined as system stability. On the other hand, in self-inhibition kinetics, ***q*** falls as ***S*** exceeds the critical substrate concentration ($S_c = \sqrt{K_S K_I}$). An accidental increase in ***S*** will thus reduce ***q***, interfering in recovery to the previous steady state. In this particular situation, system stability fails and the reaction becomes unstable [10].

2.2. Evaluating relative nitritation and nitratation rates

A comprehensive model was developed in previous work [4,6], based on experimental observations, to evaluate the reaction rate of nitrifiers when considering the total ammonium nitrogen (TAN) and total nitrite nitrogen (TNN) as substrates for AOB and NOB, respectively, direct and indirect effects of pH, uncompetitive and non-competitive inhibition by FA and FNA, respectively, and DO limitations. The model was further extended by including the temperature effect (modified Ratkowsky model [11]) and alkalinity function [12], which can be expressed as

$$q = \frac{\frac{\hat{q}_{max}}{2}\left\{1+\cos\left[\frac{\pi}{w}\left(pH - pH^{opt}_{AOB/NOB}\right)\right]\right\}S_{ED}}{\left(K_{ED}\left(1+\frac{I_{FNA}}{K_{IFNA}}\right) + S_{ED}\left(1+\frac{I_{FNA}}{K_{IFNA}}+\frac{I_{FA}}{K_{IFA}}\right)\right)}\left(\frac{S_{EA}}{K_{EA}+S_{EA}}\right)\left(\frac{S_{IC}}{K_{IC}+S_{IC}}\right)\left([a(T-T_{min})]^2\{1-e^{c\cdot(T-T_{max})}\}\right) \quad (1)$$

$$\text{where } pH^{AOB/NOB}_{opt} - w \le pH \le pH^{AOB/NOB}_{opt} + w$$

$$\text{and } I_{FA} = \frac{S_{TAN}\cdot 10^{pH}}{e^{\left(\frac{6344}{273+{}^\circ C}\right)}+10^{pH}}(mgNH_3 - N/L) \quad (2a)$$

$$I_{FNA} = \frac{S_{TNN}}{\left(e^{\left(\frac{-2300}{273+{}^\circ C}\right)}\cdot 10^{pH}\right)+1}(mgHNO_2\text{-}N/L) \quad (2b)$$

In which $\hat{q}_{max}$ is the theoretical maximum specific substrate utilization rate of electron donor (mg S/mg VSS-day) obtained at optimal pH, temperature and saturated DO and inorganic carbon (IC). S_{ED}, S_{EA} and S_{IC} are the substrate concentrations (mg/L) for electron donor (i.e., TAN), electron accepter (i.e., dissolved oxygen, DO) and inorganic carbon, respectively. I_{FA}, I_{FNA}, respectively, are the concentrations of FA and FNA as the inhibitors (mg NH_3-N/L or mg HNO_2-N/L). K_{ED}, K_{EA} and K_{IC} are half-maximum-rate concentration (mg/L) for electron donor (S_{ED}), electron accepter (S_{EA}) and inorganic carbon (S_{IC}), respectively. K_I is the inhibition constant for FA or FNA (mg/L). The parameters T_{max} and T_{min} are maximum and minimum temperature at which growth is observed, while ***a*** and ***c*** are temperature dependency parameters.