

Pressurized hydrogenotrophic denitrification reactor for small water systems

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Abstract

The implementation of hydrogenotrophic denitrification is limited due to safety concerns, poor H₂ utilization and low solubility of H₂ gas with the resulting low transfer rate. The current research proposes a novel pressurized hydrogenotrophic reactor for denitrification. The main novelty of the reactor is the operation under closed headspace without any gas purging to release N₂ gas. The investigation performed refutes a prevalent notion that N₂ 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 N₂ gas is carried out by the effluent in dissolved form. Therefore, no gas purging is required and H₂ loss is limited only to the dissolved H₂ in the effluent. 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 NO₃⁻-N/L. Hydrogen gas utilization efficiencies of 92.8% and 96.9% were measured for the two effluent concentrations, respectively. Reactor modelling predicted high denitrification rates above 4 g NO₃⁻-N/(L_{reactor}·d) at reasonable operational conditions. The residual H₂ from the main reactor unit can be further consumed by ClO₄⁻ reducing bacteria, thus increasing H₂ utilization efficiency up to almost 100%.

Keywords

Drinking water; hydrogenotrophic denitrification; hydrogen utilization; nitrate removal; nitrogen accumulation; pressurized reactor

INTRODUCTION

The benefits of using H₂ gas as the electron donor for biological denitrification of groundwater were discussed previously. Among them, the clean nature and the low cell yield of hydrogenotrophic bacteria are the major advantageous features, resulting in small waste sludge production, minimal reactor clogging and reduced-cost post treatment. Moreover, H₂ gas is less expensive than other electron donors per electron-equivalent delivered for contaminant reduction (two-thirds the price of methanol). Therefore, H₂ gas is an excellent choice for decentralized and small water systems where a simple and reliable technology with minimal manpower control is required. However, the main drawbacks limiting the use of hydrogenotrophic denitrification are safety concerns, poor H₂ utilization and low denitrification rates due to low solubility of H₂ with the resulting low transfer rate (Karanasios, Vasiliadou, et al., 2010).

A summary of the prior technology available for hydrogenotrophic denitrification was given elsewhere (Epsztein, Beliaevski, et al., 2016a). Among these technologies, the membrane biofilm reactor (MBfR) gained the most attention due to its safe and economic gas delivery system with close to 100% utilization efficiency of H₂ gas. However, results from MBfRs reveal low denitrification rates due to the limited surface area available for biofilm growth (Lee and Rittmann, 2002; Ergas and Reuss, 2001; Hwang, Cicek, et al., 2010; Zhao, Valencia, et al., 2014). Moreover, MBfRs are susceptible to fouling and therefore require intensive control for cleaning and replacement of membranes (Lee and Rittmann, 2003).

To the best of our knowledge, there are no reports of hydrogenotrophic systems based on pressurized reactors without any gas discharge. The main reason is assumed to be a possible misconception suggesting that during denitrification in a closed-headspace reactor, N₂ gas build-up

occurs in the reactor's headspace and requires intermittent (Rezania, Oleszkiewicz, et al., 2007) or continuous (Grommen, Verhaege, et al., 2006) gas purging. The purging performed results in significant H₂ loss to atmosphere with the related safety and financial consequences.

The current research presents a novel pressurized hydrogenotrophic denitrification reactor based on a new concept suggesting that N₂ gas produced during denitrification does not accumulate in a closed-headspace reactor and therefore purging is not required (see explanation in the next section). The reactor is characterized by high denitrification rates, minimal hydrogen loss and low risk with safe effluent discharge. The simplicity of the new reactor may encourage its full implementation, especially in remote and small water plants, where process monitoring and control should be minimized.

EXPLANATION OF THE NEW CONCEPT

The main novelty of the reactor is the operation under a pressurized closed headspace without any gas discharge. The common concern of N₂ gas build-up in a pressurized denitrifying system is addressed by the idea that in continuous operation the effluent water carries excess N₂ gas out of the reactor. The dissolved N₂ concentration in the reactor reaches a constant level according to the concentration of NO₃⁻-N removed and therefore the partial pressure of N₂ in the reactor must also remain constant and correlate with the dissolved N₂ concentration according to Henry's law. Since N₂ reaches equilibrium and is not accumulated over time, there is no need for gas discharge and the risky and economic H₂ loss to atmosphere through gas purging of the reactor is prevented. Hydrogen loss is therefore limited only to the dissolved H₂ in the effluent. The operation under low-pressure headspace consisting uniquely of H₂ and N₂ gases prevents hazardous H₂-O₂ contact and minimizes the risk of explosion in case of failure.

