High-rate hydrogenotrophic denitrification in a pressurized reactor

Razi Epsztein *, Michael Beliavski, Sheldon Tarre, Michal Green

Faculty of Civil and Environmental Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel

**HIGHLIGHTS**

- A novel pressurized H₂-based reactor for denitrification is presented.
- The common misconception of N₂ accumulation in closed headspace is eliminated.
- At steady-state, N₂ pressure remains constant and no gas purging is required.
- The reactor presents high rates of approximately 5 g NO₃⁻-N/(Lreactor d).
- Hydrogen utilization efficiencies of up to 96.9% are achieved.

**ABSTRACT**

Most conventional hydrogenotrophic denitrification reactors based on packed- or fluidized-bed present a similar H₂ delivery scheme of continuous gas purging to the atmosphere in order to improve H₂ transfer rates and enable discharge of N₂ gas produced during denitrification. This operation results in a significant release of H₂ 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 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. 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 NO₃⁻-N/L. Average denitrification rates of 2.1 ± 0.2 and 1.06 ± 0.06 g NO₃⁻-N/(Lreactor d) with H₂ utilization efficiencies of 92.8% and 96.9% were measured for the two effluent concentrations, respectively. Higher denitrification rates of up to 5 g NO₃⁻-N/(Lreactor d) were observed at higher recirculation flow rates and higher partial pressures of H₂.

© 2015 Elsevier B.V. All rights reserved.

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 CO₂ 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 H₂ gas, also named hydrogenotrophic denitrification, is an excellent choice because of its clean nature and low biomass yield, as well as the fact that H₂ does not persist in the treated water. Moreover, H₂ is less expensive than other electron donors. 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 [6].

http://dx.doi.org/10.1016/j.cej.2015.11.004
1385-8947/© 2015 Elsevier B.V. All rights reserved.
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 \( \text{H}_2 \) and present a similar \( \text{H}_2 \) delivery scheme of gas sparging in either a separate \( \text{H}_2 \) 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 \( \text{H}_2 \) 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 \( \text{H}_2 \) production \([17]\).

Table 1 shows that \( \text{H}_2 \)-based reactors reach denitrification rates above 0.5 g NO\(_3\)-N/(L reactor d) only when a wasteful \( \text{H}_2 \) 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, \( \text{N}_2 \) 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 \( \text{N}_2 \) gas and without any \( \text{H}_2 \) 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 \( \text{H}_2 \) gas, high denitrification rates are achieved \([18]\).

The main objective of the following research is to prove the suggested concept that during continuous operation \( \text{N}_2 \) 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 \( \text{H}_2 \) delivery schemes.

<table>
<thead>
<tr>
<th>Reactor type/H2 delivery scheme</th>
<th>Denitrification rate [g NO(_3)-N/(L reactor d)]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BER/as described above</td>
<td>0.06</td>
<td>[14]</td>
</tr>
<tr>
<td>MBBR/as described above</td>
<td>0.393</td>
<td>[23]</td>
</tr>
<tr>
<td>Packed-bed/( \text{H}_2 ) saturation in separate tank with electrolysis</td>
<td>0.182</td>
<td>[11]</td>
</tr>
<tr>
<td>Packed-bed/( \text{H}_2 ) saturation in separate tank with gas-permeable membrane</td>
<td>0.25</td>
<td>[17]</td>
</tr>
<tr>
<td>Packed-bed/direct bubbling</td>
<td>0.471</td>
<td>[24]</td>
</tr>
<tr>
<td>Fluidized-bed/bubbling in separate saturation tank</td>
<td>2.5(^a)</td>
<td>[8]</td>
</tr>
<tr>
<td>Fluidized-bed/direct bubbling</td>
<td>0.036</td>
<td>[25]</td>
</tr>
<tr>
<td>Suspended growth with MBR/saturation in separate tank under pressure</td>
<td>0.552</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>0.6–0.7</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>[27]</td>
</tr>
</tbody>
</table>

