Hydrogenotrophic Denitrification of Groundwater in a Membrane Bioreactor Assisted by Membrane Gas Diffusion

by

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A Thesis submitted to the Faculty of Graduate Studies of

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ABSTRACT

A hydrogenotrophic denitrification system, comprising of a suspended growth membrane bioreactor (MBR) and a membrane hydrogen gas diffuser, was developed to remove nitrate from groundwater. A hollow fiber gas permeable membrane module was designed for hydrogen delivery and a commercially available hollow fiber membrane module was used for solid/liquid separation. The MBR was operated at an SRT of 20 days and at room temperature for 420 days. Four nitrate loading rates of 24, 48, 96, 192 and 384 NO_3^--N mg/L·d were applied to the system. As the nitrate loading was increased, pH increased due to increased denitrification and release of OH^- ions. ORP remained fairly stable when full denitrification was achieved; however, it increased in the initial period of the fourth and the last stage as residual nitrate was present in the reactor. It later decreased when sufficient $NaHCO_3$ was provided. Nitrate removal was complete (100%) in the first three nitrate loadings and average of 91% and 96% of nitrate removal was achieved in the system with 192 and 384 NO_3^--N mg/L·d with sufficient carbon source supply, respectively. Nitrate utilization rate (NUR) of 30.6, 23.4, 37.7, and 184.2 mg NO_3^--N/L·d were achieved in the first four nitrate loadings, respectively. Effluent DOC concentration of approximately 8 mg/L was observed in all five nitrate loading regimes. It was found that the inorganic carbon source plays an important role in the nitrate removal efficiency when higher nitrate loading is applied to the system.

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INTRODUCTION

High nitrate concentration is of primary concern in groundwater which plays a substantial role in public water supply in many countries (Zekster, 2000). A high nitrate levels in groundwater sources were reported worldwide of increasing rates (Gayle et al., 1989).

Due to the adverse health effects associated with nitrate in drinking water including methemoglobinemia and the link to cancer (Health Canada, 1987), various environmental agencies have set a nitrate and nitrite limit in drinking water. The United States Environmental Protection Agency (USEPA) and Health Canada currently have nitrate and nitrite drinking water regulations of 10 mg NO_3^--N/L and 1 mg NO_2^--N/L, respectively (Health Canada, 1987; USEPA, 2002). European Union (EU) has set the maximum level of nitrate in drinking water at 11.3 mg NO_3^--N/L and a stricter limit on nitrite at 0.03 mg NO_2^--N/L (Urbain et al., 1996).

To comply with these strict standards, various nitrate removal methods have been used. Commonly used nitrate treatment methods include ion exchange, reverse osmosis and electrodialysis; however, they often require high capital and operating costs and generate concentrated wastes (Sorg, 1980; Dahab, 1987; Kapoor and Viraraghavan, 1997). Biological denitrification has been an alternative process for nitrate treatment to physico-chemical methods. Biological denitrification is the conversion of nitrate to nitrogen gas by denitrifying bacteria under anoxic conditions. It can be carried out by both heterotrophic denitrifiers (heterotrophic denitrification) and autotrophic

denitrifiers (autotrophic denitrification). In groundwater, nitrate treatment in which sufficient carbon source is often not present, heterotrophic denitrification often has to rely on external carbon sources such as methanol and acetate. Such treated groundwater carries a risk of being contaminated with the biomass generated in the process or with residual external carbon additives which can also become disinfection by-product (DBP) precursors. These problems can be eliminated by using hydrogenotrophic (autotrophic) denitrification in which hydrogen serves as an electron donor and nitrate as an electron acceptor in lieu of oxygen.

Advantages of hydrogenotrophic denitrification include (1) the elimination of carryover of organic compounds to the treated water as hydrogen is not an organic compound, (2) less excess biomass generation, (3) easy removal of residual hydrogen by sparging due to its relatively low water solubility, and (4) lower cost of hydrogen compared to methanol or acetate (Ergas and Reuss, 2001; Fang et al., 2002; Lee, 1999). The major limitation of hydrogenotrophic denitrification is the low solubility of hydrogen gas resulting in difficulty of hydrogen dissolution and possible accumulation of hydrogen gas in a confined space, thus creating an explosive environment (Mansell and Schroeder, 2002). Several researchers have reported that a process using hollow fiber gas diffusing membranes could be operated with up to 100 % gas transfer efficiency (Semmens and Gantzer, 1993; Pankhania et al., 1994; Lee, 1999). Other researchers have also demonstrated effective hydrogenotrophic denitrification with gas permeable hollow fiber membranes, which were used to enhance the hydrogen delivery efficiency and limit explosion risks through the bubble-less introduction of hydrogen (Lee and Rittmann,

2000; Ergas and Reuss, 2001; Falk, 2002; Pierkiel, 2002). Advantages of the hollow fiber membrane bioreactor over systems employing conventional gas sparging include higher gas transfer rates, higher biomass densities and bubble-less operation, which prevents the waste of excess H_2 and the accumulation of explosive gases in a confined space (Gantzer, 1995; Brindle and Stephenson, 1996; Stephenson et al., 2000). Combining hydrogenotrophic denitrification with hollow fiber membrane gas diffusion technology has the potential for the production of high quality drinking water from groundwater.

Additional concerns regarding the use of hydrogenotrophic denitrification are the relatively slow growth of the autotrophic denitrifying bacteria compared to heterotrophic denitrifying bacteria and the loss of particular strains of denitrifiers in the effluent which will have an impact on the process efficiency. The use of a membrane bioreactor (MBR) can address these concerns and also provide additional pathogen reduction in the effluent. Most of the research conducted on hydrogenotrophic denitrification has been with attached growth systems, owing to the low biomass yield of hydrogenotrophic denitrifiers (Ergas and Reuss, 2000; Lee and Rittman, 2000; Falk, 2002; Pierkiel, 2002). However, attached growth systems have shown problems such as the difficulty of biofilm control, limited mass transfer and decreasing biomass activity due to thick biofilm formation (Brindle and Stephenson, 1996; Freitas dos Santos et al., 1997; Falk, 2002).

