Progress and Prospect of Research on N_2O Dynamics Model in Wastewater Biological Treatment Process

Yutian LIU[1, a], Shoubin ZHANG[1, b*], Liping QIU[1, c] and Yuanyuan ZHANG[1, d]

[1] School of Civil Engineering & Architecture, University of Jinan, NO.336, Nanxinzhuang West Road., Jinan 250022, P.R.China

[a]liuyutian1010@163.com, [b*] Corresponding author: cea_zhangsb@ujn.edu.cn, [c]cea_qiulp@ujn.edu.cn, [d]zyyzhangxiaolan@126.com

Keywords: wastewater biological denitrification；nitrous oxide；N_2O dynamics model； Activated Sludge Model 3.

Abstract. Nitrous oxide (N_2O) is a kind of strong greenhouse gas, which can cause the composite pollution effect to the atmospheric environment. Wastewater biological treatment process is considered to be one of the important anthropogenic source of N_2O. Therefore, the research on the generation of N_2O in wastewater treatment process is of great theoretical significance and engineering application value. Based on a brief description of the mechanism of N_2O generation in wastewater treatment process, the research progress of N_2O dynamics model is deeply analyzed. And then the feasibility of building the N_2O dynamic model which based on the Activated Sludge Model 3 (ASM3) is proposed and the endogenous respiration of microorganisms associated with N_2O generation is emphasized in dynamic modelling process. And on these bases, a reasonable prospect of the N_2O dynamic modelling is put forward.

Introduction

Nitrous oxide (N_2O) is a kind of strong greenhouse gas, which can cause the composite pollution effect to the atmospheric environment. Wastewater biological treatment process is considered to be one of the important anthropogenic sources of N_2O[1]. Therefore, the research on the generation of N_2O in wastewater treatment process is of great theoretical significance and engineering application value. Based on this, more and more scholars began to pay attention to the mechanism of N_2O generation and build the N_2O dynamic model through describing various N_2O generation pathways. However, these models usually good fit with own data but fail with foreign data. Hence, the N_2O dynamics model also has a great development space.

Mechanism of N_2O production

During biological nitrogen removal process, the generation of N_2O mainly has three kinds of pathways: namely the hydroxylamine (NH_2OH) oxidation, ammonia-oxidizing bacteria (AOB) denitrification and heterotrophic denitrification pathways [2].

In the process of traditional aerobic nitrification, two pathways can lead to produce N_2O: First, due to the NH_2OH incomplete oxidation, intermediate can produce N_2O by chemical decomposition or enzymatic reactions and then N_2O appeared as a form of byproduct [3]; Second, if the concentration of dissolved oxygen (DO) is insufficient, it will result a higher concentration of NO_2^- and make the NO_2^- instead of O_2 as electron acceptor, and then NO_2^- reduction to NO or N_2O. This process is also named AOB denitrification.

As is known to all, heterotrophic denitrification process is mainly divided into four steps reaction and the four steps reaction can produce three kinds of intermediate: namely NO_2^-, NO and N_2O. Therefore, N_2O is generated as an intermediate in heterotrophic denitrification pathway.

Modeling of N_2O production

According to the mechanism of N_2O production, N_2O dynamics model mainly has four categories: (1) Single-pathway models by AOB; (2) Two-pathway models by AOB; (3) N_2O models by heterotrophs; (4) Integrated N_2O models. The Single-pathway models include NH_2OH oxidation or AOB denitrification and the Two-pathway models integrate NH_2OH oxidation and AOB denitrification. Furthermore, the Integrated N_2O models couple of nitrification and denitrification process.

Single-pathway models by AOB.

NH_2OH/NOH model. NH_2OH/NOH model is proposed by Law et al [4] (Fig.1C).In this model, NOH is the intermediate of NH_2OH oxidation and N_2O is produced by NOH chemical decomposition.

