

Hydrogen-driven denitrification of wastewater in an anaerobic submerged membrane bioreactor: potential for water reuse

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Abstract An anaerobic submerged membrane bioreactor was coupled with a novel hydrogen delivery system for hydrogenotrophic denitrification of municipal final effluent containing nitrate. The biological treatment unit and hydrogen delivery unit were proven successful in removing nitrate and delivering hydrogen, respectively. Complete hydrogen transfer resulted in reducing nitrate below detectable levels at a loading of $0.14 \text{ kg N m}^{-3} \text{ d}^{-1}$. The produced water met all drinking water guidelines except for color and organic carbon. However, the organic carbon was removed by 72% mostly by membrane rejection. To reduce the organic carbon and color of the effluent, post treatment of the produced water is required.

Keywords Groundwater; hydrogenotrophic denitrification; membrane gas diffuser; nitrate; reuse

Introduction

The increased water demand in the world is putting more pressure on water resources. Water and wastewater professionals are looking at reusing final effluent for irrigation and agriculture as well as for indirect and even direct potable water supply. One example for direct water reuse is in Windhoek in Namibia, where treated wastewater is blended with water from other sources prior to distribution (Asano and Levine, 1996). Water experts around the world agree that the implementation of wastewater reuse will be a major challenge in the 21st century (Marsalek, 2002). Currently, wastewater reuse is mainly practiced in areas that have the most stressed water resources. This includes the Middle East, Japan, Korea, Australia, and the southwest United States. Currently, there are no guidelines for direct water reuse, but for indirect water reuse, the reclaimed water is required to meet drinking water guidelines (USEPA, 2004).

Many final wastewater treatment effluents contain high levels of nitrate due to low C/N ratio in the raw wastewater, which requires incorporating denitrification and addition of exogenous electron donor (Barnard and Abraham, 2006). Depending on the choice of exogenous substrate, either heterotrophic or autotrophic denitrification can be stimulated. In contrast to heterotrophic denitrification, where a variety of organic carbon sources can be used as electron donors, the donors for autotrophic denitrification include reduced sulphur compounds and hydrogen. Hydrogen is the preferred donor, since denitrification with sulphur compounds produces sulfate as a by-product residue. The advantages of autotrophic denitrification using hydrogen include: lower cost of hydrogen, when produced on-site (Gantzer, 1995), elimination of the organic carbon carry over to the reclaimed water, which can also become disinfection by-product (DBP) precursors, and

lower sludge production (Ergas and Reuss, 2001). However, low solubility of hydrogen and effective hydrogen delivery pose a challenge and need to be addressed in the reactor design.

The objective of this study was to design and evaluate a system for producing reusable water from municipal final effluent containing nitrate. An innovative hydrogen delivery system was designed and coupled with an anaerobic submerged membrane bioreactor to address both effective hydrogen delivery and biological treatment.

Materials and methods

Nitrate removal from municipal final effluent

The experimental system used in this study is illustrated in Figure 1. The system was composed of a hydrogen delivery unit and a biological reactor. The hydrogen delivery unit was composed of a super-saturator tank with a total volume of 8.5 l, a chemical feed pump, a pressure regulator valve, a mixer and a hydrogen cylinder. The reactor unit was configured as a membrane bioreactor, which consisted of a cylindrical plexiglas reactor with the total volume of 10.1 l and working volume of 5.6 l, two hollow fiber membrane filters (ZW-1, by Zenon Env. Inc.) with nominal pore size of 0.04 μm and a total surface area of 0.094 m^2 , two permeate pumps, a gas recycle pump and a pressure regulator valve.

The MBR was operated under anaerobic conditions. The reactor was fed municipal final effluent containing nitrate, which was obtained from Winnipeg's North End Wastewater Treatment Plant, which is a pure oxygen BOD removal plant. A feed tank with the total volume of 25 litres was used to feed both the super-saturator and the biological reactor. The feed with the average flow rate of 32 ml min^{-1} was split and directed to the MBR and the hydrogen saturator. The directed feed to the saturator was supersaturated with hydrogen at a pressure of 120 psi and released to the reactor to provide hydrogen for autotrophic denitrification.

