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Mathematical Modeling of Effects of Nanomaterials on N_2O Emission during Denitrification

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ABSTRACT

Effects of nanomaterials on N_2O emission during denitrification have previously been reported experimentally. A new mathematical model considering such effects is developed to describe the N_2O production by heterotrophic denitrifiers for the first time. The model is successfully calibrated and validated using the data under different conditions. The model satisfactorily describes the nitrogen conversion data from the system. Modeling results show a much lower inhibition constant of nanomaterials for N_2O reduction compared to those for nitrate and nitrite reduction, indicating a significant contribution of nanomaterials on N_2O accumulation during denitrification.

Keywords: Denitrification; N_2O; nanomaterials; mathematical modelling

1. INTRODUCTION

Biological nitrogen removal (BNR) is the most widely practiced approach for nitrogen control during wastewater treatment, which involves both nitrification and denitrification. During autotrophic nitrification, ammonium (NH_4^+) is first converted to nitrite (NO_2^-) by ammonia oxidizing bacteria (AOB), followed by nitrite oxidation to nitrate (NO_3^-) by nitrite oxidizing bacteria (NOB). Heterotrophic denitrification process includes sequential reductions of NO_3^- to dinitrogen gas (N_2) with NO_2^-, nitric oxide (NO) and nitrous oxide (N_2O) as intermediates, carried out by heterotrophic denitrifiers. Each reduction step is catalyzed by the corresponding denitrification reductase, namely nitrate reductase (Nar), nitrite reductase (Nir), NO reductase (Nor) and N_2O reductase (Nos), respectively (Zumft, 1997). Recently, N_2O emissions during BNR have raised increasing concern owing to its potent greenhouse gas effect and its ability to deplete stratospheric ozone (Ravishankara et al., 2009). Although it is commonly believed that nitrification is the main contributor of N_2O production in wastewater treatment plants (WWTPs) (Ni et al., 2014; Peng et al., 2014, 2015). N_2O, formed as an obligatory intermediate during denitrification cannot be overlooked due to the fact that low levels of N_2O accumulation during anoxic phase would lead to spike of N_2O emission during subsequent aeration.

Recently, nanomaterials such as zinc oxide nanoparticles (ZnO NPs), have been widely used in industrial applications and consumer products. The increasing manufacture and

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utilization of nanomaterials have accelerated their releases into aquatic environments. As such, WWTPs usually receive substantial amounts of nanomaterials in the influent. For example, Zheng et al. (2014) reported that the release of ZnO NPs into WWTPs causes negative effects on nitrate removal and N_2O emissions during microbial denitrification process.

Mathematical modelling is of great significance towards understanding metabolic mechanism of N_2O production during denitrification as well as estimating site-specific N_2O production in real WWTPs. So far, several N_2O models based on heterotrophic denitrification have been proposed (Hiatt and Grady, 2008; Liu et al., 2014, 2015; Pan et al., 2013; Schulthess and Gujer, 1996). However, none of the currently available N_2O models by heterotrophic denitrifiers are able to provide a well-rounded description of N_2O production during denitrification with respect to the effect of nanomaterials.

This study aims to develop a new denitrification model that takes effects of nanomaterials on N_2O accumulation into consideration. The model is calibrated and validated using experimental data previously reported in Zheng et al. (2014). It is expected that the developed model would provide support for better understanding of N_2O emission during the wastewater treatment.

2. MATERIALS AND METHODS

2.1 Model development

A new mathematical model that synthesizes all relevant reactions in the conventional three-step denitrification model and incorporates the effect of nanomaterials on denitrification process is presented in Table 1 and 2. The model describes the relationships among five soluble compounds: NO_3^- (S_{NO_3}), NO_2^- (S_{NO_2}), N_2O (S_{N_2O}), N_2 (S_{N_2}), and biodegradable substances (Ss). Heterotrophic denitrifiers are modeled together (X_H) according to previous studies (Hiatt and Grady, 2008; Ni et al., 2011). Table 3 lists the definitions, values, units, and sources of all parameters used in the developed model.