\(^a\) 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 \( \text{H}_2 \) and the \( \text{N}_2 \) formed during denitrification. An additional source of \( \text{N}_2 \) gas is atmospheric \( \text{N}_2 \) 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 \( \text{H}_2 \) and \( \text{N}_2 \) gases without further accumulation of \( \text{N}_2 \) gas over time. This ability is achieved only under continuous operation where effluent water carries excess of \( \text{N}_2 \) gas out of the reactor. At the beginning of the process, \( \text{N}_2 \) in the liquid phase includes only atmospheric \( \text{N}_2 \) (i.e. dissolved \( \text{N}_2 \) originating from air), thus partial pressure of \( \text{N}_2 \) in the gas phase is approximately 0.8 bars (as in normal air mixture). The reactor is then pressurized by \( \text{H}_2 \) gas to the desired total pressure. Over time \( \text{N}_2 \) gas is produced by hydrogenotrophic denitrification and exchanges \( \text{H}_2 \) gas in the gas phase, so the partial pressure of \( \text{N}_2 \) gas increases and the partial pressure of \( \text{H}_2 \) gas decreases. At some point, the partial pressure of \( \text{N}_2 \) gas reaches a level correlating with the terminal \( \text{N}_2 \) concentration in the liquid phase according to Henry’s law, a gas–liquid equilibrium is achieved and the partial pressures of both \( \text{N}_2 \) and \( \text{H}_2 \) gases in the gas phase remain constant. Therefore, the final partial pressure of \( \text{N}_2 \) gas depends directly on \( \text{N}_2 \) concentration in the influent (i.e. the atmospheric \( \text{N}_2 \)) and the concentration of NO\(_3\)-N removed and converted to \( \text{N}_2 \) gas.

In order to introduce \( \text{H}_2 \) gas and enable denitrification, the total pressure applied (i.e. pressure of \( \text{N}_2 \) and \( \text{H}_2 \)) must be higher than the partial pressure of \( \text{N}_2 \) at gas–liquid equilibrium. Fig. 2 presents the partial pressure of \( \text{N}_2 \) 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, \( \text{P}_{\text{NO}_3} \) is the partial pressure of NO\(_3\)-N in the reactor, \( \text{P}_{\text{N}_2, \text{atm}} \) is the \( \text{N}_2 \) pressure resulting from atmospheric \( \text{N}_2 \) (i.e. ~0.8 bars) and \( \text{P}_{\text{N}_2, \text{denitrification}} \) is the \( \text{N}_2 \) pressure resulting from \( \text{N}_2 \) gas produced during denitrification and calculated by Eq. 2. In Eq. 2, \( \text{C}_{\text{N}_2, \text{denitrification}} \) is the concentration of NO\(_3\)-N converted to \( \text{N}_2 \) and \( \text{H}_2 \) is Henry’s constant (17 mg \( \text{N}_2\)/L bar at 25°C). The calculations for \( \text{C}_{\text{N}_2, \text{denitrification}} \) are based on previous suggested stoichiometry of hydrogenotrophic denitrification according to Eq. 3.

\[ \text{P}_{\text{N}_2} = \text{P}_{\text{N}_2, \text{atm}} + \text{P}_{\text{N}_2, \text{denitrification}} \] (1)

\[ \text{P}_{\text{N}_2, \text{denitrification}} = \text{C}_{\text{N}_2, \text{denitrification}} / \text{H}_2 \] (2)

\[ \text{NO}_3^- + 3.03\text{H}_2 + \text{H}^+ + 0.229\text{H}_2\text{CO}_3^- \quad \rightarrow \quad 0.477\text{N}_2 + 3.6\text{H}_2\text{O} + 0.0458\text{C}_8\text{H}_8\text{O}_2\text{N} \] (3)

For lower concentrations of NO\(_3\)-N removed, less \( \text{N}_2 \) is produced by denitrification per volume of water so the resulting partial pressure of \( \text{N}_2 \) is lower. Alternatively, for a specific total pressure of \( \text{N}_2 \) and \( \text{H}_2 \), a lower NO\(_3\)-N concentration removal will result in a lower partial pressure of \( \text{N}_2 \) with a corresponding higher partial pressure of \( \text{H}_2 \). 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 \( \text{N}_2 \) in the reactor at gas–liquid equilibrium is calculated to be 1.7 bars (see Fig. 2). Therefore, the minimal total...
pressure applied to the pressurized reactor must be above this value. For example, applying a total pressure of 2 bars leaves room for 0.3 bars of H₂.

