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Simultaneous removal of sulfide, nitrate and acetate under denitrifying sulfide removal condition: Modeling and experimental validation

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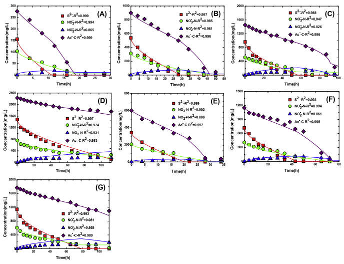
HIGHLIGHTS

- This work developed a mathematical model for DSR process.
- Kinetics of sulfur–nitrogen–carbon and interactions between denitrifiers were studied.
- Kinetic parameters of the model were estimated via data fitting.
- The model described kinetic behaviors of DSR processes over wide parametric range.

GRAPHICAL ABSTRACT

Model evaluation applied to case study 1: (A-G) S^{2-}, NO_3^--N, NO_2^--N, and Ac^--C profiles under initial sulfide concentrations of 156.2 (A), 539 (B), 964 (C), 1490 (D), 342.7 (E), 718 (F), and 1140.7 (G) mg L^{-1}. The solid line represents simulated result and scatter represents experimental result.



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ABSTRACT

Simultaneous removal of sulfide (S^{2-}), nitrate (NO_3^-) and acetate (Ac^-) under denitrifying sulfide removal process (DSR) is a novel biological wastewater treatment process. This work developed a mathematical model to describe the kinetic behavior of sulfur–nitrogen–carbon and interactions between autotrophic denitrifiers and heterotrophic denitrifiers. The kinetic parameters of the model were estimated via data fitting considering the effects of initial S^{2-} concentration, S^{2-}/NO_3^--N ratio and Ac^--C/NO_3^--N ratio. Simulation supported that the heterotrophic denitratation step (NO_3^- reduction to NO_2^-) was inhibited by S^{2-} compared with the denitritation step (NO_2^- reduction to N_2). Also, the S^{2-} oxidation by autotrophic denitrifiers was shown two times lower in rate with NO_2^- as electron acceptor than that with NO_3^- as electron acceptor. NO_3^- reduction by autotrophic denitrifiers occurs 3–10 times slower when S^0 participates as final electron donor compared to the S^{2-}-driven pathway. Model simulation on continuous-flow DSR reactor suggested that the adjustment of hydraulic retention time is an efficient way to make the reactor tolerating high S^{2-} loadings. The proposed model properly described the kinetic behaviors of DSR processes over wide parametric ranges and which can offer engineers with basis to optimize bioreactor operation to improve the treatment capacity.

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1. Introduction

Sulfide, nitrate and organic compounds are pollutants in receiving waters. Nitrogenous compounds in water bodies afford the risks associated with toxicity and bad odors in waters [1,2]. Sulfide is a toxic, corrosive and odorous compound that is harmful to human health that concentrations as low as 10 mg L^{-1} [3,4]. Biological process to remove these pollutants from water has received increasing interests [5]. Autotrophic denitrifiers use reduced sulfur compounds (S^{2-}, S^0, $S_2O_3^{2-}$) as an energy source [6–16], while the heterotrophic denitrifiers use numerous organic compounds as electron donor [17,18].

Reyes-Avila et al. [1] proposed that the rate of nitrate reduction to nitrite is faster via autotrophic denitrification than via heterotrophic denitrification pathway, while the rate of nitrite reduction to nitrogen gas is faster via heterotrophic pathway than via autotrophic pathway. With sufficiently incubated symbiotic heterotrophs and autotrophs, these authors achieved simultaneous removal of sulfide, nitrogen and carbon under well defined denitrifying conditions at loading rates of 0.294 kg S m^{-3} d^{-1}, 0.209 kg N m^{-3} d^{-1}, and 0.303 kg C m^{-3} d^{-1}. Chen et al. [5] promoted these loadings to 3.0 kg S m^{-3} d^{-1}, 1.45 kg N m^{-3} d^{-1}, and 2.77 kg Ac m^{-3} d^{-1} using a novel sludge cultivation strategy. Show et al. [19] reviewed those studies for simultaneous removal of N, S and C.

Kinetic models on heterotrophic denitrifiers alone [2,20–23] or autotrophic denitrifiers alone [24–29] were available. Simultaneous removal of sulfide, nitrate, and acetate in wastewater can be attributed to the mixed culture denitrification [1,2,14]. Limited efforts have been dedicated to model this mixed culture process. Few measurements, with most of them limited one substrate with the rest in excess were available for parameter estimation. Kinetic models on DSR process considering complex interactions between autotrophic and heterotrophic denitrifiers are desired. This study aims at developing a comprehensive kinetic model on autotrophic/heterotrophic denitrification dynamics. The kinetic processes for simultaneous sulfide, nitrate, and carbon (acetate) removal via mixed-culture autotrophic and heterotrophic denitrification were evaluated and validated by comparison with experimental data obtained in this work and in literature.

2. Materials and methods

2.1. Experimental setup and analysis

Sludge sample was collected from a bench-scale expanded granular sludge bed (EGSB) which has been operated for more than six months. The EGSB reactor has a working volume of 4 liter, height of 120 cm and internal diameter of 50 mm. The temperature was maintained at 30 ± 1 °C. The reactor was fed with a synthetic wastewater containing as follows (in mg L^{-1}): S^{2-}, 200; NO_3^--N, 105; Ac^--C, 113.4; NH_4Cl, 50; K_2HPO_4, 50; $NaHCO_3$, 1500; $MgSO_4$, 50; and trace element solution (in mg L^{-1}): EDTA, 50; NaOH, 11; $CaCl_2\cdot 2H_2O$, 7.34; $FeCl_2\cdot 4H_2O$, 3.58; $MnCl_2\cdot 2H_2O$, 2.5; $ZnCl_2$, 1.06; $CoCl_2\cdot 6H_2O$, 0.5; $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 0.5; $CuCl_2\cdot 2H_2O$, 0.14.