In its original version presented in the current paper, the reactor is operated under an unsaturated flow regime as a trickling filter where water is recirculated and trickled over the biofilm carriers. Plastic carriers with high surface area are used and together with high mass transfer of H₂ gas due to the unsaturated flow, high denitrification rates are achieved. 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 effluent water is released (i.e. pulsed discharge).

An alternative version of the pressurized reactor, using a submerged bed where gas is recirculated from the reactor's headspace to the bottom and bubbled through the submerged bed, was tested in another research (Epsztein, Beliavski, et al., 2016b).

MATERIALS AND METHODS

Experimental setup

A schematic diagram of the full experimental system is illustrated in Fig. 1.

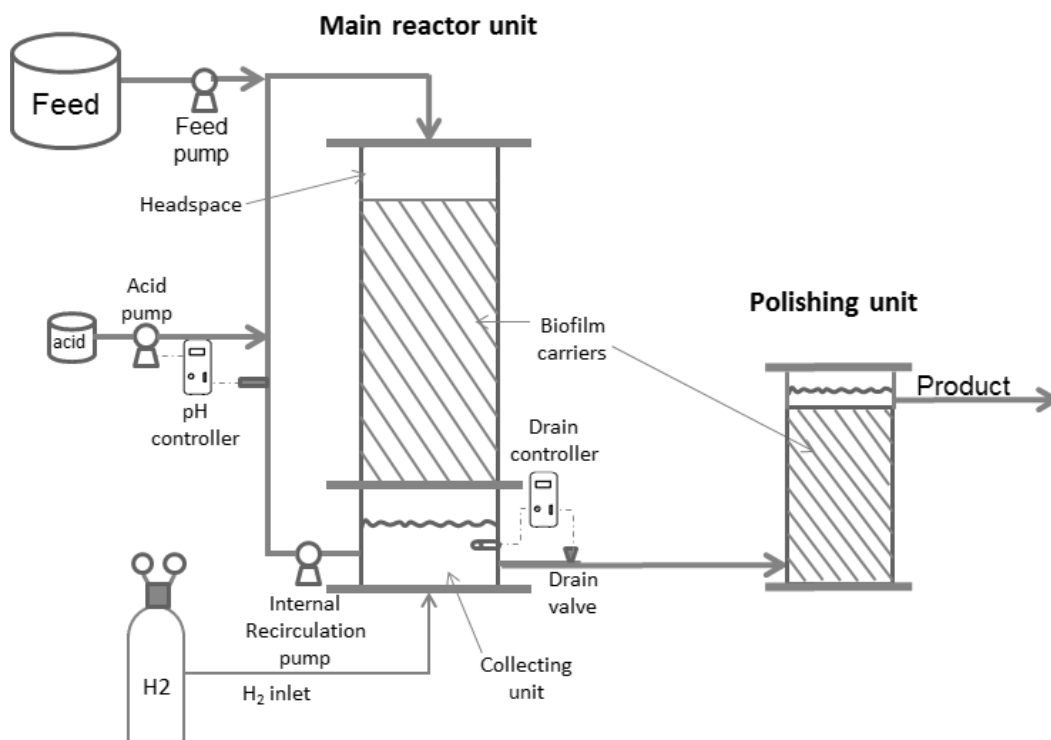


Figure 1. Schematic diagram of the full experimental system.