In terms of safety and economics, this property of maintaining constant pressure of N₂ eliminates the need for reactor gas discharge with the accompanying H₂ loss to atmosphere as occurs in conventional systems described in the former section. Moreover, at gas–liquid equilibrium the pressurized reactor contains an inert N₂–H₂ gas mixture without O₂ gas, so that the formation of an explosive atmosphere within the reactor is prevented. Finally, working under low partial pressure of H₂ minimizes risks in case of failures and reduces H₂ loss to the liquid phase, i.e. residual H₂ that was not consumed.

In addition to the above mentioned advantages of safety and economics, the proposed reactor allows for high denitrification rates in comparison to existing hydrogenotrophic systems. The reactor contains carriers with high surface area that allows for better dispersal and thin biofilm development. This leads to a more effective biomass at relatively low H₂ partial pressures with a corresponding low dissolved H₂ concentration. The large gas–liquid contact area provided by the carriers together with the high diffusion coefficient of H₂ in the gas phase of the reactor ensures that a high mass transfer rate of H₂ is achieved.

3. Materials and methods

3.1. Experimental setup

The reactor system used for all tests is shown in Fig. 1. It 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 area of 900 m²/m³, 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 (H₂ 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 reactor start-up, a 2 L solution consisting of tap water enriched with nitrate, bicarbonate (added as 2 g of NaHCO₃) and phosphate with 0.5 L bacteria originating from a former hydrogenotrophic reactor was prepared and recirculated through the reactor under a constant H₂ pressure of 2 bars by purging. The feed solution for all experiments was tap water mixed with concentrated stock solutions of NaNO₃ and KH₂PO₄ (influent concentration of 1 mg P/L). Except for the experiment of checking the influence of recirculation flow rate on denitrification rates, recirculation flow rate was 2500 mL/min for all trials. Water
temperature was maintained constant at 25.5 ± 1 °C. pH was kept at 7.1 by dosing hydrochloric acid. The relatively low pH was aimed to prevent an extreme pH increase within the biofilm, which leads to NO3-N accumulation [19,20]. Influent and effluent water were collected for further analyses.

3.2. Analyses

Nitrate concentration was 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 CO2/HCO3- eluent. Nitrite-N concentration and alkalinity were measured according to Standard Methods (Method 4500 and Method 2320, respectively). H2 concentration in gas phase was measured by gas chromatography (TCD detector; column: HP-Plot-Q 30 m; 0.53 mm, 40µ, 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 min with gas flow rate of 250 mL/min to ensure exchange of the entire gas volume in the bottle. The dissolved H2 concentration in liquid phase was measured by headspace analysis of effluent samples immediately sealed within a serum bottle using the same gas chromatograph.

3.3. Test protocols

3.3.1. Effect of total pressure and NO3-N concentration on denitrification rates

Denitrification rates of the proposed reactor were initially tested for various combinations of total pressure and effluent NO3-N concentration with constant recirculation flow rate of 2500 mL/min. For each total pressure tested, the system was first operated to steady state with high effluent NO3-N concentration (>15 mg/L). The time required to reach a steady state ranged between 1 and 2 days. The total pressures applied were 1.5, 2, 2.5 and 3 bars. For the current research purposes, steady state was defined as an operational state presenting constant denitrification rate during extended operation. After reaching steady state, the effluent NO3-N concentration was decreased gradually by adjusting the influent NO3-N concentration and the denitrification rate was calculated for each combination of total pressure and effluent NO3-N concentration (see Section 4.1). Due to relatively short time (see Section 4.2), the measurements for each total pressure could be performed during a short period of less than 3 h. In such a short time, it was assumed that gas phase composition remained constant. The influent NO3-N concentration was operated in the range of 3–35 mg/L (added as NaN03), and the influent flow rate was kept constant on 450 mL/min. Reactor cleaning by flushing with water was carried out every few days to remove excess biomass growth. The frequency of cleaning depended on the denitrification rate achieved for different operational parameters.

3.3.2. Effect of recirculation flow rate on denitrification rates

In a set of experiments, the influence of recirculation flow rate on denitrification rates was tested. In this case, the H2 pressure applied was 3 bars and the effluent NO3-N was kept constant on 5 mg/L by adjusting the inlet NO3-N concentration in the range of 15–40 mg NO3-N/L (added as NaN03). In this specific experiment (as opposed to the standard operation of the proposed reactor), the H2 pressure was kept constant by continuous flushing of the reactor headspace with H2 gas. The reactor was first operated at the highest recirculation flow rate of 8000 mL/min. After reaching steady state, the recirculation flow rate was decreased gradually and denitrification rates and effluent dissolved H2 concentrations were measured for each recirculation flow rate applied.

