

Total nitrogen removal in an aerobic/anoxic membrane biofilm reactor system

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Abstract The hydrogen-based membrane biofilm reactor (MBfR) is effective for reducing nitrate-N to N₂ gas, but most wastewaters contain ammonium-N. Here, we document that an aerobic/anoxic MBfR system achieves nearly total N removal (<2 mgN/L) when the influent N is ammonium. The aerobic/anoxic MBfR couples two MBfR modules. The aerobic MBfR is supplied O₂ and brings about nitrification of ammonium to nitrate or nitrite. The anoxic MBfR is supplied H₂ and brings about denitrification to N₂ gas. Total N removal is most strongly influenced by the O₂ pressure in the aerobic module: too low O₂ caused poor nitrification, while too high O₂ inhibited denitrification in the anoxic module. Hydrogen pressure does not strongly affect total-N removal, and the best total-N removal occurs when the H₂ and O₂ pressures are similar.

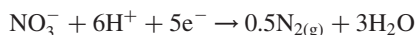
Keywords Biofilm; denitrification; membrane; nitrification; nitrogen removal

Introduction

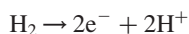
Ammonium (NH₄⁺) is the most usual form of nitrogen in wastewaters. Two microbiological reactions must take place in sequence when the input N is NH₄⁺ and total-N removal is the goal (Rittmann and McCarty, 2001): nitrification and denitrification. Nitrification is an oxidation reaction in which NH₄⁺ is transformed to nitrate (NO₃⁻) by nitrifying bacteria that reduce O₂:



Denitrification is the microbiologically catalyzed reduction of NO₃⁻ to nitrogen gas (N₂):



The N-containing product, N₂, evolves from the water, thereby eliminating N. An electron donor must be oxidized to provide the electrons (e⁻). In our work, H_{2(g)} is the electron donor:



Combining the two half reactions gives the overall denitrification reaction:



A novel and promising technology for carrying out denitrification using H₂ is the membrane biofilm reactor, MBfR (Lee and Rittmann, 2000, 2002; Rittmann and Lee, 2002; Rittmann *et al.*, 2004). H₂ gas is delivered to the denitrifying bacteria by diffusing through the wall of a bubble-less membrane. A biofilm naturally develops on the outside of the

membrane wall, removes electrons from H_2 that diffuses through the membrane, and uses those electrons to reduce NO_3^- to N_2 gas.

The H_2 -based MBfR is an ideal system for reducing NO_3^- to N_2 , but the NH_4^+ normally present in wastewater must first be oxidized to NO_3^- (or nitrite, NO_2^-) by aerobic nitrifying bacteria. We seek a means to carry out both steps of complete N removal in the MBfR setting. We created just such a process, the aerobic/anoxic MBfR, which consists of two MBfRs coupled together to operate as one integrated system that achieves nitrification, denitrification, and total-N removal. One MBfR is supplied with O_2 gas to achieve nitrification. The other MBfR is supplied with H_2 gas to achieve denitrification and complete N removal.

Our laboratory prototype of the aerobic/anoxic is shown schematically in Fig. 1. Each MBfR had 32 hollow fibers of length 25 cm, giving a total biofilm surface area of 70.6 cm^2 . The volume of each MBfR was approximately 10 cm^3 . The influent pumping rate was set to $0.11\text{ cm}^3/\text{min}$, giving a detention time of the MBfR system of approximately 3 hours. The recycle flow rates shown in Figure 1 were used to couple the two MBfRs and to ensure that the system behaved as a completely mixed system.

The objectives of this study were to: (1) document simultaneous nitrification and denitrification in the prototype aerobic/anoxic MBfR system, (2) determine the effects of O_2 and H_2 gas pressures, and (3) evaluate under what conditions the integrated MBfR could achieve an effluent total-N concentration from 1 to 3 mgN/L when the influent N was 50 mg/L , all as NH_4^+ .

Methods and materials

The medium was a synthetic wastewater containing $50\text{ mg } NH_4^+ \text{-N/l}$ and buffered with $0.252\text{ g/l } HCO_3^-$, $0.136\text{ g/l } H_2PO_4^-$, and $1.134\text{ g/l } HPO_4^{2-}$. The medium composition is given in Table 1. The medium was fed from an N_2 -gas-sparged bottle to prevent uncontrolled changes in the carbonate system. The parameters measured were NH_4^+ , NO_3^- , and NO_2^- , which were assayed by Hach methods using a Spectronic Spec 20. Due to the small size and closed nature of the system, we were not able to take samples to measure the dissolved concentrations of O_2 or H_2 internal to the aerobic/anoxic MBfR. H_2 and O_2 flows were too small to measure.

