



Direct delivery of CO₂ into a hydrogen-based membrane biofilm reactor and model development



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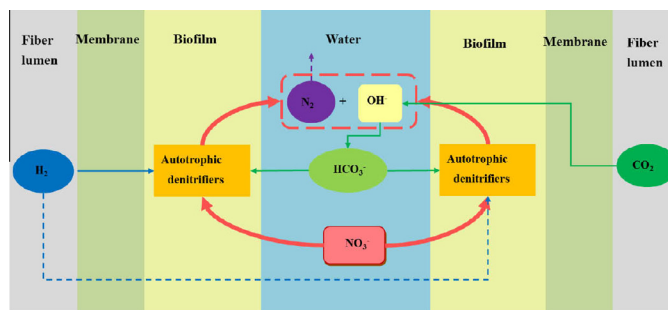
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HIGHLIGHTS

- Direct delivery of CO₂ into fibers improved the hydrogen-based MBfR performance.
- A mathematical model was built up to predict pH and LSI in the system.
- Mis-distributions of H₂ and CO₂ caused disparity of biomass communities on different modules.
- Functional bacteria existed on both H₂ and CO₂ modules.

GRAPHICAL ABSTRACT



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ABSTRACT

A new hydrogen-based hollow fiber membrane biofilm reactor (MBfR) with double membrane technique was developed in this work and systematic research was conducted. A mathematical model was built up to predict pH and Langelier Saturation Index (LSI) in the hydrogen-based autotrophic denitrification system with minimal error. The model tested with varied CO₂ pressures identified that increasing CO₂ pressure resulted in pH decrease and prevention from precipitation. Long-term performance of the new MBfR was also evaluated. When CO₂ was delivered at 0.05 MPa, 99% nitrate was removed with a constant neutral pH in the reactor. In the long-term experiment, mis-distributions of H₂ and CO₂ caused disparity of biomass communities on the H₂ and CO₂ modules, but functional bacteria existed on both modules; this suggested that despite of mis-distribution, bubbleless H₂ was still able to be transported by recirculation to the CO₂ module and became available for the bacteria on the module.

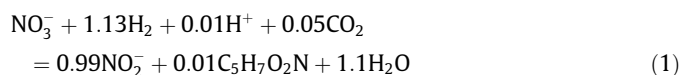
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1. Introduction

Nitrate is introduced into groundwater from a variety source, such as agricultural activities, poor sewer systems, wastewater, and industrial activities. Nitrate in drinking water is a cause of methemoglobinaemia in infants, and the permissible limit of the World Health Organization (WHO) is 10 mgN/L [1,2]. NO₃⁻ spurs

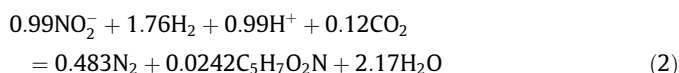
eutrophication of surface waters, and wastewater standards often are much lower than 10 mgN/L [3].

The H₂-based membrane biofilm reactor (MBfR) was developed to remove nitrate using hydrogen gas as a clean electron-donor substrate for autotrophic denitrifiers [4–7]. One major characteristic of denitrification is base production that can lead to pH increase [7]. Base production in autotrophic denitrification is illustrated in Eqs. (1) and (2) [8],



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in which hydrogen gas (H_2) is the electron donor and biomass synthesis is indicated by $\text{C}_5\text{H}_7\text{O}_2\text{N}$. Nitrite reduction is the predominant source of alkalinity, consuming 1 H^+ equivalent per N equivalent of NO_2^- . Denitrification also consumes some inorganic carbon for biomass synthesis, although its impact is small compared to the generation of base.

One risk from proton consumption is high-pH inhibition [9]. For example, Lee and Rittmann (2003) reported that the optimal pH for autotrophic denitrification is in the range 7.7–8.6, and a significant decrease in nitrate removal rate and a dramatic increase in nitrite accumulation occur with pH over 8.6. Another risk of high pH is the precipitation of hardness cations with common basic anions. Common mineral precipitates in biological denitrification processes include calcium carbonate (CaCO_3), calcium hydrogen phosphate (CaHPO_4), calcium dihydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$), hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) [10]. Precipitation of mineral solids on the membrane can lead to long-term loss of gas permeability and to embrittlement of the membrane in an MBfR [4,7]. Consequently, pH control is necessary for autotrophic denitrification.

Phosphate buffer ($\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$) has been used extensively as a pH buffer in bench-scale MBfR studies [11–18]. However, phosphate also can lead to surface-water eutrophication [19,20] when the effluent is discharged to a surface water, and it also has been reported to stimulate microbial growth in distribution systems in special circumstances [21]. According to stoichiometry, when the influent nitrate is 10 mg N/L, the concentration of phosphate buffer must be above 100 mg P/L buffer ($\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$) to keep the effluent pH below 8.0.

A better alternative for pH control is carbon dioxide gas (CO_2), which also is the inorganic carbon source for H_2 -based autotrophic denitrification and is not harmful to humans or the aquatic environment. Tang et al. (2011) sparged CO_2 directly into pilot-scale MBfRs and successfully maintained the effluent pH below 8.0. Commercial-scale MBfRs use CO_2 sparging to control pH. A pH probe actuates CO_2 sparging whenever the pH inside the MBfR exceeds a set point, such as 7.5–8.0.