The full system included the main reactor unit and a following polishing unit to remove the residual H_2 in the reactor effluent. Except for the experiment testing the polishing unit performance (last section in ‘Results and discussion’), only the main reactor unit was used. The main reactor unit comprised of a clear PVC cylindrical reactor 71 cm in height and 10.5 cm in diameter divided into two unequal parts. The top part of the reactor (height 51 cm) contained plastic biofilm carriers (total surface of $900 \text{ m}^2/\text{m}^3$, Aqwise) and was separated by a metal screen from the bottom part (height 20 cm) of the reactor where recirculating water collected. The reactor was connected to a gas supply (H_2 cylinder with pressure regulator), feed pump (Diaphragm pump model 7090-42, Cole-Palmer), recirculation pump (FL-2403, ProPumps) and pH controlling unit (standard pH electrode, pH controller – pH190, Alpha; hydrochloric acid tank and acid pump – gamma/ L, ProMinent).

For the last experiment described in the ‘Results and discussion’, the main reactor unit was connected in a row to a PVC cylindrical polishing unit 21 cm in height and 10.5 cm in diameter, filled with the same plastic biofilm carriers as in the main reactor unit (see Fig. 1). The effluent water from the main reactor unit was introduced at the bottom of the polishing unit and released at the top part. The polishing unit was operated under a saturated-flow mode and its product pipeline was open to atmosphere.

A detailed description of reactor start-up was given in an earlier publication (Epsztein, Beliavski, et al., 2016a). Water temperature in the main reactor unit was maintained constant at $27.5 \pm 1 \text{ }^\circ\text{C}$ and bulk pH was kept at 7 ± 0.1 by dosing hydrochloric acid. The feed solution was tap water mixed with concentrated stock solutions of NaNO_3 and KH_2PO_4 . For the experiment with perchlorate, the feed solution was mixed with stock solution of NaClO_4^- .

All rate calculations in this work were based on the packing volume of the carriers in the main reactor unit (see packing volumes used for each experiment in the ‘Results and discussion’). The packing volume of the carriers in the polishing unit was 2 L.

Analyses

Nitrate and perchlorate were determined using a Metrohm 761 ion chromatograph (IC) equipped with a 150 mm Metrosep A Supp 5 column with column guard and suppressor using a $\text{CO}_3^{2-}/\text{HCO}_3^-$ eluent. Nitrite-N and alkalinity were measured according to Standard Methods (Method 4500 and Method 2320, respectively). H_2 concentration in gas phase was measured by gas chromatography (TCD detector; column: HP-PLOT-Q 30m; 0.53mm. 40u, Agilent 7890A). Samples for the gas phase analysis by gas chromatography were taken by direct injection of fresh gas mixture from the reactor headspace into a 20 mL sealed serum bottle. The bottle was first flushed with the same gas mixture from the reactor headspace for 1 minute with gas flow rate of 250 mL/min to ensure exchange of the entire gas volume in the bottle.

RESULTS AND DISCUSSION

Proof of concept – reaching a gas-liquid equilibrium

Two operational modes with different effluent NO_3^- -N concentration were chosen for proving the concept of reaching gas-liquid equilibrium in the pressurized reactor. Operation (i) simulates the common treatment process aimed to meet the worldwide regulations for NO_3^- -N in drinking water. A common alternative practice is to treat a portion of NO_3^- -N containing groundwater to very low concentrations (e.g. ~1 mg/L) and to mix the low concentration product water with untreated groundwater to meet the drinking water standard. This type of operation, sometimes called split treatment process, is represented by operation (ii).

The inlet NO_3^- -N concentration was 25 mg/L for both operations. The influent flow rates applied for operation mode (i) and (ii) were 430 and 130 mL/min, respectively. The recirculation flow rate was 2500 mL/min for both operations. The packing volume of the carriers in the main reactor unit was 4.4 L. Each operation started with pressurizing the reactor with H_2 gas to a total pressure of 3 bars (2 bars of H_2 gas were added above the atmospheric pressure). The total pressure was maintained constant throughout the experiment by keeping the H_2 cylinder connected to the reactor through a pressure regulator. The concentration of H_2 gas in the reactor headspace was measured over time and converted to partial pressure. Assuming H_2 and N_2 are the only gases in the reactor (after initial oxygen depletion), the partial pressure of N_2 gas could also be calculated by subtracting the partial pressure of H_2 from the total pressure.

Table 1 presents the main results achieved at steady state for the two operation modes.