The NH_2OH/NOH model has five reaction stages, i.e: Reaction stage 1 (R1): NH_3 oxidation to NH_2OH, this process consumes O_2 and O_2 as a substrate exists; Reaction stage 2 (R2): NH_2OH oxidation to NOH; Reaction stage 3 (R3): NOH oxidation to NO_2^-; Reaction stage 4 (R4): generate N_2O by NOH chemical decomposition; Reaction stage 5 (R5): O_2 as the final electron acceptor.

In addition, R1 process needs two electrons which come from (R2 + R3) process. NH_2OH oxidation can produce four electrons, two electrons among them returns to ammonia monooxygenase (AMO) and the remaining two electronics used for the growth of microbial cells. However, in this model ignored biological growth and CO_2 reduction.

NH_2OH/NO model. NH_2OH/NO model is established by Ni et al and NO is the intermediate of NH_2OH oxidation [3] (Fig.1D). And NH_2OH/NO model also has five reaction stages:Reaction stage 1 (R1): NH_3 oxidation to NH_2OH; this process consumes O_2 and O_2 as a substrate exists; Reaction stage 2 (R2): NH_2OH oxidation to NO; Reaction stage 3 (R3): NO oxidation to NO_2^-; Reaction stage 4 (R4): NO reduction to N_2O; Reaction stage 5 (R5): express attenuation process of the AOB .

It is import to note the reaction rate of AOB will reduce when NO replace O_2 as the electron acceptor and then this model introduces a hypoxia correction factor h_{AOB} to describe this phenomenon. Furthermore, NH_2OH/NO consider the growth and decay of nitrite oxidizing bacteria (NOB).

4 steps AOB denitrification model. Ni et al think the AOB denitrification need four steps to produce N_2O in this model [9]. And as shown in Fig.1A, four biochemical processes are as follows:

Reaction stage 1 (R1): NH_3 oxidation to NH_2OH, O_2 is consumed, NH_3 and O_2 are the final electron acceptor;Reaction stage 2 (R2+R3): NH_2OH oxidation to NO_2^-, O_2 is the final electron acceptor;Reaction stage 3 (R2+R4): AOB denitrification, NO_2^- is the final electron acceptor; Reaction stage 4 (R2+R5): produce N_2O by AOB denitrification. Moreover, it is important to note the R2 process provides four electrons and two electrons among them used for NH_3 oxidation, the remaining electrons used for the growth of microbial cells. On the other hand, Reaction stage 2 includes the growth and decay of microorganism.In addition, if the concentration of DO is insufficient and contains a large amount of NO_2^-, NO_2^- will replace O_2 as the final electron acceptor. In other words, R4 (NO_2^- reduction to NO) and R5 (NO reduction to N_2O) processes will happen.

3 steps AOB denitrification model. As shown in Fig.1B, there is no intermediate production in oxidation process [7] and three biochemical reactions are as follows:

Reaction stage 1 (R1): NH_4^+ oxidation to NO_2^-, but does not consider if there have some intermediates; Reaction stage 2 (R2): NH_4^+ oxidation to NO; Reaction stage 3 (R3): NH_4^+ oxidation to N_2O. On these bases, Mampaey et al think that 6 electrons will be providing in the Reaction stage 1 (R1) of this model and 4 electrons of them are used for O_2 oxidation, the remaining two electrons are used to reduce NO_2^- to NO or reduce NO to N_2O. And the growth and decay process of microorganisms were considered in the above three reaction stages.

Two-pathway models by AOB. Ni et al established the N_2O dynamics model by integrating nitrification pathway [8] and this model defines two new concepts: namely the Mred(electron carrier in reduced form) and Mox (in oxidized form), and Mred and Mox fit with the following two relations:

$S_{Mred}+S_{Mox}=C_{TOT}$ (1)

$Mred=Mox+2e^-+2H^+$ (2)