Liquid retention times for different recirculation flow rates were measured by the following procedure: (1) reactor was completely drained and then was filled with the carriers (covered with biomass); (2) an influent flow rate of 450 mL/min was applied without recirculation and the time till the first reactor drain was measured. This measurement gave the liquid retention time without recirculation; (3) recirculation flow rate was then increased gradually and the lag between two drains was measured. This lag was the addition to the liquid retention time due to the increase in recirculation flow rate.

3.3.3. Proof of concept – reaching a gas–liquid equilibrium

After investigating the effect of total pressure, NO3-N concentration and recirculation flow rate on denitrification rates, the concept of reaching a steady state with constant partial pressures of both H2 and N2 gases was further tested for two operational modes: (i) operation with high effluent NO3-N concentration of 10 mg/L, and (ii) operation with low effluent NO3-N concentration of 1 mg/L. The inlet NO3-N concentration was 25 mg/L for both operations. The influent flow rates applied for operations (i) and (ii) were 430 and 130 mL/min, respectively. For each operation, the total pressure applied was determined by summing the theoretical N2 partial pressure developed (Fig. 2) with the H2 partial pressure needed (Fig. 3) as will be described in Section 4.2. The recirculation flow rate was 2500 mL/min for both operations.

Each operation started with pressurizing the reactor with H2 gas to the desired total pressure above the atmospheric pressure (e.g. for total pressure of 3 bars, 2 bars of H2 gas were added above the atmospheric pressure). The total pressure was maintained constant throughout the experiment by keeping the H2 cylinder connected to the reactor through a pressure regulator. The concentration of H2 gas in the reactor headspace was measured over time and converted to partial pressure. Assuming H2 and N2 are the only gases in the reactor (after initial oxygen depletion), the partial pressure of N2 gas could also be calculated by subtracting the partial pressure of H2 from the total pressure. At the beginning of the process, this subtraction gives the partial pressures of both N2 and O2.

All denitrification rates in this paper were calculated based on the empty reactor volume excluding the volume of the collecting unit.

4. Results and discussion

4.1. Effect of total pressure and NO3-N concentration on denitrification rates

Fig. 3 presents the denitrification rates calculated after reaching steady state, as a function of effluent NO3-N concentration for 4 different total pressures as described in Section 3.3.1.

A similar trend was observed for all total pressures tested. Nitrate was limiting at low NO3-N concentrations (e.g. NO3-N < ~5 mg/L for the experiment with total pressure of 2.5 bars). At higher NO3-N concentrations (e.g. NO3-N > ~5 mg/L for the experiment with total pressure of 2.5 bars), total pressure was found to govern denitrification rate. This is due to the different H2 partial pressures achieved (with the corresponding different dissolved H2 concentration) for each total pressure applied. The H2 partial pressure could be estimated using the theory proposed in Section 2 and summarized in Fig. 2. For example, for the lowest total pressure of 1.5 bars, a denitrification rate of 0.7 g N/(L reactor d) was achieved at steady state. The removal of NO3-N in this case was approximately 5 mg/L that correlates to a N2 partial pressure buildup of 1.1 bars according to Fig. 2. Therefore the H2 partial
Denitrification rates increased significantly with higher recirculation flow rates. These increased rates can be partially explained by the moderate increase in liquid retention time. The main reason for the improved denitrification rate is probably the increase in media wetting which results in higher surface area of active biofilm exposed to both NO$_3$-$N$ and H$_2$. The lowest denitrification rate was observed for operation without any recirculation (i.e. $Q_R = 0$).

The gradual decrease in effluent dissolved H$_2$ at higher recirculation flow rates is a result of the higher H$_2$ consumption rate in the biofilm. This supports the assumption that higher denitrification rates were achieved due to better media wetting rather than better gas (H$_2$)-liquid transfer and deeper penetration of H$_2$ in the biofilm. Further increase of $Q_R$ was not possible due to technical issues. Water recirculation is also known to be a crucial feature in the process design of trickling filters for BOD and ammonia degradation. When the hydraulic load is too low, recirculation of water is applied to enhance the reactor efficiency by maximizing media wetting and minimizing channeling and poor horizontal mixing [21,22].

