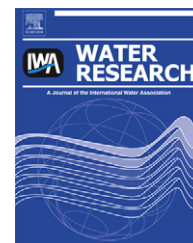


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A pH-control model for heterotrophic and hydrogen-based autotrophic denitrification

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ABSTRACT

This work presents a model to predict the alkalinity, pH, and Langelier Saturation Index (LSI) in heterotrophic and H₂-based autotrophic denitrification systems. The model can also be used to estimate the amount of acid, e.g. HCl, added to the influent (method 1) or the pH set point in the reactor (method 2: pH can be maintained stable by CO₂-sparge using a pH-control loop) to prevent the pH from exceeding the optimal range for denitrification and to prevent precipitation from occurring. The model was tested with two pilot plants carrying out denitrification of groundwater with high hardness: a heterotrophic system using ethanol as the electron donor and an H₂-based autotrophic system. The measured alkalinity, pH, and LSI were consistent with the model for both systems. This work also quantifies: (1) how the alkalinity and pH in Stage-1 significantly differ from those in Stage-2; (2) how the pH and LSI differ significantly in the two denitrification systems while the alkalinity increase is about the same; and (3) why CO₂ addition is the preferred method for autotrophic system, while HCl addition is the preferred method for the heterotrophic system.

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1. Introduction

Heterotrophic and H₂-based autotrophic denitrification processes have been widely tested at the pilot-scale for drinking water treatment, and a few full-scale plants have been built and operated in Europe (Richard, 1989; Rogalla et al., 1990). One important characteristic of denitrification is that it produces approximately one equivalent of strong base for each equivalent of N reduced beyond nitrite (Lee and Rittmann, 2003). One risk from base production is high-pH inhibition. The optimal pH range reported for denitrification is 7–9; values outside this range can retard the denitrification process and lead to accumulation of intermediates: NO₂⁻, NO₂, and N₂O (Kurt et al., 1987; Janda et al., 1988; Lee and Rittmann, 2003; Baeseman et al., 2006; Sengupta and Ergas, 2006).

A second risk is precipitation of hardness cations with common basic anions. Common mineral precipitates in biological denitrification processes includes calcium carbonate (CaCO₃), calcium hydrogen phosphate (CaHPO₄), calcium dihydrogen phosphate (Ca(H₂PO₄)), hydroxyapatite (Ca₅(PO₄)₃OH), and β-tricalcium phosphate (Ca₃(PO₄)₂) (Snoeyink and Jenkins, 1980; Lee and Rittmann, 2003). For example, CaCO₃ precipitation was observed in bench-scale and pilot-scale denitrification reactors using real groundwater (Adham et al., 2004; Ziv-El and Rittmann, 2009).

Inorganic precipitates can have negative impacts on biological denitrification processes. For the H₂-based membrane biofilm reactor, build-up of mineral solids inside the biofilm and at its interface with the membrane can increase mass-transport resistance for H₂ diffusion within the biofilm and

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out of the biofilm, and it also decreases the efficiency of NO_3^- and nutrients transport into the biofilm (Lee and Rittmann, 2003). Another problem is the calcification of fibers, which results from the deposition and accumulation of CaCO_3 (up to 25% of the biofilm mass) on the outside of the biofilm and appears to induce fiber breakage as the fiber becomes inflexible (Adham et al., 2004). Though the negative impact of precipitation on heterotrophic denitrification processes has not been studied as systematically, it is susceptible to precipitation-induced increases in mass-transport resistance, medium clogging, and poor flow distribution.

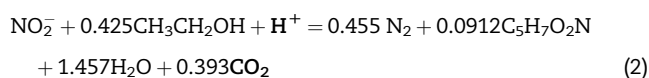
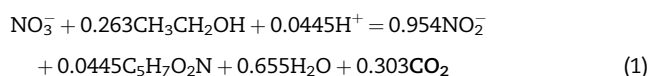
When problems associated with base production and high pH are significant, pH control is necessary for a denitrification process. The pH can be controlled using either of two methods. One is to add acid (e.g., HCl) in the influent at a concentration that balances excessive base production from denitrification (method 1); and the other is to sparge CO_2 into the reactor to control the pH in the reactor at a set point using a pH-control loop (method 2) (Adham et al., 2004).