The mechanism of this model is shown in Fig.3, which contains 6 biochemical processes, i.e:Reaction stage 1 (R1): NH_3 oxidation to NH_2OH;Reaction stage 2 (R2): NH_2OH oxidation to NO;Reaction stage 3 (R3): NO oxidation to NO_2^-;Reaction stage 4 (R4): NO reduction to N_2O;Reaction stage 5 (R5): O_2 reduction to H_2O;Reaction stage 6 (R6): NO_2^- reduction to N_2O.What should we know is that in reaction stage 1 (R1), an O atom from the O_2 molecule is reduced to NH_2OH and the second O atom is reduced to H_2O. Furthermore, Mred donated 2 electrons to the O atoms in reaction stage 1 (R1) and donate 1 electron to the NO in reaction stage 4, and then Mred is oxidized to Mox. On the other hand, Mox received a total of 4 electrons in reaction stage 2 and 3. The electron transfer process in reaction stage 5 is also an energy producing process. In reaction stage 6, NO_2^- as the final electron acceptor joins the reaction process. In addition, $NO2^-$ reduction to N_2O needs only 1 step and this model ignores the microbial growth.

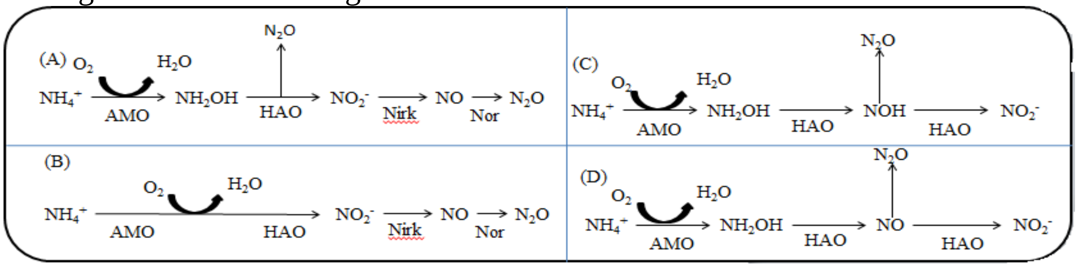

Fig.1 N_2O models by nitrification process. A: 4 steps AOB denitrification model; B: 3 steps AOB denitrification model; C: NH_2OH/NOH pathway; D: NH_2OH/NO pathway;

N_2O models by heterotrophs.

ASMN model. Hiatt and Grady et al used the direct coupling method for building this model[9] and the biochemical stages are as follows:

Reaction stage 1 (R1): NO_3^- reduction to NO_2^-; Reaction stage 2 (R2): NO_2^- reduction to NO; Reaction stage 3 (R3): NO reduction to N_2O; Reaction stage 4 (R4): N_2O reduction to N_2. And on these bases, N_2O is generated as an intermediate in this model.

ASM-ICE model. Unlike ASMN model, Pan et al used the indirect coupling method for building ASM-ICE model and used methanol as carbon source[10]. Moreover, this model also uses the Mred and Mox to describe the electron carrier. As shown in Fig.2, the biochemical reactions are as follows:

Carbon oxidation process:Reaction stage 1 (R1): methanol conversion to CO_2;Reaction stage 2 (R2): methanol assimilation to biomass. Nitrogen reduction processes:Reaction stage 3 (R3): NO_3^- reduction to NO_2^-;Reaction stage 4 (R4): NO_2^- reduction to NO; Reaction stage 5 (R5): NO reduction to N_2O;Reaction stage 6 (R6): N_2O reduction to N_2. Moreover, this model suppose the carbon oxidation and electron transfer are important condition for the N_2O production. So this model introduced anabolic and catabolic process, and simultaneously increases the electron competition theory in 4 steps denitrification process.