Providing hydrogen and nitrate to the reactor creates a favorable condition for the growth of hydrogenotrophic denitrifying bacteria. Hydrogenotrophic denitrifiers metabolize hydrogen and nitrate, converting nitrate to nitrogen gas. The biomass produced in the reactor is separated from the treated wastewater by the submerged membrane filters. The headspace, which is filled with nitrogen produced during denitrification, is recycled through a recycle pump for both reactor mixing and membrane surface scouring.

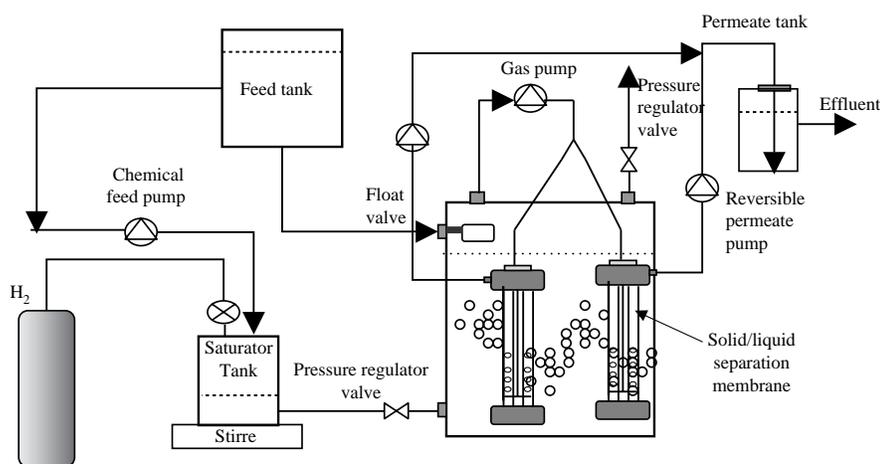


Figure 1 Schematic of laboratory scale bioreactor

The excess nitrogen is released automatically to the atmosphere through a pressure release valve. The membrane filters were operated under 300 s filtration and 30 s back-wash mode using two separate permeable pumps. The reactor was operated at room temperature (25–28 °C) with an SRT of 20 days and HRT of 3 hours.

Both influent and effluent were sampled and analyzed for nitrate, nitrite, total and soluble chemical oxygen demand, pH, alkalinity, true colour, turbidity, hardness, total dissolved solids and total coliform. The mixed liquor from the reactor was analyzed for volatile and total suspended solids and soluble COD. These analyses were performed according to *Standard Methods* (APHA, 1998). The dissolved hydrogen in the permeate tank was monitored using an Orbisphere online dissolved hydrogen analyzer.

Mass transfer study

An experiment was conducted to study the mass transfer of the supersaturated water released to the reactor, where the reactor was filled with pure water. Mass transfer of hydrogen into the water is the worst case scenario, since biological hydrogen consumption increases mass transfer rate.

In order to study the mass transfer of hydrogen into the water, the feed tank and reactor (shown in Figure 1) were filled with water and the reactor head space was filled with nitrogen gas. Some portion of the feed (water) from the feed tank was pumped to the saturator tank with a flow rate of 37 ml min^{-1} . The saturator was already filled with hydrogen having a pressure of 120 psi. The working pressure of the regulator valve, which is located between the saturator and the reactor, was adjusted to 125 psi. The supersaturated water was introduced to the reactor through the pressure regulator valve. At steady-state, the flow rate of the feed pump was equal to the flow rate of the supersaturated feed released to the reactor. The supersaturated water from the saturator and the water from the feed tank were mixed in the reactor and pumped out with a flow rate of 480 ml min^{-1} . The dissolved hydrogen concentration in the reactor was monitored using an online dissolved hydrogen analyzer. The dissolved hydrogen in the saturator was measured by sampling headspace gas. The mass transfer efficiency was calculated by applying a hydrogen mass balance using dissolved hydrogen concentration in the saturator and in the reactor.

