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High-rate hydrogenotrophic denitrification in a pressurized reactor

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HIGHLIGHTS

- A novel pressurized H_2-based reactor for denitrification is presented.
- The common misconception of N_2 accumulation in closed headspace is eliminated.
- At steady-state, N_2 pressure remains constant and no gas purging is required.
- The reactor presents high rates of approximately 5 g NO_3^--N/($L_{reactor}$ d).
- Hydrogen utilization efficiencies of up to 96.9% are achieved.

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ABSTRACT

Most conventional hydrogenotrophic denitrification reactors based on packed- or fluidized-bed present a similar H_2 delivery scheme of continuous gas purging to the atmosphere in order to improve H_2 transfer rates and enable discharge of N_2 gas produced during denitrification. This operation results in a significant release of H_2 gas to atmosphere with its related economic and safety concerns. The current research proposes a novel pressurized high-rate hydrogenotrophic reactor for denitrification without gas purging. The investigation performed refutes a prevalent notion that N_2 gas accumulates in the headspace of a closed reactor during denitrification. Instead, this research shows that during continuous operation a gas–liquid equilibrium is established in the reactor according to Henry's law and excess N_2 gas is carried out by the effluent in dissolved form. Therefore, no gas purging is required and H_2 loss is limited only to the dissolved H_2 in the effluent. As a consequence, a simple low-cost and high-rate reactor with closed headspace can be designed for denitrification. The proposed reactor is operated as a trickling filter where water is recirculated over biofilm carriers with high surface area.

The feasibility of the proposed reactor was shown for two effluent concentrations of 10 and 1 mg NO_3^--N/L. Average denitrification rates of 2.1 ± 0.2 and 1.06 ± 0.06 g NO_3^--N/($L_{reactor}$ d) with H_2 utilization efficiencies of 92.8% and 96.9% were measured for the two effluent concentrations, respectively. Higher denitrification rates of up to 5 g NO_3^--N/($L_{reactor}$ d) were observed at higher recirculation flow rates and higher partial pressures of H_2.

1. Introduction

Biological denitrification of nitrate-contaminated groundwater has been widely investigated with both heterotrophic [1,2] and autotrophic [3] cultures. The more common process of heterotrophic denitrification, where nitrate is reduced by various organic compounds, is characterized by high efficiency and high denitrification rates [4]. However, the main drawbacks of biological denitrification of drinking water using heterotrophic cultures are the potential risk of microbial contamination of the treated water, the remaining of organic metabolites and microbial products, excess waste biomass and reactor clogging, formation of disinfection by-products (DBP) and costly post-treatment [5].

Autotrophic denitrification using reduced inorganic compounds as electron donor and CO_2 as carbon source, overcomes most of the above disadvantages. Reactor clogging, waste sludge production and post-treatment costs are reduced due to significantly less biomass growth. Autotrophic denitrification using H_2 gas, also named hydrogenotrophic denitrification, is an excellent choice because of its clean nature and low biomass yield, as well as the fact that H_2 does not persist in the treated water. Moreover, H_2 is less expensive than other electron donors. However, the main drawbacks limiting the use of hydrogenotrophic denitrification are safety concerns, poor H_2 utilization and low denitrification rates due to low solubility of H_2 with the resulting low transfer rate [6].

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A summary of the prior research on hydrogenotrophic denitrification is shown in Table 1. Most of the investigated packed/fluidized-bed hydrogenotrophic systems lack efficient and safe delivery of H_2 and present a similar H_2 delivery scheme of gas sparging in either a separate H_2 saturation tank [7] or a main reactor tank [8]. Membrane biofilm reactors (MBfRs) and bio electrochemical reactors (BERs) were both designed to enable more efficient, safer and high-rate H_2 delivery to biofilm. The MBfR technology has already been proven successfully on both pilot scale and even full scale. However, results from MBfRs reveal low denitrification rates due to the limited surface area available for biofilm growth [9–12]. Moreover, MBfRs are costly due to the high cost of membrane replacement and cleaning because of fouling [13]. BERs also suffer from limited surface area available for biofilm growth and low denitrification rates [14–16]. Additionally, a gradual scale formation on the surface of the cathode suppresses H_2 production [17].

Table 1 shows that H_2-based reactors reach denitrification rates above 0.5 g NO_3^--N/($L_{reactor}$ d) only when a wasteful H_2 delivery scheme of bubbling was applied (e.g. packed- and fluidized-bed systems with bubbling). Safe and economic systems (e.g. BERs and MBfRs) could not reach high rates, mainly due to a limited surface area for biofilm growth. In other words, a process combines high rates with safe and economic operation is yet to be achieved.

To the best of our knowledge, there are no reports of hydrogenotrophic systems based on pressurized reactors without gas purging. The main reason is assumed to be a possible misconception claiming that during denitrification in a closed-headspace reactor, N_2 gas build-up occurs in the reactor's headspace and requires intermittent or continuous gas purging.

The current work presents a novel pressurized high-rate hydrogenotrophic reactor without gas purging, as shown in Fig. 1. The reactor is described in detail in Section 2. Briefly, the operation of the reactor maintains a gas–liquid equilibrium without pressure build-up of N_2 gas and without any H_2 gas loss from the gas phase. The reactor is operated under an unsaturated-flow regime as a trickling filter where water is recirculated over the biofilm carriers. Plastic carriers with large surface area are used and together with high mass transfer of H_2 gas, high denitrification rates are achieved [18]. The main objective of the following research is to prove the suggested concept that during continuous operation N_2 gas reaches a gas–liquid equilibrium without further accumulation in the closed headspace of denitrifying reactor. The second goal is to show how the new concept facilitates the design of an applicable reactor capable of operating at high denitrification rates.