Table 1 Process kinetic rate equations for the developed model

Process	Kinetics rates expressions
1. Anoxic growth of HB with nitrate	$\mu_{NO3}\frac{S_S}{K_{S1}+S_S}\frac{S_{NO3}}{K_{NO3}+S_{SNO3}}\frac{K_{I1,NO2}}{K_{I1,NO2}+S_{NO2}}\frac{K_{I1,Zn}}{K_{I1,Zn}+S_{Zn}}X_H$
2. Anoxic growth of HB with nitrite	$\mu_{NO2}\frac{S_S}{K_{S2}+S_S}\frac{S_{NO2}}{K_{NO2}+S_{SNO2}}\frac{K_{I2,NO2}}{K_{I2,NO2}+S_{NO2}}\frac{K_{I2,Zn}}{K_{I2,Zn}+S_{Zn}}X_H$
3. Anoxic growth of HB with N_2O	$\mu_{N2O}\frac{S_S}{K_{S3}+S_S}\frac{S_{N2O}}{K_{N2O}+S_{SN2O}}\frac{K_{I3,NO2}}{K_{I3,NO2}+S_{NO2}}\frac{K_{I3,Zn}}{K_{I3,Zn}+S_{Zn}}X_H$
4. Decay of HB	$b_H X_H$

Table 2 Stoichiometric matrix for the developed model

Variable / **Process**	**S_{NO_3}** **N**	**S_{NO_2}** **N**	**S_{N_2O}** **N**	**S_{N_2}** **N**	**Ss** **COD**	**X_H** **COD**	**X_I** **COD**
1	$-\frac{1-Y_H}{1.14Y_H}$	$\frac{1-Y_H}{1.14Y_H}$	-	-	$-\frac{1}{Y_H}$	1	-
2	-	$-\frac{1-Y_H}{1.14Y_H}$	$\frac{1-Y_H}{1.14Y_H}$	-	$-\frac{1}{Y_H}$	1	-
3	-	-	$-\frac{1-Y_H}{0.57Y_H}$	$\frac{1-Y_H}{0.57Y_H}$	$-\frac{1}{Y_H}$	1	-
4	-	-	-	-	-	-1	f_I

Table 3 Kinetic and stoichiometric parameters of the developed model

Parameter	**Definition**	**Value**	**Unit**	**Source**
Stoichiometric parameters				
Y_H	yield coefficient for growth on Ss	0.67	g COD/ g COD	(1)
f_I	Fraction of residual inert biomass (X_I)	0.1	g COD/ g COD	(2)
Kinetic parameters				
μ_{NO_3}	maximum anoxic growth rate on nitrate	0.053	1/h	(1)
μ_{NO_2}	maximum anoxic growth rate on nitrite	0.056	1/h	(1)
μ_{N_2O}	maximum anoxic growth rate on N_2O	0.134	1/h	(1)
b_H	decay rate coefficient of HB	0.026	1/h	(1)
K_{S1}	half saturation coefficients of S_S for nitrate reduction	5	g COD/m^3	(1)
K_{S2}	half saturation coefficients of S_S for nitrite reduction	1.5	g COD/m^3	(1)
K_{S3}	half saturation coefficients of S_S for N_2O reduction	2	g COD/m^3	(1)
K_{NO_3}	half saturation coefficients of S_{NO_3}	0.251	g N/m^3	(1)
K_{NO_2}	half saturation coefficients of S_{NO_2}	0.81	g N/m^3	(1)
K_{N_2O}	half saturation coefficients of S_{N_2O}	0.005	g N/m^3	(1)
K_{I1,NO_2}	NO_2^- inhibition constant for nitrate reduction	12	g N/m^3	(3)
K_{I2,NO_2}	NO_2^- inhibition constant for nitrite reduction	10	g N/m^3	(3)
K_{I3,NO_2}	NO_2^- inhibition constant for N_2O reduction	8	g N/m^3	(3)

Source: (1) Ni et al., 2011; (2) Hiatt and Grady, 2008; (3) Schulthess and Gujer, 1996

2.2 Experimental data for model evaluation

Experimental data from a denitrifying culture previously reported in Zheng et al. (2014) are used for the model calibration and validation. To examine the possible effects of ZnO NPs on microbial denitrification, the culture was exposed to 0, 1 and 10 mg/L ZnO NPs in a mineral medium. The concentrations of NO_3^-, NO_2^- and N_2O were estimated at intervals of 4 h for a total time of 24 h. The gaseous and dissolved N_2O was analyzed using gas chromatography with an electron capture detector (ECD). More details of the reactor operation and performance can be found in Zheng et al. (2014).

