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Simplified model for hydrogenotrophic denitrification in an unsaturated-flow pressurized reactor

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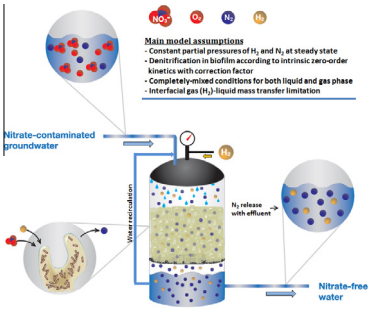
HIGHLIGHTS

- A model for H_2-based denitrifier unsaturated-flow pressurized reactor is presented.
- The rate constant and k_La were determined for different recirculation flow rates.
- A correction factor for the rate constant was successfully developed.
- High correlation between model and experimental results was achieved.
- Max. denitrification rate of 7.5 gNO_3^--N/($L_{reactor}$·d) was predicted by the model.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel unsaturated-flow pressurized reactor (UFPR) for hydrogenotrophic denitrification was recently developed. The reactor is characterized by safe and economic operation since gas purging intrinsic to conventional H_2-based systems is not required and H_2 loss is limited only to the dissolved H_2 in the effluent. Additionally, high denitrification rates are achieved by high water recirculation over plastic carriers with high surface area.

This paper focuses on mathematical modeling of the novel reactor, based on its unique and specific characteristics. The continuously stirred hydraulic regime formed due to the relatively high recirculation flow rate required for efficient media wetting and the homogeneous gas phase in the closed reactor headspace, simplified the model design for the UFPR. The reaction rate constant and the overall volumetric gas (H_2)-liquid mass transfer coefficient (k_La) were determined for different recirculation flow rates at steady state. A rate constant correction factor β was developed to compensate for pH changes within the biofilm, deviation from intrinsic zero-order degradation kinetics and non-homogeneity of the biofilm. Model validation tests showed a high correlation between experimental and model results for various combinations of operational parameters. Results from the model showed that high denitrification rates of up to 7.5 g NO_3^--N/($L_{reactor}$·d) together with H_2 utilization efficiencies above 90% can be achieved by the UFPR.

1. Introduction

Hydrogen-based denitrification systems for treating nitrate-contaminated groundwater have gained a lot of attention in recent years. The clear advantages of hydrogenotrophic systems over reactors using traditional organic compounds as electron donors for reducing NO_3^- have been extensively discussed in previous works and include mainly low biomass yield, minimization of reactor clogging and reduction of post-treatment costs. However, safety concerns, poor utilization of H_2 gas and low denitrification rates are the main drawbacks still limiting the implementation of this method in full scale [1].

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Nomenclature

A	total active surface area for bacterial growth [m^2/m^3]
β_H	empirical correction factor for K_H
β_N	empirical correction factor for K_N
C_{H_2}	Henry's constant for H_2 gas [mg/(L·bar)]
C_{N_2}	Henry's constant for N_2 gas [mg/(L·bar)]
$D_{f,H}$	diffusion coefficient of H_2 in the biofilm [m^2/d]
$D_{f,N}$	diffusion coefficient of NO_3^- in the biofilm [m^2/d]
H^*	equilibrium concentration of dissolved H_2 [mg/L]
H_{av}	average concentration of dissolved H_2 along the filter [mg/L]
H_e	effluent concentration of dissolved H_2 [mg/L]
H_i	inlet concentration of dissolved H_2 [mg/L]
K_H	half-order coefficient for H_2 degradation [$(mg/L)^{0.5}$/d]
K_N	half-order coefficient for NO_3^--N degradation [$(mg/L)^{0.5}$/d]
$k_{0f,H}$	degradation rate of H_2 in the biofilm [g/($L_{biofilm}$·d)]
$k_{0f,N}$	degradation rate of NO_3^--N in the biofilm [g/($L_{biofilm}$·d)]
k_La	overall volumetric gas-liquid mass transfer coefficient of H_2 [1/d]
N_{av}	average concentration of NO_3^--N along the filter [mg/L]
N_e	effluent concentration of NO_3^--N [mg/L]
N_i	inlet concentration of NO_3^--N [mg/L]
$N_{2,T}$	total dissolved N_2 concentration [mg/L]
$N_{2,atm}$	dissolved N_2 concentration originated from atmospheric N_2 gas [mg/L]
$N_{2,denit}$	dissolved N_2 concentration originated from denitrification [mg/L]
P_{H_2}	partial pressure of H_2 gas in the reactor [bar]
P_{N_2}	partial pressure of N_2 gas in the reactor [bar]
P_T	total pressure in the reactor [bar]
$q_{max,N}$	maximal specific degradation rate of NO_3^--N [g/(gVSS·d)]
Q	volumetric flow rate [mL/min]
Q_R	recirculation flow rate [mL/min]
r_H	overall degradation rate of H_2 [g/($L_{reactor}$·d)]
r_N	overall degradation rate of NO_3^--N [g/($L_{reactor}$·d)]
t	time component [d]
V	reactor volume [L]
υ	stoichiometric mass ratio [g H_2/g NO_3^--N]
X_f	biofilm density [gVSS/mL]

