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Mathematical modeling of nitrous oxide (N_2O) production in anaerobic/anoxic/oxic processes: Improvements to published N_2O models

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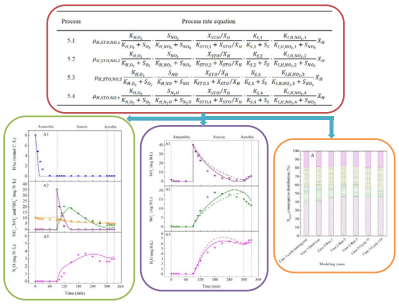
HIGHLIGHTS

- An improved model was proposed for N_2O production modeling in the A^2O process.
- Competition for electrons among four denitrification reductases was considered.
- One affinity constant for X_{STO} was divided into four constants in the model.
- The improved model better predicted N_2O production and nitrite accumulation.
- N_2O accumulation resulted from the more rapid decline of the N_2O reduction rate.

GRAPHICAL ABSTRACT



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ABSTRACT

Competition for electrons among different steps of denitrification on intracellular polymers (X_{STO}) plays a significant role in nitrous oxide (N_2O) accumulation in the biological nitrogen removal process. In this work, this electron competition was considered in a mathematical model to predict N_2O production in anaerobic/anoxic/oxic sequencing batch reactors (A^2O-SBR) for the first time. The affinity constant for intracellular polymers of heterotrophs (K_{STO}) that was used in previously published models was divided into four affinity constants ($K_{STO,1}$, $K_{STO,2}$, $K_{STO,3}$ and $K_{STO,4}$) to represent the ability of each denitrification reductase to compete for intracellular polymers. The improved model was calibrated and validated using experimental data from three independent A^2O-SBR systems. The results demonstrated that the modeling predictions strongly agreed with the measured data from all experimental tests under various operational conditions. The modeling results indicated that N_2O accumulation resulted from the more rapid decline of the N_2O reduction rate than the nitrite reduction rate for the inadequate X_{STO} in these A^2O-SBR systems. The modeling results also suggested that distinguishing affinity constants for intracellular polymers during the four-step denitrification felicitously described a different X_{STO} distribution in each reduction step, thereby better predicting nitrogen dynamics and N_2O production in A^2O processes than the published model. The improved model is therefore a preferable tool to gain insight into N_2O accumulation in A^2O processes.

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1. Introduction

Nitrous oxide (N_2O) is one of the most important greenhouse gases. Although its proportion in total greenhouse gas emissions is only 0.03%, it has a global warming potential more than 300-fold greater than carbon dioxide (CO_2) [1]; it significantly contributes to the carbon footprint of greenhouse gas emissions [2]. Measurements have demonstrated that substantial amounts of N_2O can be emitted from lab-scale experiments and full-scale wastewater treatment plants (WWTPs) [2] during both autotrophic nitrification and heterotrophic denitrification processes [3–6]. Low dissolved oxygen (DO) concentrations, high nitrite accumulations during nitrification and denitrification processes, and a limited availability of biodegradable organic compounds during denitrification are the most significant causes leading to N_2O accumulation and emission in biological nitrogen removal (BNR) processes [2,4,7].

Moreover, when carbon sources are limited or carbon/nitrogen (C/N) ratios are low [8,9], the electron supply cannot meet the electron demand for complete denitrification. Under these circumstances, electron competition may occur among four denitrification reductases [10]. Pan et al. [10] also revealed that competition for electrons occurs under carbon-limited as well as carbon-abundant conditions. Furthermore, the slower degradation of polyhydroxybutyrate (PHB) cannot provide adequate electrons for denitrification. Therefore, electron competition likely also occurs when PHB is used as an electron donor [2,7]. Specifically, under electron-competitive conditions, nitrate reductase may have great advantages in capturing electrons when compared to nitrite and N_2O reductases [2], which easily leads to nitrite and N_2O accumulation [11,12]. As N_2O reduction is the last step of denitrification, N_2O reductase cannot gain enough electrons, resulting in N_2O production during denitrification [2,11,13]. Additionally, some environmental conditions, such as pH, temperature, carbon source and free nitrous acid (FNA) inhibition, can intensify electron competitions and eventually lead to N_2O accumulation [10,14]. Therefore, the mechanisms of electron completion on N_2O production in the denitrification process are of great importance and deserve more attention in research.