2.3 Model calibration and validation

The developed model includes 18 stoichiometric and kinetic parameters. Fifteen of these model parameter values are well established in previous studies. Thus, literature values were directly adopted for these parameters (Table 3). The remaining three parameters, i.e., ZnO NPs inhibition constant for nitrate reduction ($K_{I1,Zn}$), ZnO NPs inhibition constant for nitrite reduction ($K_{I2,Zn}$) and ZnO NPs inhibition constant for N_2O reduction ($K_{I3,Zn}$), which are unique to the proposed model and the key parameters governing the denitrification and N_2O production, are then calibrated using experimental data.

Experimental data (nitrate, nitrite, N_2O) from the denitrifying culture exposed to 0 and 1 mg/L ZnO NPs were used to calibrate the model. The parameter values were estimated by minimizing the sum of squares of the deviations between the measured data and the model predictions using the secant method embedded in AQUASIM 2.1d (Reichert, 1998). Model validation was then carried out with the calibrated model parameters using the other set of experimental data (nitrate, nitrite, N_2O) from the culture in the presence of 10 mg/L ZnO NPs.

3. RESULTS

3.1 Model calibration

A two-step procedure was applied to calibrate the model. In the first step, anoxic growth kinetics in the absence of ZnO NPs was tested using the nitrate, nitrite and N_2O data (Fig. 1A). Then the nanomaterial-related parameters was further calibrated using the nitrate, nitrite and N_2O production data in the presence of 1 mg/L ZnO NPs in the second step (Fig. 1B). The calibration of the new model involved optimizing key parameter values by fitting simulation results to the experimental data. The nitrate, nitrite, and N_2O dynamics simulated with the established model are illustrated in Fig. 1. Our model captured all these trends well. The good agreement between these simulated and measured data supported that the developed model properly captures the relationships among N_2O dynamics, nitrate and nitrite concentrations. The calibrated parameter values giving the optimum model fittings with the experimental data are listed in Table 4. The calibrated values show a much lower inhibition constant of ZnO NPs for N_2O reduction compared to those for nitrate and nitrite reduction, indicating a significant contribution of ZnO NPs on N_2O accumulation during denitrification.

3.2 Model validation

Model and parameter validation was performed based on the comparison between the model predictions (using the same parameters shown in Table 3 and 4) and the experimental data under 10 mg/L ZnO NPs (not used for model calibration). The model predictions and the experimental results are shown in Fig. 1C. The validation results show that the model predictions mostly match the measured data in

the validation experiment, which supports the validity of the developed model, further suggesting that N_2O reduction is significantly inhibited by the addition of ZnO NPs.