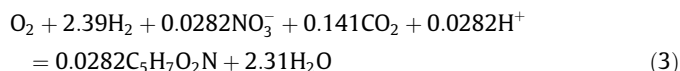
While effective for pH control, CO_2 sparging can lead to CO_2 loss in the off-gas, which wastes CO_2 and increases operating costs. Here we apply a novel double-membrane technique to overcome the drawbacks of CO_2 sparging. CO_2 is delivered to hollow-fibers simultaneously with H_2 so that it diffuses into water in the same “bubbleless” way as H_2 [22]. This approach offers a means to eliminate CO_2 loss by off-gasing. We investigated the performance of an MBfR when using different CO_2 pressures and developed a model to predict the effluent pH and precipitation risk.

2. Model development

2.1. Model overview

Three major factors affect the pH in our MBfR system. The first factor is the alkalinity present in feed water. For natural water, the carbonate system dominates the alkalinity due to the common occurrence and dissolution of carbonate minerals and the presence of CO_2 in the atmosphere [10]. The second factor is the CO_2 addition (via membrane diffusion). CO_2 is the acid form of inorganic carbon, and its addition lowers the pH while increasing the total inorganic carbon. The third factor is the denitrification and oxygen respiration processes in our system. The base production and consumption of CO_2 in denitrification were illustrated in Eqs. (1) and (2). 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 consumption in an autotrophic system (Eq. (3)) [23]:



When coupled with an alkalinity mass balance (via the proton condition) in the influent and effluent, the factors mentioned above can be used to create a model to predict the effluent pH and alkalinity, from which the Langelier Saturation Index (LSI) can be computed to give an indication of the precipitation potential for CaCO_3 , the most common mineral precipitate.

2.2. Assumptions and simplifications

The model makes the following simplifying assumptions, which are based on Tang et al. (2011):

- (1) The pH inside the biofilm does not differ greatly from that in the bulk liquid. Therefore, the conditions in the bulk liquid can be used to assess alkalinity, pH, and LSI based on denitrification reactions occurring in the biofilm.
- (2) Inorganic-carbon species are the only buffers, since phosphate concentrations normally are low [24].
- (3) Calcium carbonate (CaCO_3) is the only precipitate. Calcium phosphate species are neglected, since the phosphate concentration typically is low. $\text{Mg}(\text{OH})_2$ also is neglected, because it is super-saturated only at pH values that are too high to be relevant for biological treatment [10].
- (4) The reactor is a closed system, which means that CO_2 does not exchange between the reactor and the atmosphere.
- (5) Activity coefficients are ignored, since most waters for denitrification have a low salinity.

2.3. Theoretical approach

The alkalinity in the influent and effluent of the reactor is tabulated by coupling the proton condition, the total concentration of inorganic carbonate species (C_T), and the hydrogen-ion concentration (Eq. (4)).

$$[\text{Alk}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \\ = 2[C_T] \frac{1}{1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2}} \\ + [C_T] \frac{1}{1 + \frac{[\text{H}^+]}{K_1} + \frac{[\text{H}^+]}{K_2}} + \frac{10^{-14}}{[\text{H}^+]} - [\text{H}^+] \quad (4)$$

in which K_1 , K_2 = acid/base equilibrium constants for H_2CO_3 and HCO_3^- ($K_1 = 10^{-6.3}$, $K_2 = 10^{-10.3}$ at 2 °C); and C_T = total concentration of inorganic carbon species in the influent and effluent (mole/L).

Eq. (4) can be used to obtain $C_{T,\text{in}}$, since $[\text{Alk}]_{\text{in}}$ and $[\text{H}^+]_{\text{in}}$ can be measured. Then $C_{T,\text{out}}$ can be solved by calculating the change of total concentration of inorganic carbon species due to denitrification (Eqs. (1) and (2)), oxygen respiration (Eq. (3)), precipitation, and external CO_2 addition. $[\text{NO}_3^-]_{\text{in}}$, $[\text{NO}_3^-]_{\text{out}}$, $[\text{Ca}^{2+}]_{\text{in}}$, $[\text{Ca}^{2+}]_{\text{out}}$, $[\text{O}_2]_{\text{in}}$, and $[\text{O}_2]_{\text{out}}$ are experimentally measured model inputs and the concentration of the external CO_2 addition $[\text{CO}_2]$ can be calculated via CO_2 permeability, which can be obtained from Siqing et al. (2015) [25].

$[\text{Alk}]_{\text{out}}$ can be solved by calculating the change of alkalinity due to denitrification (Eqs. (1) and (2)), oxygen respiration (Eq. (3)), precipitation, and external acid addition. $[\text{NO}_3^-]_{\text{in}}$, $[\text{NO}_3^-]_{\text{out}}$, $[\text{Ca}^{2+}]_{\text{in}}$, $[\text{Ca}^{2+}]_{\text{out}}$, $[\text{O}_2]_{\text{in}}$, and $[\text{O}_2]_{\text{out}}$ are experimentally measured model inputs and the external acid addition is not involved in our research.

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