Mathematical modeling has been demonstrated to be helpful for testing the mechanisms of pollutant removal in wastewater treatment [15]. Firstly, the Activated Sludge Model for Nitrogen (ASMN) proposed by Hiatt and Grady [16] was successfully developed to predict N_2O production by describing heterotrophic denitrification as a four-step process. Subsequently, the Activated Sludge Model for Indirect Coupling of Electrons (ASM-ICE) was developed to represent the electron competition among four denitrification steps [17,18]. However, both the four-step ASMN model and the ASM-ICE model did not consider the role of intracellular polymers in N_2O production in denitrification processes. Afterward, the relations between denitrification on intracellular polymers (X_{STO}, an internal cell storage product of heterotrophic organisms [15]) and N_2O accumulation were investigated in several published models [19–21]. These models satisfactorily described X_{STO} synthesis/consumption, nitrogen removal, and N_2O production in denitrification on intracellular polymers, denitrifying phosphorus removal and anaerobic/oxic/anoxic (AOA) processes. However, due to the lack of recognition of the electron competition in denitrification, none of these models considered the competition for electrons in denitrification processes with the intracellular polymers being the sole electron donors. More information should be provided to explore the reaction kinetics for the models aiming to predict N_2O production during denitrification on intracellular polymers.

The anaerobic/anoxic/oxic (A^2O) process, in which phosphorus and nitrogen can be removed simultaneously [22,23], is the most commonly used process in wastewater treatment [24]. In the WWTPs of China, the A^2O process accounted for the biggest design treatment capacity of 33.2% [25]. The A^2O process undergoes alternating anaerobic/anoxic/oxic conditions to achieve internal cell product storage/consumption and nitrogen removal. Firstly, the readily biodegradable organics (S_S) are stored as intracellular polymers by heterotrophic bacteria under anaerobic conditions. Next, nitrate (NO_3^-) is reduced to nitrite (NO_2^-), then nitric oxide (NO), N_2O, and finally nitrogen gas (N_2) in the anoxic stage, using the intracellular polymers as electron donors. Nitrate reductase (Nar), nitrite reductase (Nir), NO reductase (Nor) and N_2O reductase (Nos) are the four functional enzymes in this four-step denitrification process [26]. During the aerobic stage, ammonium (NH_4^+) is successively oxidized to nitrite and nitrate by ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB), respectively. A significant amount of nitrite could accumulate under oxygen-limited conditions. Due to the utilization of the aerobically synthesized PHB for denitrification in the anoxic stage, N_2O could be emitted from WWTPs running the A^2O process [27]. Moreover, N_2O emissions from the full-course BNR processes operated at the oxidation ditch (OD), University of Cape Town (UCT), AO and AOA modes have been previously modeled [19,28–30], but N_2O production in an A^2O system has never been modeled. Since the application of the A^2O process is popular in wastewater treatment, modeling efforts should begin now.

In this work, an improved model, in which the competition for storage polymers among four denitrification reductases was firstly introduced, was proposed to investigate the competition for electrons and the mechanisms of N_2O production during denitrification in A^2O processes. The improved model was verified using experimental data from three independent A^2O-SBR systems with different operation characteristics. The new model is expected to be beneficial for improving the prediction of N_2O production in A^2O processes.

2. Materials and methods

2.1. Model description

The mechanisms of X_{STO} synthesis/consumption and nitrogen conversion dynamics in the A^2O process are the same as that in the AOA process. Therefore, the published model for predicting N_2O production in AOA systems (the published model for short [19]) was employed in this work. The component definitions, stoichiometry and composition matrix, kinetic rate expression matrix of the published model are presented in Supplementary Material Tables S.1–S.3.

The published model by Ding et al. [19], as well as other reported models describing N_2O production during denitrification on intracellular polymers [20,21], did not consider the electron competition among the four reduction steps under starving conditions [2,3,11,13]. The affinity constants (K_{STO}) regarding storage polymers (electron donor) were uniformly used in all four denitrification steps [19–21]. This limitation potentially restrains the model application for N_2O prediction in endogenous denitrification processes. In this work, the key kinetic parameter of K_{STO} was divided into four independent affinity constants, i.e., $K_{STO,1}$, $K_{STO,2}$, $K_{STO,3}$ and $K_{STO,4}$, to describe the distinct electron capturing ability of each denitrification reductase. These four affinity constants, which govern the distributions of intracellular polymers, were introduced into the denitrification process in this study for the first time. Modifications of the kinetic rate expressions (R5.1, R5.2, R5.3 and R5.4) in the published models are presented in Table 1. The parameter values of $K_{STO,1}$, $K_{STO,2}$, $K_{STO,3}$ and $K_{STO,4}$ were calibrated using the experimental data from the anaerobic/anoxic/oxic