We fed the medium continuously for several weeks while the biofilms accumulated on the outside of the hollow fiber membranes and to establish the baseline performance. Once a visible layer of biofilm was present and N removal was stable for the

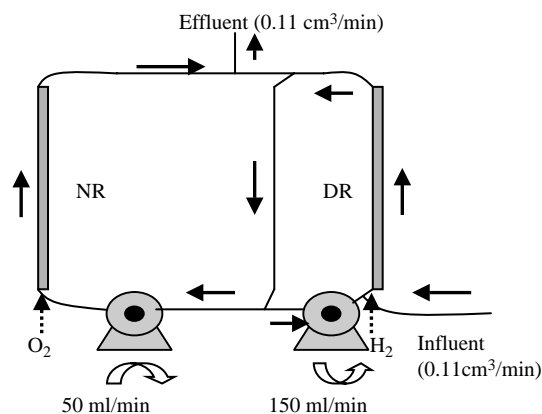


Figure 1 Configuration of the aerobic/anoxic MBfR system as a laboratory prototype

Table 1 Composition of the synthetic-wastewater medium

Media ingredient	Quantity
Distilled water	5 L
NaHCO ₃	1.26 g
(NH ₄) ₂ SO ₄	1.179 g
KH ₂ PO ₄	0.681 g
NaHPO ₄	5.678 g
Trace minerals	7.5 ml
Ca-Fe solution	7.5 ml
MgSO ₄ ·7H ₂ O	7.5 ml

baseline conditions, we began the experiments to determine N removal under different gas-pressure conditions. Applying a constant H₂ pressure (2.5 psi = 0.17 atm), we determined the N removal for the following O₂ pressures: 1.25 psi, 2.0 psi, and 6.0 psi, which correspond to 0.085, 0.14, and 0.41 atm, respectively. Applying a constant O₂ pressure (3.6 psi = 0.24 atm), we determined N removal for 1.25 psi (0.085 atm) and 5.0 psi H₂ pressure. We allowed the system to reach steady state before changing the O₂ or H₂ pressure, took at least three samples for each gas pressure, and filtered each sample (0.45- μ m membrane filter) to remove any suspended microbes that detached from the biofilm.

Results and discussion

The first 100 hours of results in Figure 2 show the baseline removal of N when the H₂ pressure was 2.5 psi (0.17 atm) and the average O₂ pressure was 2.0 psi (0.14 atm). The concentrations of all N species were low: near to or less than 1 mgN/L for NH₄⁺ and NO₃⁻, with NO₂⁻ nearly zero. The total N concentration (i.e., the sum of NH₄⁺ + NO₃⁻ + NO₂⁻ as N) was always less than 3 mgN/L and typically was less than 2 mgN/L. These results clearly demonstrate that the aerobic and anoxic MBfR system could achieve very low concentrations of all N species and total N.

The results between 110 and 280 hours in Figure 2 illustrate the general trends for NO₃⁻ and NH₄⁺ as we changed the O₂ pressure. The NH₄⁺ concentration greatly increased with low oxygen pressure (1.25 psi), due to O₂ limitation of nitrification in the aerobic MBfR. On the other hand, the NO₃⁻ concentration was high when the O₂ pressure was

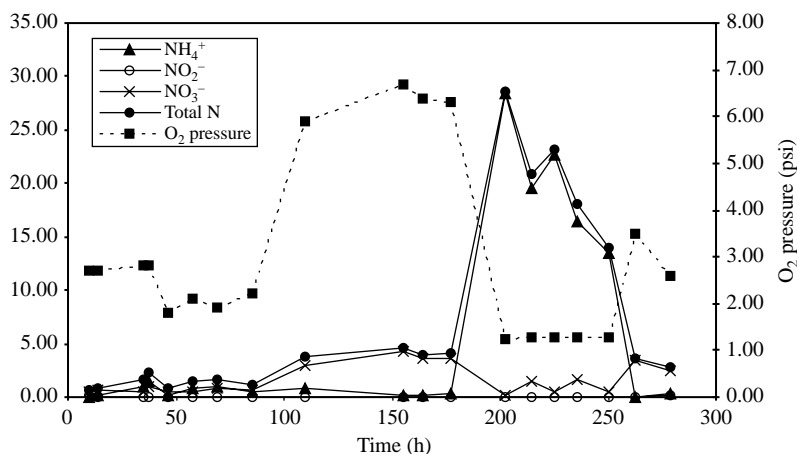


Figure 2 Effects of O₂ pressure on N species concentrations when the H₂ pressure was 2.5 psi (0.17 atm). The first 100 hours represent the baseline operation