Table 1. Main results achieved at steady state for the two operation modes under the constant conditions described.

	Operation (i)	Operation (ii)
Inlet NO_3^- -N concentration [mg/L]	25	25
Effluent NO_3^- -N concentration in reactor [mg/L]	10.1 ± 1.2	1.3 ± 0.6
Denitrification rate [$\text{g N}/(\text{L}_{\text{reactor}} \cdot \text{d})$]	2.1 ± 0.2	1.06 ± 0.06
Total pressure [bars]	3	3
*Theoretical N_2 pressure at steady-state [bars]	1.7	2.3
Measured N_2 pressure at steady-state [bars]	1.6	2.1
Effluent dissolved H_2 concentration [mg/L]	0.5	0.34
H_2 utilization efficiency [%]	92.8	96.9

* Full theory was given previously (Epsztein, Beliaevski, et al., 2016a)

Gas-liquid equilibrium was achieved after 23 h and 105 h for operation (i) and (ii), respectively, and proved the novel concept. The small deviation of the experimental results for the steady-state partial pressures of N_2 from the theoretical calculations can be attributed to the fact that the reactor is not a true completely mixed system. This results in higher NO_3^- -N concentration at the top of the reactor (i.e. where less NO_3^- -N is removed) with the corresponding lower partial pressure of N_2 produced according to the reactor's theory. Alternatively, the deviation mentioned may be explained by the density differences of H_2 and N_2 gases. The concentration of H_2 , the lighter gas, at steady state was a bit higher than expected at the top of the reactor where the gas was sampled. The lower denitrification rate calculated for operation (ii) was due to NO_3^- -N limitation with the resulting lower penetration to biofilm. Nitrite concentrations were always below detected levels for both operations. According to the stoichiometry suggested by McCarty (McCarty, 1972), the dissolved H_2 concentrations measured correlate with H_2 utilization efficiencies of 92.8 and 96.9% for operation (i) and (ii), respectively. The high H_2 utilization efficiencies were achieved due to the fact that H_2 gas was not wasted through gas purging. Further enhancement of H_2 utilization efficiency is possible using the polishing unit as described below.

Denitrification rates in the pressurized reactor

As mentioned above, on top of the inherent advantages of safety and economics, the new reactor was designed to ensure high denitrification rates in comparison to existing hydrogenotrophic systems due to the use of high-surface-area carriers and the maintenance of high gas (H_2)-liquid transfer rate by the unsaturated flow. A mathematical model based on simple mass balances for steady-state and completely stirred hydraulic conditions was developed and validated for evaluating the performance of the pressurized reactor. Detailed description of model development was given in another publication (Epsztein, Beliaevski, et al.). Denitrification rates and H_2 utilization efficiencies were evaluated by the model for reasonable operational conditions of effluent NO_3^- -N concentration of 10 mg/L, recirculation ratio (Q_R/Q) of 5 and different total pressures. The model results are shown in Fig. 2.

