Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Evaluating two concepts for the modelling of intermediates accumulation during biological denitrification in wastewater treatment

Yuting Pan [a], Bing-Jie Ni [a], Huijie Lu [b], Kartik Chandran [c], David Richardson [a,d], Zhiguo Yuan [a,*]

[a] Advanced Water Management Centre (AWMC), The University of Queensland, St. Lucia, Brisbane, QLD 4072, Australia

[b] Department of Civil and Environmental Engineering, University of Vermont, Burlington, VT 05405, USA

[c] Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA

[d] Centre for Molecular Structure and Biochemistry (CMSB), School of Biological Sciences, University of East Anglia, Norwich, NR4 7TJ, UK

ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form
8 December 2014
Accepted 16 December 2014
Available online 25 December 2014

Keywords:
Denitrification modelling
Electron competition
Carbon source
Nitrous oxide
ASMN
ASM-ICE

ABSTRACT

The accumulation of the denitrification intermediates in wastewater treatment systems is highly undesirable, since both nitrite and nitric oxide (NO) are known to be toxic to bacteria, and nitrous oxide (N_2O) is a potent greenhouse gas and an ozone depleting substance. To date, two distinct concepts for the modelling of denitrification have been proposed, which are represented by the Activated Sludge Model for Nitrogen (ASMN) and the Activated Sludge Model with Indirect Coupling of Electrons (ASM-ICE), respectively. The two models are fundamentally different in describing the electron allocation among different steps of denitrification. In this study, the two models were examined and compared in their ability to predict the accumulation of denitrification intermediates reported in four different experimental datasets in literature. The N-oxide accumulation predicted by the ASM-ICE model was in good agreement with values measured in all four cases, while the ASMN model was only able to reproduce one of the four cases. The better performance of the ASM-ICE model is due to that it adopts an "indirect coupling" modelling concept through electron carriers to link the carbon oxidation and the nitrogen reduction processes, which describes the electron competition well. The ASMN model, on the other hand, is inherently limited by its structural deficiency in assuming that carbon oxidation is always able to meet the electron demand by all denitrification steps, therefore discounting electron competition among these steps. ASM-ICE therefore offers a better tool for predicting and understanding intermediates accumulation in biological denitrification.

* *Corresponding author*. Tel.: +61 7 3365 4374; fax: +61 7 3365 4726.
E-mail address: zhiguo@awmc.uq.edu.au (Z. Yuan).

http://dx.doi.org/10.1016/j.watres.2014.12.029
0043-1354/

1. Introduction

Denitrification is an important process of the global nitrogen cycle. Nitrate reduction consists of four consecutive reduction steps, with nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O) as three obligatory intermediates (Zumft, 1997). Each reduction step is catalysed by one or more specific enzymes, including nitrate reductase (Nar), nitrite reductase (Nir), NO reductase (Nor) and N_2O reductase (Nos). In wastewater treatment systems, denitrification, together with nitrification, are the key processes to remove nitrogen pollutants from wastewater (Tchobanoglous et al., 2003).

A long-existing operational issue of wastewater denitrification is the accumulation of N-oxide intermediates. Nitrite and NO are known to be toxic, which could suppress the activity of denitrifiers (Ni and Yu, 2008; Zumft, 1997). In recent years, the emission of nitrous oxide from wastewater treatment plants (WWTPs) has become an emerging problem, because N_2O is a potent greenhouse gas with a 300-fold stronger radiative force than carbon dioxide, and is also a primary ozone depleting substance in the 21st century (IPCC, 2007; Ravishankara et al., 2009).

It has been demonstrated that the accumulation of denitrification intermediates is often a result of electron competition among N-reductases involved in the four denitrification steps (Pan et al., 2013a; Schalk-Otte et al., 2000). Pure culture-based studies of electron transport network in typical denitrifying bacteria, such as *Paracoccus denitrificans*, have proven that all denitrification enzymes derive their electrons from a common electron supply source, i.e., the ubiquinol pool of the respiratory electron transport chain (Richardson et al., 2009). The structure of this electron transport network sets the stage for the electron competition between the four denitrification steps. The electron competition occurs when the electron supply rate is rate-limiting during denitrification.