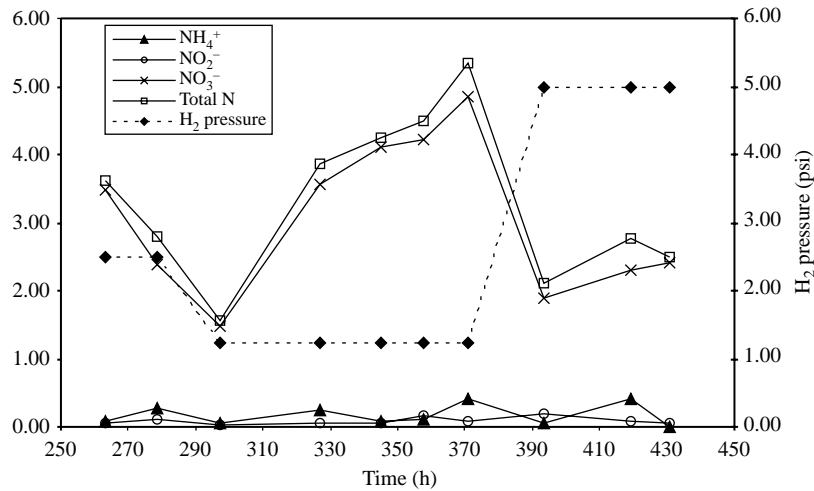


Figure 3 Effects of H₂ pressure on N-species concentrations when the O₂ pressure was held constant at 3.6 psi (0.24 atm)

increased (6 psi), because dissolved-oxygen carryover from the aerobic MBfR to the anoxic MBfR inhibited denitrification. The NO₂⁻ concentration was always small and hardly affected by the gas pressures. The total-N concentration mirrored the concentration of an N species that had an increased concentration due to the change in O₂ pressure.

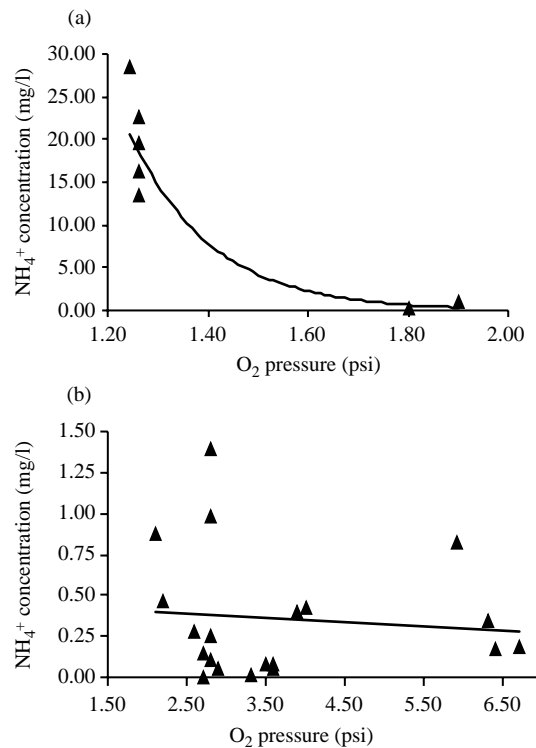


Figure 4 The effects of O₂ gas on NH₄⁺ concentrations when a) O₂ < 2.0 psi and b) O₂ > 2.0 psi. The curves are to visualize the major trends and show significance (Note: The trend in (a) is exponential and the trend line in (b) is linear)

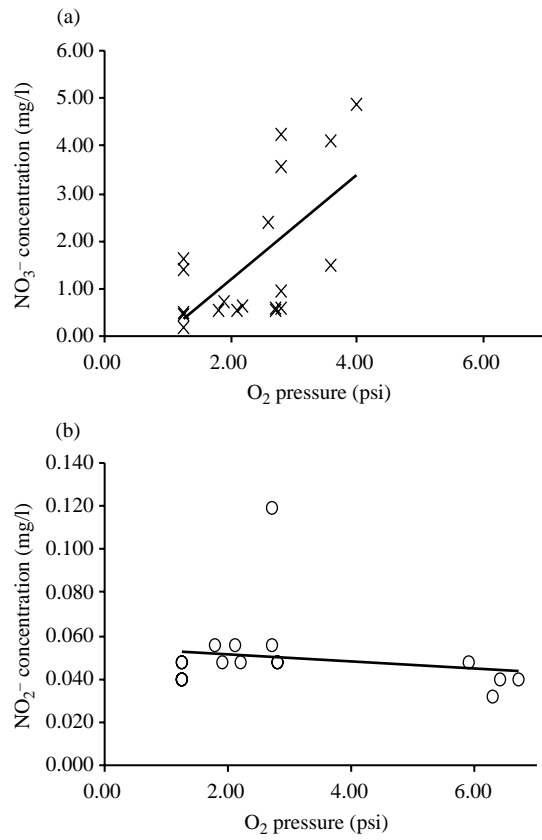


Figure 5 The effects of O₂ pressures on a) NO₃⁻ concentration and b) NO₂⁻ concentration. The curves are to visualize the major trends and significance