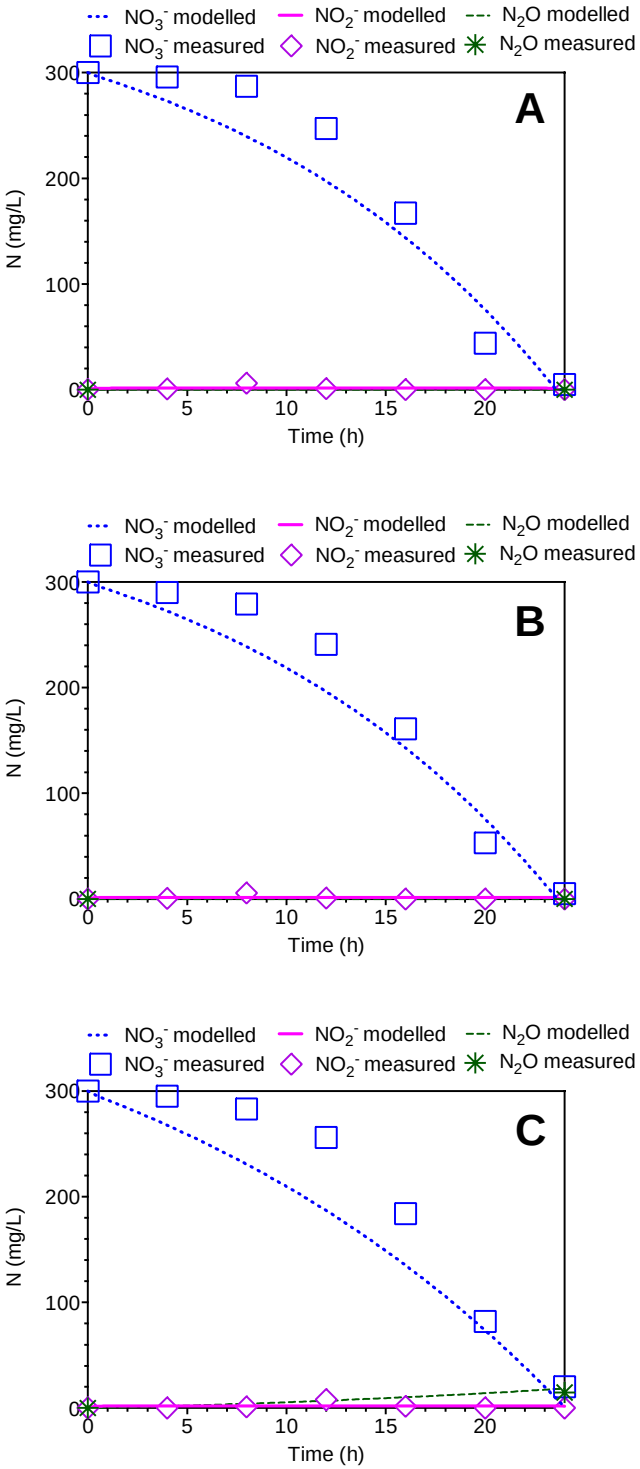

Figure 1 Model calibration and validation results using the experimental data in the presence of: (A) 0 mg/L; (B) 1 mg/L; (C) 10 mg/L ZnO NPs

Table 4 Best-Fit Parameters Describing N_2O Accumulation during Denitrification Process

Parameter	Definition	Values	Unit
$K_{I1,Zn}$	ZnO NPs inhibition constant for nitrate reduction	99	g Zn/m^3
$K_{I2,Zn}$	ZnO NPs inhibition constant for nitrite reduction	32	g Zn/m^3
$K_{I3,Zn}$	ZnO NPs inhibition constant for N_2O reduction	1	g Zn/m^3

4. DISCUSSION

Increasing evidence shows that nanomaterials have a significant influence on N_2O production by heterotrophic denitrifiers. However, the previously proposed N_2O models by heterotrophic denitrifiers are without consideration of nanomaterial effect (Hiatt and Grady, 2008; Ni et al., 2011). These models have been shown to fail to predict N_2O data in the presence of nanomaterials. In this work, a new mathematical model considering the inhibition effect of nanomaterials on denitrification is developed to describe the N_2O production by heterotrophic denitrifiers for the first time. The set of best-fit parameter values are shown in Table 4. The parameter values obtained were robust in their ability to predict nitrate, nitrite, and N_2O dynamics. The validity of this developed model was confirmed by independent data sets under different initial conditions. In addition, the model can be integrated with other wastewater treatment models such as the well-accepted activated sludge models (ASM) to describe plant-wide performance rather than parts of the plant (Kaelin et al., 2009; Ni et al., 2011, 2013).

Modeling results indicated that a much higher amount of N_2O could accumulate in the presence of nanomaterials during denitrification. The reason is that the inhibition effect of nanomaterials on N_2O reduction is much higher than those of nitrate and nitrite reduction. This information could be very useful for future wastewater treatment design. Nevertheless, more verification using other wastewater treatment systems including full-scale applications are still needed for the model to be developed into a useful tool for practical applications. In addition, effects of nanomaterials on nitrification process should also be considered in future study.