Results and discussion

Mass transfer

Results of the mass transfer study are presented in Figure 2. In the first part of the experiment, the mixer in the saturator was turned off and there was no circulation of the

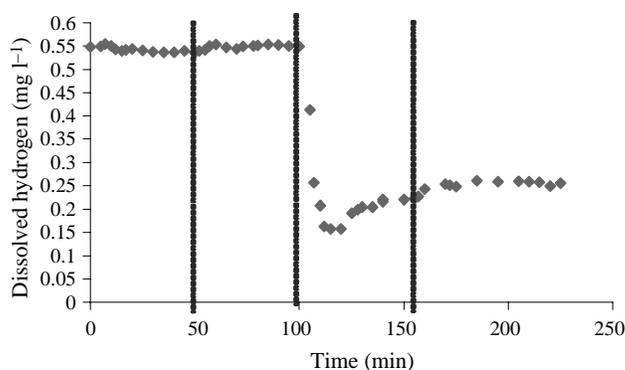


Figure 2 Dissolved hydrogen concentration in the reactor under steady state conditions

head-space gases. In this case, the dissolved hydrogen in the reactor was around 0.55 mg l^{-1} . In order to calculate the mass transfer efficiency, the dissolved hydrogen concentration in the saturator is needed. The dissolved hydrogen concentration in the saturator was measured by taking samples from the pressure regulator valve, resulting in 7.18 mg l^{-1} of hydrogen. Hydrogen mass balance showed that 100% hydrogen delivery was achieved. As the second part of the experiment shows, mixing in the saturator did not increase dissolved hydrogen concentration. This is due to the high natural flow rate maintained through the saturator (very low retention time) which renders the effect of additional mixing negligible. In the second part of the experiment, the headspace was circulated through the membrane module with the rate of 30 l min^{-1} . The dissolved hydrogen in the reactor decreased from 0.55 to 0.2 mg l^{-1} . The circulated gas stripped out some portion of the dissolved hydrogen, however as the system is closed, the stripped gas will eventually be available to the bacteria. Another way to eliminate the need for headspace recirculation and subsequent hydrogen stripping is to use external membranes for water filtration. The cost of high flow recirculation, however, can be prohibitive to the use of external membranes in many applications. In the last step of testing, decreasing the headspace gas recirculation flow rate from 30 l min^{-1} to 15 l min^{-1} resulted in an increase in the dissolved hydrogen concentration from 0.2 to 0.25 mg l^{-1} .

Nitrate removal

At the start up, some portion of the feed (16 ml min^{-1}) was directed to the saturator and the rest (17 ml min^{-1}) was introduced into the reactor. The clogging of the miniature pressure regulator valve introducing the supersaturated feed to the reactor was a problem. The particular valve used in this study was designed for liquids, free of suspended solids and could not handle the bacteria grown in the saturator. However, the clogging is not anticipated to be of great concern in full scale applications as similar valves are used in full scale dissolved air flotation systems working under the same concept. As shown in Figure 3, the membrane bioreactor system was effective in complete nitrate removal from the synthetic feed where the nitrate was reduced from $33 \pm 4 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ to below detectable level with an average loading of $0.14 \text{ kg N m}^{-3} \text{ d}^{-1}$. No nitrite accumulation was observed throughout the experiment. The dissolved hydrogen concentration in the effluent changed between $0.1 \pm 0.03 \text{ mg l}^{-1}$, however complete denitrification was achieved at dissolved hydrogen concentrations as low as 0.001 mg l^{-1} . The dissolved

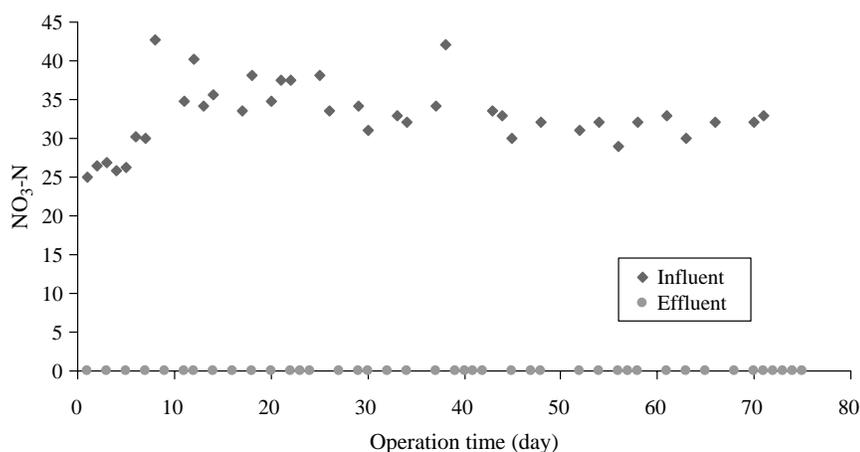


Figure 3 Reactor performance regarding nitrate removal from water under steady-state

hydrogen concentration in the effluent was changing due to the fact that supersaturated flow rate was decreasing over time. The hydrogen delivery system was operated in a way which gave hydrogen pressure of 120 psi and extra pressure for opening of the pressure regulator valve was provided by chemical feeding pump. Over time the partial pressure of hydrogen in the headspace was decreasing due to hydrogen dissolution causing the level of water in the saturator to rise. Controlling the water level in the saturator is the key for continuous dissolution of gas into the water in the saturator.