A novel unsaturated-flow pressurized reactor (UFPR) for hydrogenotrophic denitrification of groundwater operating at high denitrification rates together with minimal hydrogen loss and low risk was presented and described in an earlier publication [2]. The main novelty of this reactor is the operation under a pressurized closed headspace without any gas discharge. The common concern of N_2 gas build-up in a pressurized denitrifying system is addressed by the idea that in continuous operation a gas-liquid equilibrium is achieved according to Henry's law and the effluent water carries excess N_2 gas out of the reactor. Since N_2 reaches equilibrium and is not accumulated over time, there is no need for gas discharge and H_2 loss to atmosphere is limited only to the dissolved H_2 in the effluent. The operation under low-pressurized headspace consisting uniquely of H_2 and N_2 gases prevents hazardous H_2—O_2 contact and minimizes the risk of explosion in case of failure.

On top of the inherent advantages of safety and economics, the UFPR was designed to ensure high denitrification rates in comparison to existing hydrogenotrophic systems. The reactor is operated under an unsaturated-flow regime as a trickling filter where water is recirculated over plastic biofilm carriers with high surface area. The high surface area of the plastic carriers serves as a platform for both bacterial growth and gas (H_2)-liquid mass transfer, thus enabling high denitrification rates. Utilization of plastic carriers with very high surface area in unsaturated-flow reactors is susceptible to reactor clogging and is more commonly implemented in autotrophic trickling filters with low cell yield as in nitrification or the UFPR. In these systems very often a relatively high recirculation flow rate is applied in order to achieve full media wetting [3]. The recirculation ratio (Q_R/Q) applied in the UFPR varies between 3 and 18, which is about one order of magnitude higher than the recirculation ratio in traditional trickling filters [4]. This high recirculation ratio, together with the assumption of a well-mixed and homogeneous gas phase in the closed headspace, differentiates the UFPR from traditional trickling filters; especially in terms of reactor hydraulics.

Trickling filter models attempt to take into account various processes affecting the contaminant degradation such as gas flow, phase transfer, diffusion within the biofilm, biological growth and structural changes of the biofilm. Due to the problematic characterization of the unsaturated flow through the carriers and its poorly understood mechanics, most of the models and design approaches of trickling filters are empirical and therefore case specific [4–6]. The main objective of the current study is to develop a simplified and easy-to-use model for basic design and performance forecast of the UFPR, based on its unique operational conditions of unsaturated flow with high recirculation flow rate and operation in a closed headspace. Special focus is given to the effect of recirculation flow rate on reactor performance.

2. Considerations and guidelines for model design

Based on model objectives, the following assumptions were taken for model design: (1) steady-state conditions exist for all phases (gas, liquid and biofilm); (2) the biofilm is planar, one dimensional and completely homogeneous with uniform density X_f; (3) the diffusion layer near the biofilm surface is neglected, i.e., the substrate concentrations on the biofilm surface equals the bulk concentration; (4) mathematical models of hydrogenotrophic denitrification are generally described by zero-order kinetics when substrate concentrations are much higher than the half-saturation constants (i.e. $S_{NO_3} \gg K_{NO_3}$ and $S_{H_2} \gg K_{H_2}$) [7–9]. Therefore, a NO_3^--N reduction based on zero-order kinetics in the biofilm is assumed. Importantly, application of a zero-order kinetic model in biofilm reactors should be considered more carefully due to the gradual decrease of substrate concentration with increasing depth of the biofilm, as was also discussed by Atkinson et al. [10]. Moreover, in the case of denitrification, the pH gradient formed within the biofilm might also affect the maximal specific degradation rate q_{max} along the biofilm. Accordingly, a correction factor is added to the standard zero-order-based reaction rate constant for degradation in the biofilm to take into account these factors as will be explained later; (5) due to the high diffusivity of H_2 in the gas phase of the UFPR, the rate limiting step for H_2 transfer is the interfacial gas-liquid transfer; (6) in the UFPR a high recirculation ratio is applied so that the entire trickling filter may be considered as a single CSBR (continuously stirred biofilm reactor) unit with a uniform concentration of NO_3^--N throughout the reactor. This assumption can be applied also for the dissolved H_2 concentration due to the following reason: since the reactor headspace is sealed (i.e. pressurized), no natural gas convection (i.e. air draft) occurs as in traditional trickling filters. Therefore, assuming good mixing of the gas phase by molecular diffusion, any gradient of