To assess the effect of initial sulfide concentration on DSR process, seven different sets of experiments (I–VII) were conducted at substrate levels of 156, 539, 962, 1490 mg S^{2-} L^{-1} for parameter values estimation and of 343, 718, 1140 mg S^{2-} L^{-1} for model verification with S^{2-}/NO_3^--N = 5/6 and Ac^--C/NO_3^--N = 1.26 to meet the stoichiometric requirement for maintaining high performance of DSR process (Table S1) [19]. The inoculums were sampled from the reactor under the steady state (variation of substrate effluent concentrations less than 10% over three HRT's), centrifuged at 10,000 rpm for 20 min, and the pellets anaerobically collected were washed twice with distilled water to remove residual substrates eliminating the disturbance of background. The batch tests were carried out in 250 mL serum bottles and inoculated with 200 mL inoculums with 10,000 mg L^{-1} volatile suspended solids (VSS). The bottles were flushed with argon gas for 5 min to remove oxygen from both the aqueous phase and headspace, and sealed with butyl rubber stoppers and aluminium crimps. Then, the sterile anaerobic stock solution was syringe injected to generate a final substrate concentration as listed above. All serum bottles were regularly sampled anaerobically for the analysis of S^{2-}, NO_3^-, NO_2^-, Ac^- and VSS. The experiments were conducted at 30 °C and pH of 7.5. In order to assess the steady state of the system, successive batch experiments under each tested condition were carried out until the residual substrate concentrations in serum bottle varied less than 10% and then the averaged results of the steady state were recorded and reported herein. The effect of Ac^--C/NO_3^--N molar concentrations ratio (1.26, 2, and 3) on DSR process was determined by conducting additional experiments in serum bottles containing 200 mg L^{-1} S^{2-}, 105 mg L^{-1} NO_3^--N, and 113.4, 180 or 270 mg L^{-1} Ac^--C. All other conditions were similar to those described above. To further validate the proposed model, another experiment was conducted with 200 mg L^{-1} S^{2-}, 140 mg L^{-1} NO_3^--N, and 151.2, 240 or 360 mg L^{-1} Ac^--C (Table S1). Experimental data from Zhou et al. [30] concerning DSR process under different S^{2-}/NO_3^--N molar ratio were used for testing the validity and applicability of the model. Zhou et al. [30] carried out a series of batch experiments with 200 mg L^{-1} S^{2-}, 240 mg L^{-1} Ac^-, and 194, 387.5, 542.5, 620 or 775 mg L^{-1} NO_3^- giving sulfide to nitrate molar ratios of 5/2.5, 5/5, 5/7, 5/8 and 5/10 (Table S1) and the inoculum was obtained from Chen et al. [16].

The concentrations of sulfate, thiosulfate, nitrate, nitrite and acetate in liquor samples after 0.45 μm filtration were measured using ion chromatography (ICS-3000, Dionex, Bannockburn, IL, USA). Aqueous sulfide was determined spectrophotometrically (UV759S, Shanghai, China) with N, N dimethyl-p-phenylene diamine [31]. Concentrations of nitrogenous species (NO, N_2O, N_2) were determined by gas chromatography (GC-6890, Agilent, Foster City, CA, USA). Both the measurement of VSS and COD were performed according to the standard methods [32].

2.2. Model development

A mathematical model was developed on the kinetics involving NO_3^-, NO_2^-, S^{2-} and Ac^- (Fig. S1) [1]. Although the heterotrophic denitratation (NO_3^- to NO_2^-) and denitritation (NO_2^- to N_2) are complicated biological processes [23], the overall heterotrophic denitrification reaction was illustrated as that in Fig. S1. Moreover, since there is sufficient support for S^0 as the dominant end-product of S^{2-} oxidation at high S^{2-}/NO_3^- (or O_2) ratio (about 1.6) [11,33–35], the autotrophic denitrifiers mediating SO_4^{2-} production from S^0 oxidation with NO_3^- or NO_2^- reduction was ignored. NO_3^- was the preferred electron acceptor for S^{2-} oxidation compared NO_2^- [36], thus when NO_3^- was presented in the medium, S^{2-} oxidation coupling NO_2^- reduction process was ignored (except for the S^{2-}/NO_3^--N = 5:2.5 with insufficient nitrate as electron acceptor which would be discussed latter).

The model describes the relationships between three bacterial groups: autotrophic denitrifiers (X_A), heterotrophic denitrifiers (X_H), and residual inert biomass (X_I) and four soluble compounds: NO_3^- (concentration referred to as $S_{NO_3^-}$ for the remaining part of this paper), NO_2^- ($S_{NO_2^-}$), S^{2-} ($S_{S^{2-}}$), and Ac^- (S_{Ac^-}). The units are in mg-S L^{-1} for all sulfur species, mg-N L^{-1} for all nitrogen species, mg-COD L^{-1} for carbon species, and mg-VSS L^{-1} for each biomass. In the present model, there are two processes catalyzed by autotrophic denitrifiers and heterotrophic denitrification, modeled as two sequential processes with individual, reaction-specific