Biomass concentration

At steady-state condition the average concentration of suspended solids was $1127 \pm 235 \text{ mg l}^{-1}$ for VSS and $1645 \pm 327 \text{ mg l}^{-1}$ for TSS (Figure 4)

The inert fraction of total suspended solids comes from two sources of particulate inserts in the feed and precipitated inorganics. The inorganic fraction of TSS can be attributed to the precipitation of Ca^{2+} and Mg^{+2} with carbonate, phosphate or hydroxide (OH^-) due to increase in pH during biological denitrification. The reduction of total dissolved solids is another indicator of precipitation in the reactor.

Organic carbon mass balance

Under steady state condition the organic carbon mass balance can be written as follows:

$$0 = \text{COD(In)} - \text{COD(Out)} + \text{COD(generation)} - \text{COD(degradation)} \quad (1)$$

The feed contained $39 \pm 9 \text{ mg l}^{-1}$ soluble organic carbon. Since the feed water has undergone secondary treatment, the remaining organic carbon can be attributed to the non-biodegradable fraction of raw wastewater and the slowly biodegradable soluble COD produced during substrate utilization. During autotrophic denitrification, generation of organic carbon also occurs due to release of soluble microbial products. Soluble microbial products (SMP) can be categorized into utilization-associated products (UAP) and biomass associated products (BAP). UAPs are associated with substrate metabolism and are produced at a rate proportional to substrate utilization. BAPs are associated with biomass decay and are produced at a rate proportional to biomass concentration (Barker and Stuckey, 1999). In order to assess the fate of organic carbon, the biodegradability kinetics of organic carbon is required.

The degradation of organic carbon requires heterotrophic activity. Although the conditions in the reactor are favorable to autotrophic growth, the degradation of SMPs in the reactor is possible. It has been found that all of hydrogen-dependent denitrifiers are mixotrophic as they are able to use inorganic carbon under autotrophic and organic carbon