Table 1
Denitrification rates of various systems and H_2 delivery schemes.

Reactor type/H_2 delivery scheme	Denitrification rate [g NO_3^--N/($L_{reactor}$ d)]	References
BER/as described above	0.06	[14]
	0.393	[23]
MBfR/as described above	0.182	[11]
	0.2–0.5	[9]
Packed-bed/H_2 saturation in separate tank with electrolysis	0.25	[17]
Packed-bed/H_2 saturation in separate tank with gas-permeable membrane	0.471	[24]
Packed-bed/direct bubbling	2.5[a]	[8]
Packed-bed/unsaturated flow (trickling filter)	0.036	[25]
Fluidized-bed/bubbling in separate saturation tank	0.552	[7]
Fluidized-bed/direct bubbling	0.6–0.7	[26]
Suspended growth with MBR/saturation in separate tank under pressure	0.11	[27]

[a] The denitrification rate is 6.2 g NO_3^--N/(L d) based on media porosity.

2. Description of the proposed reactor

A schematic diagram of the proposed reactor is illustrated in Fig. 1. The reactor is operated under an unsaturated flow regime where water is recirculated and trickled over biofilm carriers. The reactor is continuously fed with nitrate-contaminated groundwater. When enough liquid collects at the reactor's bottom and reaches a level switch, a drain valve is opened and treated water is released (i.e. pulsed discharge). The reactor's gas phase is closed to the atmosphere and pressurized by the supplied H_2 and the N_2 formed during denitrification. An additional source of N_2 gas is atmospheric N_2 dissolved in the influent water and carried into the reactor, where it can desorb.

The key feature of the proposed reactor is its ability to reach a gas–liquid equilibrium and maintain constant partial pressures of both H_2 and N_2 gases without further accumulation of N_2 gas over time. This ability is achieved only under continuous operation where effluent water carries excess of N_2 gas out of the reactor. At the beginning of the process, N_2 in the liquid phase includes only atmospheric N_2 (i.e. dissolved N_2 originating from air), thus partial pressure of N_2 in the gas phase is approximately 0.8 bars (as in normal air mixture). The reactor is then pressurized by H_2 gas to the desired total pressure. Over time N_2 gas is produced by hydrogenotrophic denitrification and exchanges H_2 gas in the gas phase, so the partial pressure of N_2 gas increases and the partial pressure of H_2 gas decreases. At some point, the partial pressure of N_2 gas reaches a level correlating with the terminal N_2 concentration in the liquid phase according to Henry's law, a gas–liquid equilibrium is achieved and the partial pressures of both N_2 and H_2 gases in the gas phase remain constant. Therefore, the final partial pressure of N_2 gas depends directly on N_2 concentration in the influent (i.e. the atmospheric N_2) and the concentration of NO_3^--N removed and converted to N_2 gas.

In order to introduce H_2 gas and enable denitrification, the total pressure applied (i.e. pressure of N_2 and H_2) must be higher than the partial pressure of N_2 at gas–liquid equilibrium. Fig. 2 presents the partial pressure of N_2 in the reactor at gas–liquid equilibrium and 25 °C, as a function of NO_3^--N concentration removed according to Eq. (1). In Eq. (1), P_{N_2} is the partial pressure of N_2 in the reactor, $P_{N_2,atm}$ is the N_2 pressure resulting from atmospheric N_2 (i.e. ~0.8 bars) and $P_{N_2,denitrification}$ is the N_2 pressure resulting from N_2 gas produced during denitrification and calculated by Eq. (2). In Eq. (2), $C_{N_2,denitrification}$ is the concentration of NO_3^--N converted to N_2, and H_{N_2} is Henry's constant (17 mg N_2/(L bar) at 25 °C). The calculations for $C_{N_2,denitrification}$ are based on previous suggested stoichiometry of hydrogenotrophic denitrification according to Eq. (3). For simplification and due to low biomass yield, it was assumed that all NO_3^--N consumed was converted to N_2 [6].

$$P_{N_2} = P_{N_2,atm} + P_{N_2,denitrification} \tag{1}$$

$$P_{N_2,denitrification} = C_{N_2,denitrification}/H_{N_2} \tag{2}$$

$$\begin{aligned} &NO_3^- + 3.03H_2 + H^+ + 0.229H_2CO_3 \\ &\quad \rightarrow 0.477N_2 + 3.6H_2O + 0.0458C_5H_7O_2N \end{aligned} \tag{3}$$

For lower concentrations of NO_3^--N removed, less N_2 is produced by denitrification per volume of water so the resulting partial pressure of N_2 is lower. Alternatively, for a specific total pressure of N_2 and H_2, a lower NO_3^--N concentration removal will result in a lower partial pressure of N_2 with a corresponding higher partial pressure of H_2. For typical conditions of an inlet NO_3^--N concentration of 25 mg/L and a projected reactor effluent at drinking water regulations of 10 mg NO_3^--N/L (15 mg/L NO_3^--N removed), the partial pressure of N_2 in the reactor at gas–liquid equilibrium is calculated to be 1.7 bars (see Fig. 2). Therefore, the minimal total