Figure 3 presents the results for when we varied the H₂ pressure while keeping the O₂ pressure at 3.6 psi (0.24 atm). Varying the H₂ pressure did not alter the concentrations as dramatically as did changing the O₂ pressure. The NH₄⁺ and NO₂⁻ concentrations were almost completely unaffected by the H₂ pressure. On the other hand, the NO₃⁻ concentrations increased substantially when the H₂ pressure was low (1.25 psi). Too little H₂ availability slowed denitrification in the anoxic MBfR, leaving NO₃⁻ unreduced. However, increasing the H₂ availability in the anoxic MBfR did not have a negative

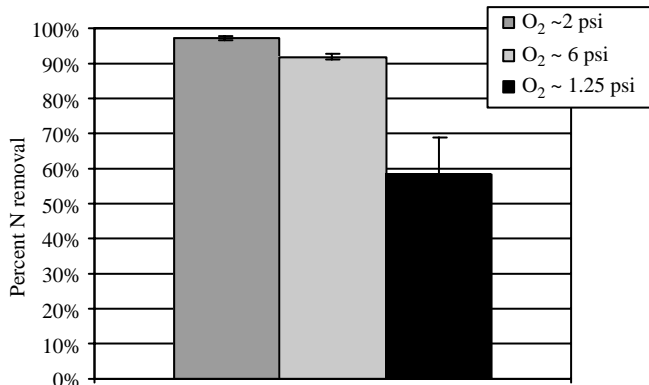


Figure 6 Percent total-N removals for constant H₂ pressure (2.5 psi = 0.17 atm) and an influent NH₄⁺ concentration of 50 mgN/L

impact on nitrification in the aerobic MBfR. This good result probably occurred because H_2 has low water solubility, which precludes significant carry over to the aerobic MBfR. The total-N concentration paralleled the NO_3^- concentration.

Figures 4 and 5 summarize how O_2 pressure affected the NH_4^+ , NO_2^- , and NO_3^- concentrations for all experiments. The NO_2^- concentration hardly varied from 0.04 mgN/L; the linear regression slope is -0.0007 mgN/L-psi, with $R^2 = 0.002$. The NH_4^+ concentration dramatically decreased when the O_2 pressure was greater than 1.25 psi (exponent on O_2 pressure is -2.56 , with $R^2 = 0.60$), since O_2 delivery was insufficient to support full nitrification in the aerobic module. Once the O_2 pressure was greater than 2.5 psi, NH_4^+ removal did not correlate with O_2 pressure (linear slope is -0.005 mgN/L-psi, with $R^2 = 0.005$), and the NH_4^+ concentration was mostly less than 0.5 mgN/L. Clearly, NO_3^- increased with higher O_2 pressure due to carry over of dissolved oxygen to the anoxic MBfR module (linear slope is 1.1 mgN/L-psi), with $R^2 = 0.4$.

Figure 6 summarizes the total-N removal efficiencies for the different O_2 pressures when the influent N was 50 mgN/L of NH_4^+ and the H_2 pressure was 2.5 psi. The changes were small for different H_2 pressures and are not shown. The total-N removal was greatest (97.1%) for the intermediate O_2 pressure (2 psi, or 0.14 atm). This corresponds to an effluent total N of only 1.5 mgN/L. At 6 psi (0.41 atm), the total-N removal decreased to 92%, due to increased NO_3^- , giving an effluent total N of 4 mgN/L. By far the poorest removal (58%) was for 1.25 psi (0.085 atm O_2), and most of the total N was NH_4^+ . Thus, the O_2 pressure to the aerobic MBfR module was the most critical control parameter for total-N removal. For these experiments, the best total-N removal occurred when the pressures of O_2 and H_2 were similar, but this is not necessarily a generalized trend.

Conclusions

We documented that a novel aerobic/anoxic MBfR system gave nearly complete N removal (<2 mgN/L) when the influent N was 50 mg/L of NH_4^+ . Total-N removal was most strongly influenced by the O_2 pressure: the most likely explanation is that too low O_2 pressure caused poor nitrification in the aerobic MBfR, while too high O_2 pressure inhibited denitrification in the anoxic MBfR. Total-N removal was less strongly influenced by H_2 pressure, although increasing the H_2 pressures provided better denitrification without affecting nitrification. For the conditions of these experiments, the best total-N removal occurred when the H_2 and O_2 pressures were similar, around 2–2.5 psi (0.14–0.17 atm).

The most significant findings of this research are that total-N removal to an effluent concentration less than 2 mgN/L can be achieved in a totally autotrophic MBfR system. Thus, it is possible to achieve an advanced N removal standard without encountering the costs and hazards of adding organic electron donors.

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