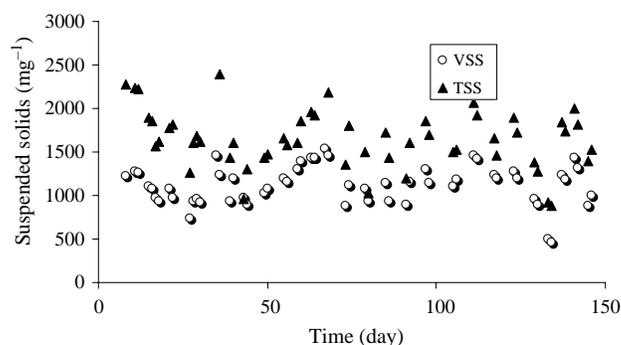


Figure 4 Suspended solids concentration at steady-state conditions

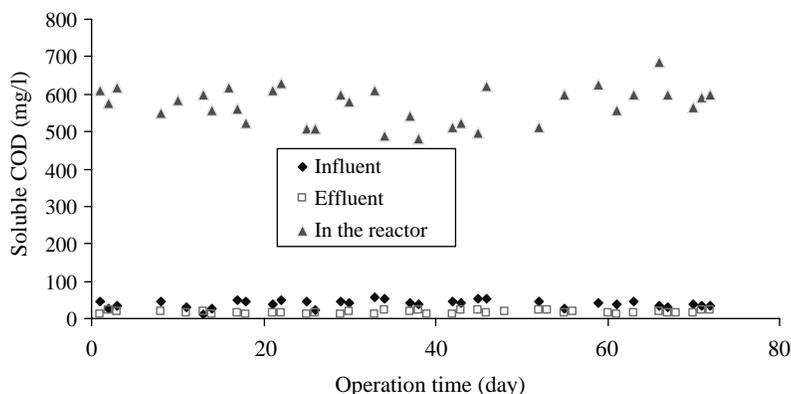


Figure 5 Soluble COD concentration at steady state conditions

under heterotrophic conditions (Szekeres *et al.*, 2002). Soluble microbial products (SMP) are slowly biodegradable and the kinetics of their degradation is well understood under aerobic conditions (Henze *et al.*, 1987; Rittmann and McCarty, 2001; Lu *et al.*, 2002). SMPs were shown to have high saturation coefficients and low utilization rates, and therefore require long hydraulic retention times to degrade. When nitrate is the electron acceptor, even lower degradation rates can be expected. In this study it was assumed that there is no degradation of SMP within three hours hydraulic retention time. To confirm this assumption, the wasted biomass from the reactor was transferred to a batch reactor and spiked with nitrate. No hydrogen was provided and nitrogen gas was bubbled into the reactor to provide anoxic conditions. As SMPs were the only electron donor, nitrate consumption rate represents the biodegradability of SMP. Negligible amount of nitrate was consumed during the 3 hr batch test, which validates the assumption of non-biodegradable SMP.

As shown in Figure 5 the organic carbon content of the effluent ($17 \pm 4 \text{ mg l}^{-1}$ as COD) was consistently lower than that of the influent feed. The mass balance for COD is presented in Table 1. The organic carbon removal was mostly achieved by membrane rejection. The organic carbon, which passed the membrane, could either originate from the incoming feed or from SMP produced during denitrification. A greater portion is expected to come from the feed, since in a previous study using the same membrane, 81% of SMP was rejected by the membrane (Rezania *et al.*, 2005).

Produced water quality

Table 2 shows physical and chemical characteristics of the influent feed and produced water.

The produced water could not meet the all of the drinking water guidelines. However, it was successful in completely removing coliform and nitrate, reducing hardness, color, organic carbon and turbidity. Color and dissolved organic carbon can be reduced below USEPA guidelines for potable water by using granular activated carbon as the post treatment.

Table 1 Organic carbon mass balance

Parameter	Unit	Value
Total COD removed	%	72
Soluble COD removed	%	56
SPM produced	mg COD mg N ⁻¹	0.41

Table 2 Produced water quality

Parameters	Unit	Influent	Effluent	US EPA guidelines
Soluble COD	mg l ⁻¹	39 ± 9	17 ± 4	–
Total COD	mg l ⁻¹	62 ± 14	17 ± 4	–
Dissolved organic Carbon	mg l ⁻¹	16.5 ± 3	9 ± 0.3	5*
Dissolved Hydrogen	mg l ⁻¹	0	0.1 ± 0.03	–
Nitrate	mg NI – 1	33 ± 4	0	10
Alkalinity	mg CaCO ₃ l ⁻¹	237 ± 37	308 ± 48	–
pH	–	7.8 ± 0.4	9.3 ± 0.14	6.5–8.5
Turbidity	Ntu	20 ± 5	0.16 ± 0.09	1
True Color	Hu	30	25 ± 5	15
Hardness	mg l ⁻¹	324 ± 65	170 ± 10	–
Total Dissolved Solids	mg l ⁻¹	580 ± 100	76 ± 20	500
Total Coliform	CFU/100 ml	2 × 10 ⁶	ND	ND

*Level of Practice
 ND(non-detectable)

Conclusions

The concept of introducing hydrogen through super-saturation can be used for efficient gas delivery. However, the liquid level in the saturator should be kept constant by using a level controller, which assures continuous gas flow from the gas tank to the saturator tank. The hydrogen delivery system was efficient achieving almost 100% hydrogen transfer rate. The transfer of hydrogen to the membrane bioreactor effectively stimulated the growth of hydrogen-dependent denitrifiers, and complete nitrogen removal was achieved at a loading rate of 0.14 N m⁻³ d⁻¹. The nitrogen gas produced during denitrification was sufficient for membrane scouring and reactor mixing. Both membrane filters were successful in separating the biomass produced during denitrification from the treated water. In addition the membranes were effective in rejection of 52% soluble COD. The produced water met drinking water guidelines in terms of total coliforms, nitrate, hardness and turbidity. Color and dissolved organic carbon did not meet USEPA Guidelines for potable water and would thus require post treatment if water reuse was intended. The designed system showed good potential for wastewater reuse applications.

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