**4.3. Proof of concept – reaching a gas–liquid equilibrium**

After determining the effect of total pressure, NO$_3$-$N$ concentration and recirculation flow rate on denitrification rates in the hydrogenotrophic reactor, two operational modes with different effluent NO$_3$-$N$ concentrations and total pressure were chosen (Table 2) for proving the concept of reaching a gas–liquid equilibrium in a pressurized reactor without gas purging. The same recirculation flow rate of 2500 mL/min was applied as in Section 4.1. In Table 2, the total pressure in the reactor needed to achieve a maximal denitrification rate for a specific effluent NO$_3$-$N$ concentration was determined by combining the information presented in Fig. 2 (N$_2$ partial pressure) and Fig. 3 (H$_2$ partial pressure).

Operation (i) simulates the common treatment process aimed to meet the worldwide regulations for NO$_3$-$N$ in drinking water.

<table>
<thead>
<tr>
<th>Recirculation flow rate [mL/min]</th>
<th>Effluent dissolved H$_2$ concentration [mg/L]</th>
<th>Liquid retention time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9</td>
<td>6.0</td>
</tr>
<tr>
<td>1000</td>
<td>0.8</td>
<td>5.5</td>
</tr>
<tr>
<td>2000</td>
<td>0.7</td>
<td>5.0</td>
</tr>
<tr>
<td>3000</td>
<td>0.6</td>
<td>4.5</td>
</tr>
<tr>
<td>4000</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>5000</td>
<td>0.4</td>
<td>3.5</td>
</tr>
<tr>
<td>6000</td>
<td>0.3</td>
<td>3.0</td>
</tr>
<tr>
<td>7000</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>8000</td>
<td>0.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

![Fig. 3. Denitrification rate as a function of effluent NO$_3$-$N$ concentration for 4 different total pressures of 1.5, 2, 2.5 and 3 bars. For the experiment with 3 bars, the reactor was maintained at pH 6.8 (see explanation in text).](image)

![Fig. 4. Denitrification rate (diamonds), liquid retention time (triangles) and effluent dissolved H$_2$ concentration (squares) as a function of recirculation flow rate at constant effluent NO$_3$-$N$ concentration of 5 mg/L and H$_2$ pressure of 3 bars.](image)
Detailed description of operational modes tested for proving the concept of reaching a gas–liquid equilibrium.

A common alternative practice is to treat a portion of NO$_3$ to the theory presented in Section 2. Alternatively, the deviation constant increase in N$_2$ partial pressure (accompanied by constant space as a function of time for operations (i) and (ii), respectively. According to Table 2, for both operational modes operation, sometimes called split treatment process, is represented by operation (ii). According to Eq. (3), these dissolved H$_2$ concentrations correlate with H$_2$ gas utilization efficiencies of 92.8% and 96.9% for operations (i) and (ii), respectively. Further enhancement of utilization efficiency of H$_2$ is possible by passing the effluent through an additional downstream denitrifying reactor open to the atmosphere, so the residual H$_2$ can be further utilized. The average NO$_3$-N concentrations measured throughout the experiments were 10.1 ± 1.2 and 1.3 ± 0.6 mg/L for operations (i) and (ii), respectively. Nitrite concentrations were always below detected levels for both operations.

5. Conclusions

A novel unsaturated-flow pressurized hydrogenotrophic reactor for denitrification without gas purging was successfully tested. The possible misconception regarding N$_2$ gas accumulation in a closed-headspace reactor was refuted by showing that in a continuous operation H$_2$ and N$_2$ in the gas phase reach a constant steady state concentration. This approach allows for safe and economic reactor operation in terms of H$_2$ gas utilization since no 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. Nitrate concentration and H$_2$ partial pressure were found to limit denitrification rates by partial penetration to biofilm. Higher recirculation flow rate could improve significantly denitrification rates up to 5 g NO$_3$-N/(L$_{reactor}$ d) by enhancing media wetting. The high surface area of the filter media available for bacterial growth and gas transfer allowed for working under low partial pressures of H$_2$ with utilization efficiencies of more than 92%.

Acknowledgments

A significant part of the analyses in this study was carried out in the Hydrogen Technologies Research Laboratory in the Technion. The research was supported by Maccabi Carasso.

References