CONCLUSIONS

In summary, an integrated mathematical model considering inhibition effects of nanomaterials is developed to describe N_2O emission during denitrification for the first time. The model developed has been applied successfully to reproduce experimental data obtained under different conditions. This work represents a significant step forward toward a unified model for N_2O emission during denitrification.

REFERENCES

Hiatt, W.C. and Grady, C.P. (2008). An updated process model for carbon oxidation, nitrification, and denitrification. *Water Environment Research*, 80(11), 2145-2156.

Kaelin, D., Manser, R., Rieger, L., Eugster, J., Rottermann, K. and Siegrist, H. (2009). Extension of ASM3 for two-step nitrification and denitrification and its calibration and validation with batch tests and pilot scale data. *Water Research*, 43(6), 1680-1692.

Liu, Y., Peng, L., Chen, X. and Ni, B.J. (2015).

Mathematical Modeling of Nitrous Oxide Production during Denitrifying Phosphorus Removal Process. *Environmental Science & Technology*, 49(14), 8595-8601.

Liu, Y., Peng, L., Guo, J., Chen, X., Yuan, Z. and Ni, B.J. (2014). Evaluating the Role of Microbial Internal Storage Turnover on Nitrous Oxide Accumulation During Denitrification. *Scientific reports*, 5, 15138-15138.

Ni, B.J., Peng, L., Law, Y., Guo, J. and Yuan, Z. (2014). Modeling of nitrous oxide production by autotrophic ammonia-oxidizing bacteria with multiple production pathways. *Environmental Science & Technology*, 48(7), 3916-3924.

Ni, B.J., Ruscalleda, M., Pellicer-Nacher, C. and Smets, B.F. (2011). Modeling nitrous oxide production during biological nitrogen removal via nitrification and denitrification: extensions to the general ASM models. *Environmental Science & Technology*, 45(18), 7768-7776.

Ni, B.J., Ye, L., Law, Y., Byers, C. and Yuan, Z. (2013). Mathematical modeling of nitrous oxide (N_2O) emissions from full-scale wastewater treatment plants. *Environmental Science & Technology*, 47(14), 7795-7803.

Pan, Y., Ni, B.J. and Yuan, Z. (2013). Modeling electron competition among nitrogen oxides reduction and N_2O accumulation in denitrification. *Environmental Science & Technology*, 47(19), 11083-11091.

Peng, L., Ni, B.J., Erler, D., Ye, L. and Yuan, Z. (2014). The effect of dissolved oxygen on N_2O production by ammonia-oxidizing bacteria in an enriched nitrifying sludge. *Water Research*, 66(0), 12-21.

Peng, L., Ni, B.J., Ye, L. and Yuan, Z. (2015). The combined effect of dissolved oxygen and nitrite on N_2O production by ammonia oxidizing bacteria in an enriched nitrifying sludge. *Water Research*, 73(0), 29-36.

Ravishankara, A.R., Daniel, J.S. and Portmann, R.W. (2009). Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science*, 326(5949), 123-125.

Reichert, P. (1998). *Computer program for the identification and simulation of aquatic systems.* Aquasim 2.0-user manual, Swiss Federal Institute for Environmental Science and Technology (EAWAG), Dübendorf, Switzerland.

Schulthess, R.V. and Gujer, W. (1996). Release of nitrous oxide (N_2O) from denitrifying activated sludge: Verification and application of a mathematical model. *Water Research*, 30(3), 521-530.

Zheng, X., Su, Y., Chen, Y., Wan, R., Liu, K., Li, M. and Yin, D.Q. (2014). Zinc oxide nanoparticles cause inhibition of microbial denitrification by affecting transcriptional regulation and enzyme activity. *Environmental Science & Technology*, 48(23), 13800-13807.

Zumft, W.G. (1997). Cell biology and molecular basis of denitrification. *Microbiology And Molecular Biology Reviews*, 61(4), 533-616.