Mathematical modelling has been widely applied to predict nitrogen removal in wastewater treatment. Previous modelling efforts have primarily focussed on the prediction of nitrate removal (Henze et al., 2000), and in some cases, nitrite as well (Ni and Yu, 2008). However, it is increasingly recognized that N_2O accumulation should also be modelled, especially due to its detrimental influence on the atmosphere (Ni et al., 2011). It has been proposed to achieve this goal through modelling denitrification as a four-step process, using NO_3^-, NO_2^-, NO, and N_2O as the terminal electron acceptor, respectively (Hiatt and Grady, 2008; Pan et al., 2013b; Schulthess and Gujer, 1996; Vonschulthess et al., 1994). With each step being modelled with individual, reaction-specific kinetics, the accumulation of nitrite, NO and N_2O can be predicted.

To date, two distinct concepts have been proposed for modelling the four-step denitrification, with their structures shown in Fig. 1.

Model I: The "direct coupling approach", represented by Activated Sludge Model for Nitrogen (ASMN) (Hiatt and Grady, 2008), in which the carbon oxidation and nitrogen reduction processes are directly coupled. This type of model describes each of the four steps as a separate and independent oxidation–reduction reaction (Fig. 1-a), and reaction-specific kinetics are applied. Many of the multiple step denitrification models have adopted such structure (e.g., Ni et al., 2011; Schulthess and Gujer, 1996).

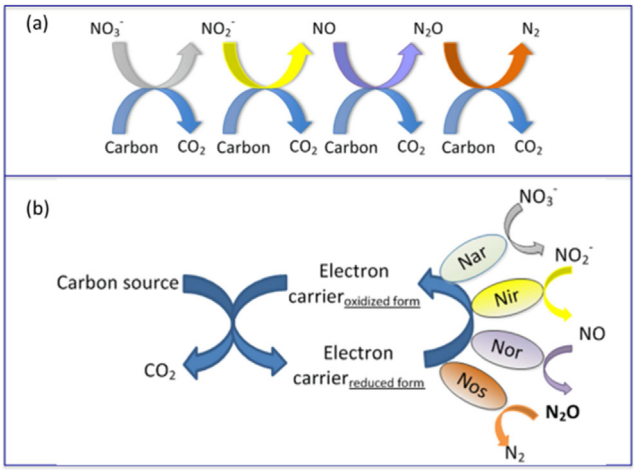

Fig. 1 – Conceptual reaction schemes used in the two 4-step denitrification models evaluated in this study: (a) The ASMN model – Using the "*direct coupling approach*" to model the carbon oxidation and nitrogen reduction processes during denitrification; (b) The ASM-ICE model – Using the "*indirect coupling approach*" to model the carbon oxidation and nitrogen reduction processes during denitrification.

Model II: The "indirect coupling approach", proposed by Pan et al. (2013a) and named Activated Sludge Model for Indirect Coupling of Electrons (ASM-ICE), in which the carbon oxidation and nitrogen reduction processes are indirectly coupled. Electron carriers are introduced as a new component in this model to link carbon oxidation to nitrogen oxides reduction (Fig. 1-b). As a result, each step of denitrification can be regulated by both the nitrogen reduction and the carbon oxidation processes.

It is of importance to evaluate the abilities of these two models in predicting denitrification activities and particularly the accumulation of denitrification intermediates. This can be done by conducting parallel comparisons with existing data reported for different denitrifying cultures and/or under different conditions. Therefore, the aim of this work is to reveal how the two model structures presented in Fig. 1 would affect their ability to reproduce experimental data reported in literature. Four distinctive denitrifying cultures were used in this examination, including one pure culture (*P. denitrificans* (N.C.1.B. 8944)) and three mixed denitrifying cultures/sludge fed with different substrates (e.g., acetate or methanol). In particular, the ability of the two models in predicting electron competition during denitrification was assessed. The findings are expected to improve the fundamental understanding of electron competition involved in specific denitrification steps, which could ultimately lead to better modelling and control of intermediate accumulation during wastewater denitrification.