Though the significance of pH control has been well established in the literature and the two pH-control methods have been proposed (Kurt et al., 1987; Janda et al., 1988; Lee and Rittmann, 2003; Adham et al., 2004; Baeseman et al., 2006; Sengupta and Ergas, 2006; Ziv-El and Rittmann, 2009), pH-control models for denitrification have not been reported to our knowledge. A reliable pH-control model should be able to predict the alkalinity, pH, and precipitation risk within the denitrification reactor. Furthermore, the model should have the ability to estimate the acid concentration in the influent in method 1 and the pH set point in method 2. Therefore, the primary objective of this study is to construct and experimentally test such a model. A second objective is to quantitatively determine the preferred pH-control methods in heterotrophic and H_2 -based autotrophic systems.

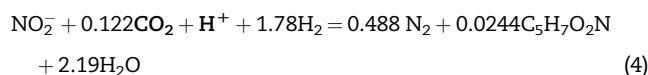
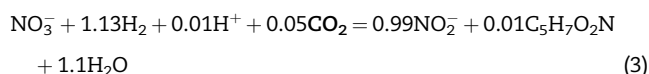
2. Model development

The alkalinity and pH increase in heterotrophic and H_2 -based autotrophic denitrification because nitrite reduction consumes protons (H^+). Proton consumption is illustrated in Eqs. (1)–(4) (based on Rittmann and McCarty (2001)), in which ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and hydrogen gas (H_2) are the heterotrophic and autotrophic electron donors, respectively, and biomass synthesis is indicated by $\text{C}_5\text{H}_7\text{O}_2\text{N}$. A typical biomass retention time of 15 days (Rittmann and McCarty, 2001) was used to develop these equations.

Heterotrophic denitrification:



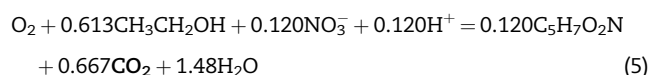
Autotrophic denitrification:



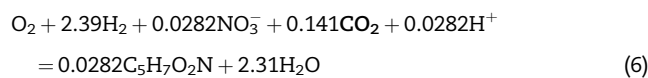
In both systems, nitrite reduction is the predominant source of alkalinity, consuming 1 H^+ equivalent per N equivalent of NO_2^- (highlighted by boldface in Eqs. (2) and (4)). Another factor that affects pH is the net production of CO_2 in heterotrophic systems (highlighted by boldface in Eqs. (1) and (2)) and net consumption of CO_2 in autotrophic systems (highlighted by boldface in Eqs. (3) and (4)). CO_2 is a weak acid, and its addition partially suppresses the pH rise from proton consumption, as well as increases the concentration of total inorganic carbon species.

Dissolved oxygen almost always is present in water to be treated by denitrification. While respiration of O_2 does not consume significant protons, oxygen respiration can affect the pH by CO_2 addition in a heterotrophic system (highlighted by boldface in Eq. (5)) and CO_2 consumption in an autotrophic system (highlighted by boldface in Eq. (6)).

Heterotrophic O_2 respiration:



Autotrophic O_2 respiration:



The feed water's alkalinity buffers pH changes and is another factor that affects pH in the reactor. For natural water, the carbonate system dominates the alkalinity due to the common occurrence and dissolution of carbonate minerals and the presence of carbon dioxide in the atmosphere (Snoeyink and Jenkins, 1980). Addition of certain chemicals to the influent or into the reactor can also affect pH. For example, HCl can be added to the influent to lower the alkalinity and pH, while CO_2 can be sparged inside the reactor to add a weak acid and increase the buffering capacity of the water.

When coupled with an alkalinity mass balance (via the proton condition) in the influent and effluent, the factors mentioned above can be used to predict the effluent pH, alkalinity, and LSI. This constitutes the model whose development is described next in a stepwise manner.

First, the following six assumptions are made:

- (1) Phosphate species are not considered as a buffer due to two factors. First, the concentration of total phosphorus in most natural groundwater is very low due to its precipitation with calcium (Snoeyink and Jenkins, 1980). Second, phosphate added as a nutrient and dosed at the stoichiometric requirement for P uptake in biomass synthesis provides negligible phosphate species in the reactor, compared to carbonate species.
- (2) Other natural buffering species (e.g., ammonium) also are neglected, because they are trivial compared to the carbonate species, which account for most of the total alkalinity (Snoeyink and Jenkins, 1980).

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