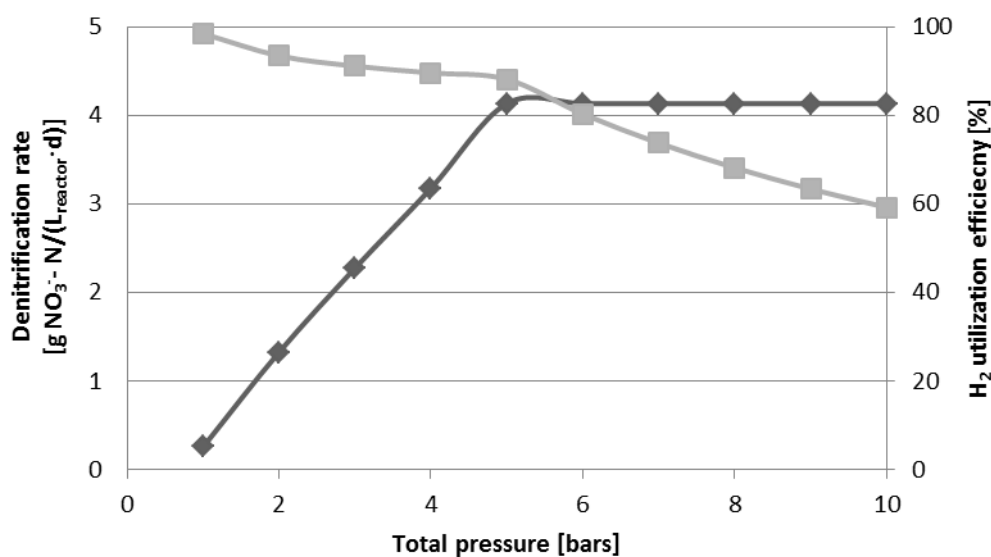


Figure 2. Model results for denitrification rates (dark grey) and H_2 utilization efficiencies (light grey) for conditions of effluent NO_3^- -N concentration of 10 mg/L, recirculation ratio (Q_R/Q) of 5 and different total pressures (X axis).

In general, Fig. 2 shows that higher denitrification rates above $4 \text{ g N}/(\text{L}_{\text{reactor}} \cdot \text{d})$ together with higher utilization efficiencies of H_2 are achieved in the pressurized reactor as compared to other hydrogenotrophic systems reviewed previously (Epsztein, Beliavski, et al., 2016a). Higher denitrification rates up to 7.5 were observed for higher recirculation ratios (Epsztein, Beliavski, et al.). Hydrogen limits denitrification rates at low pressures (< 4.5 bars). At higher pressures, NO_3^- was found to be the rate-limiting substrate since no improvement in denitrification rate was observed with increasing the pressure. Obviously, higher pressure has a negative effect on H_2 utilization efficiency. At higher pressure, a higher amount of unutilized H_2 gas is dissolved in the liquid phase and released with the effluent. The dip in the curves at total pressure of 5 bars is a result of the model transition from H_2 to NO_3^- limitation.

Feasibility study for perchlorate removal in the pressurized reactor

A feasibility study for ClO_4^- removal in the pressurized reactor using the biofilm carriers from the denitrification experiments was performed for 25 days. Inlet NO_3^- -N and ClO_4^- concentrations were approximately 15 and 20 mg/L, respectively. The total pressure was 2 bars and the recirculation flow rate was 6600 mL/min. The packing volume of the carriers in the main reactor unit was 2.5 L. The results for ClO_4^- removal rate over time are shown in Fig. 3.

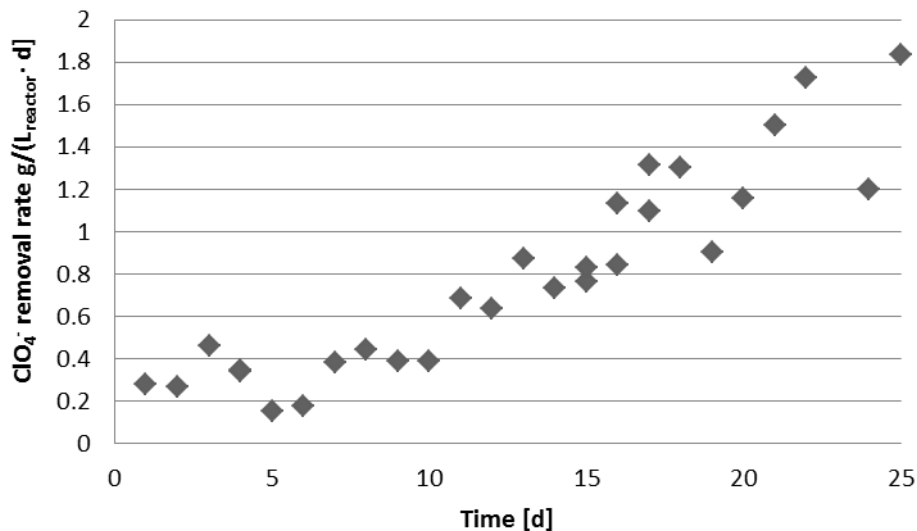


Figure 3. Perchlorate removal rate in the pressurized reactor as a function of time. At $t=0$, ClO_4^- was introduced in the reactor for the first time.