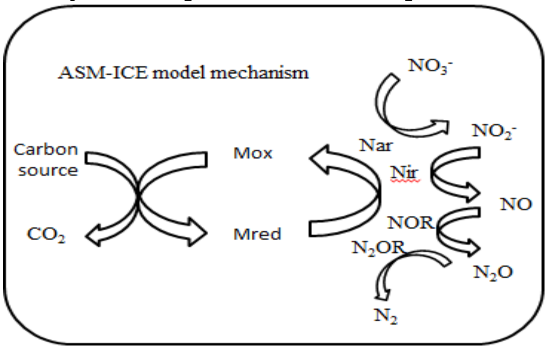

Fig.2 Mechanism of ASM-ICE model

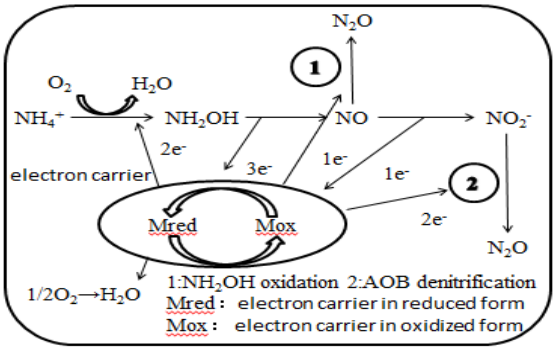

Fig.3 Mechanism of Two-pathway models by AOB

Integrated N_2O models. There have two kinds of integrated N_2O dynamics models and these models are all achieve the integration of nitrification and denitrification process [11]. The first model is proposed by combining with Single-pathway models and ASMN model [6]. And the second model is established by direct coupling Two-pathway models and ASMN model [12]. The above two kinds of models are successful in predicting N_2O production. In addition, there are also scholars believe that under the high COD, low dissolved oxygen conditions, heterotrophic denitrification process may be to store part of the N_2O and this process can affect prediction of N_2O production[11].

Conclusions and prospects

By summarizing the previous research, we can conclude that: First, there is not a clear conclusion for the mechanism of N_2O production. Second, the existing models selective describe microbial growth or decay process. Third, there is not a kind of N_2O dynamic model is recognized by the majority of researchers.

For the above problems, we should pay more attention to the microbial growth or decay processes. Well known, in ASM3 model, the conversion of nitrifying bacteria and heterotrophic bacteria are clearly separated, decay process with the unified model is described. Furthermore, the endogenous respiration of microorganisms is emphasized in ASM3 model. So, this is advantageous for the establishment of the N_2O dynamic modeling associated with ASM3. Meanwhile, ASM3 is more suitable for coding and can be simulated on computer before the actual application. So, N_2O dynamics model should be appropriate to make computer simulation process. Therefore, we should also pay more attention to the improtance of applying simulation system in early stage for building N_2O dynamic model.

Acknowledgements

This work was financially supported by the Shandong Provincial Natural Science Foundation, China (ZR2015EM021), Project of Shandong Province Higher Educational Science and Technology Program (J13LG07), Doctoral Foundation of University of Jinan (XBS1432) and partly supported by National Natural Science Foundation of China (51278225).

References

[1] J. Foley, D. de Haas and Z. Yuan: Water. Res. Vol. 44(2010), p.831-844.

[2] M.J. Kampschreur, H. Temmink: Water. Res Vol. 43 (2009), p. 4093-4103.

[3] L. Poughon, C.G. Dussap, J.B. Gros: Biotechnol Vol. 72 (2000), p. 416-433.

[4] Y.Law, B.J. Ni, P Lant: Water. Research Vol. 46 (2012), p. 3409-3419.

[5] B.J. Ni, L. Ye, Y. Law: Environ. Sci. Techno Vol. 47 (2013b), p. 7795-7803.

[6] B J Ni, M. Ruscalleda and C Pellicer-Nacher: Environ. Sci. Techno Vol. 45 (2011), p. 7768-7776.

[7] K.E.Mampaey, B.Beuckels: Environ. Techno Vol. 34(2013), p.1555-1566.

[8] B.J. Ni, L. Peng, Y. Law: Environ. Sci. Techno Vol. 48 (2014), p. 3916-3924.

[9] W.C. Hiatt, Jr. Grady, C.P.L: Water. Environ. Res Vol. 80 (2008), p. 145-2156.

[10] Y. Pan, B.J. Ni, Z. Yuan: Environ. Sci. Techno Vol. 47 (2013b), p. 11083-11091.

[11] B.J. Ni: Water. Research Vol. 87 (2015), p. 336-346.

[12] B.J. Ni, Y.Pan: Environ. Sci. Techno Vol. 49 (2015), p. 9176-9184.