Fig. 3 shows the feasibility of the pressurized reactor to remove ClO_4^- . The relatively rapid acclimation of bacteria to reduce ClO_4^- shows that no specialized inoculation is required. Maximal ClO_4^- removal rate of $1.83 \text{ g}/(\text{L}_{\text{reactor}} \cdot \text{d})$ was observed after 25 days of operation. Effluent NO_3^- -N concentration was always below 1 mg/L. Nitrite concentrations were always below detected levels.

Increasing H_2 utilization efficiency with the polishing unit

The full system (i.e. main reactor plus polishing unit) was operated for 60 days under the following conditions: inlet NO_3^- -N concentration of 25 mg/L, flow rate of 150 mL/min, recirculation flow rate of 3800 mL/min and total pressure of 2.5 bars. The packing volume of the carriers in the main reactor unit was 2.5 L. The main results at steady-state conditions are summarized in Table 2.

Table 2. Main results achieved at steady state for the full scheme under the constant conditions described.

Inlet NO ₃ ⁻ -N concentration [mg/L]	25.8 ± 0.6
Effluent NO ₃ ⁻ -N concentration in reactor [mg/L]	0.66 ± 0.2
Denitrification rate [g N/(L _{reactor} ·d)]	2.172 ± 0.15
Total pressure in main reactor unit [bars]	2.5
*Theoretical H ₂ pressure at steady-state [bars]	0.3
Measured H ₂ pressure at steady-state [bars]	0.23 ± 0.01
Effluent dissolved H ₂ concentration in reactor at saturation [mg/L]	0.345
H ₂ utilization efficiency before polishing unit [%]	96.8
Effluent NO ₃ ⁻ -N concentration in polishing unit [mg/L]	0
Effluent dissolved H ₂ concentration in polishing unit [mg/L]	0.062
H ₂ utilization efficiency after polishing unit [%]	99.4

* Full theory was given previously (Epsztein, Beliavski, et al., 2016a)

Despite the low NO₃⁻-N concentration in the reactor (i.e. with the resulting low penetration to biofilm), the denitrification rates in the main reactor unit were always above 2 g N/(L_{reactor}·d) due to the high active biofilm surface area. Nitrite concentrations were always below detected levels. According to the theory suggested by Epsztein et al. (Epsztein, Beliavski, et al., 2016a), the steady-state N₂ pressure developed at 25°C and removal of ~25 mg NO₃⁻-N/L is around 2.2 bars. This leaves room for 0.3 bars of H₂. The H₂ pressure measured at steady state was slightly lower (0.23), probably due to asymmetrical distribution of H₂ gas in the column and the accuracy level of the GC measurement. Assuming the dissolved H₂ concentration in the reactor is close to saturation (~1.5 mg H₂ / (L·bar) at 25°C) and using the suggested stoichiometry of hydrogenotrophic denitrification (McCarty, 1972), the dissolved H₂ in the reactor effluent is 0.345 with the corresponding H₂ utilization efficiency of 96.8%.

In the polishing unit, the residual NO₃⁻-N in the reactor effluent (0.66 mg/L) was removed using additional 0.283 mg/L of H₂, so that the residual H₂ after the polishing unit effluent was decreased to 0.062 mg/L with the corresponding H₂ utilization efficiency of 99.4%. It is important to note that this calculation of H₂ utilization efficiency was based on the effluent dissolved H₂ concentration in reactor at saturation, while the real dissolved H₂ concentration should be lower with the corresponding higher H₂ utilization efficiency.

CONCLUSIONS

A novel pressurized unsaturated flow hydrogenotrophic reactor for denitrification without gas purging was successfully tested. The possible misconception regarding N₂ gas accumulation in a closed reactor's headspace was refuted by showing that in a continuous operation H₂ and N₂ in the gas phase reach a constant steady-state concentration. This approach allows for safe and economic reactor operation in terms of H₂ gas utilization since no gas purging is required. Denitrification rates of one order of magnitude higher than most previously reported denitrification rates were achieved using a trickling filter with recirculation. The residual H₂ from the main reactor unit can be utilized for perchlorate reduction in a following polishing unit, thus increasing H₂ utilization efficiency up to almost 100%. Process simplicity and safety may encourage its use in remote and small water treatment plants.

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