LITERATURE REVIEW

In this section, a review of literature with the focus on hydrogenotrophic denitrification is provided. Other literatures included in this section provide a review of nitrate contamination in groundwater, membrane gas diffusion, and membrane bioreactor applications for water treatment. The objectives of this research are also stated at the end of this section.

1. Groundwater as a Drinking Water Source

Groundwater is considered as one of the most important drinking water sources world wide. At present, fresh groundwater is an essential resource for public water supply in many countries and its share to the public water supply is increasing. In the U.S.A., groundwater is a major source comprising 75% of municipal water supply systems and provides the drinking water for more than a half of the country's population (Zekster, 2000). In Europe, many countries are highly dependent on groundwater for the use of potable and domestic water supply to municipalities. This is considered to be due to advantages of groundwater over other drinking water sources including surface water. Groundwater is usually less contaminated than surface water as it is not directly exposed to external environment.

In Manitoba, groundwater plays a substantial role in drinking water supply. Many rural residents rely on this resource for most of their domestic needs. Groundwater is also used for various other purposes: livestock watering, irrigation, industrial processing, heating, and cooling. Manitoba Conservation (1997) reported that approximately 20% of

Manitoba residents are dependent on groundwater for their domestic needs. Out of the 290 communities in Manitoba, 155 rely on groundwater sources (Betchers et al., 1995). Due to this high rate of groundwater use, groundwater quality in Manitoba is becoming an increasing concern.

2. Nitrate Contamination in Groundwater

Nitrate is ubiquitous in the environment and is considered as one of the most common groundwater contaminants. Nitrate is a naturally occurring ion and the product of the oxidation of ammonia by micro-organisms in plants and soil or water. It is a very stable and highly mobile which can easily migrate and be accumulated in groundwater source. Jahan (2003) described that nitrate contamination of drinking water sources may result from both artificial and organic overfertilization in agriculture, human and animal waste disposal, discharge of wastewater from food processing, explosives manufacturing industries and NO*x* absorption in air stripping. As a drinking water source, groundwater generally has low nitrate content because it is (1) taken up in synthesis, (2) leached by water percolating through the soil; or (3) subject to denitrification activity below the aerobic top layer of soil (Canter, 1997). However, its synthesis and denitrification do not always remove all nitrates added to the soil from fertilizers and nitrified wastewater effluents. Consequently, nitrates leached from soil are a major groundwater contamination problem in many areas in the U.S.A. and elsewhere around the world (USEPA, 1993).

Nitrate can originate from various sources. These sources include decaying plant or animal material, agricultural fertilizers, manure, domestic sewage or geological formations containing soluble nitrogen compounds (Bourchard et al., 1992). In the case of nitrite, it may be produced from excess ammonia in drinking water distribution systems that use chloramines as disinfectant (Keeney, 1986). Due to its relatively stable nature, most nitrogenous materials in environment tend to be converted to nitrates; therefore, all sources of nitrogen including organic nitrogen, ammonia and fertilizers are potential sources of nitrates.

In Canada, high nitrate concentrations have been found in groundwater at many sites across the country. Manure and chemical fertilizer are thought to be two major potential sources of nitrate contamination in Manitoba groundwater (Manitoba Conservation, 1997). Health Canada (1987) reported that 60% of wells among 450 samples in 125 locations in the Fraser Valley of British Columbia (B.C.) were found to exceed the recommended nitrate level of 45 mg NO_3/L. In this survey, the maximum concentration of 182 mg/L was recorded.

3. Environmental / Health Concerns of Nitrate

High nitrate concentration in groundwater is of primary concern as it can result in potential human health effects and other environmental concerns to animals, crops, or industrial processes. The most commonly reported toxic effect of high concentration of nitrates in drinking water is the condition of methemoglobinemia and its effect on infants which is known as blue baby syndrome (Bouchard et al., 1992). Methemoglobinemia

refers to a condition resulting from the oxidation (by nitrite) of reduced iron (Fe^{2+}) in hemoglobin, the oxygen carrier of mammalian blood, to its oxidized from (Fe^{3+}). The resulting methae-moglobin (MeHb) is not capable of releasing oxygen to body tissues due to its high dissociation constant (Health Canada, 1987). The problem is caused by a reduction of nitrate to nitrite which reacts with hemoglobin in the bloodstream to produce methemoglobin, which impairs oxygen transport. Infants under three months of age and the unborn are particularly more susceptible than older infants, children or most adults.

Nitrates have also been reported to be associated with carcinogenicity, as they can react with amino acids to form various carcinogens (Tannenbaum and Green, 1998). Excessive nitrates in groundwater have also caused problems with ruminants (Canter, 1997). This can be of a particular concern in Manitoba where agriculture is a primary industry. According to Canter's report (1997), sheep and cattle can be seriously affected by nitrates from birth through adulthood. Monogastric (single stomach) animal infants such as horses, pigs, and chickens can also be prone to nitrate associated health problems. Symptoms of nitrate-nitrite poisoning in livestock include cyanosis, shortness of breath, rapid heartbeat, frequent urination, and collapse. In severe cases, death may occur within hours. A loss of milk production in cows and aborted calves are also signs of possible nitrate poisoning (Chandler, 1989).

4. Limits of Nitrate in Drinking Water

Due to these adverse health effects described in the previous section, various environmental agencies have set a nitrate and nitrite limit in drinking water. In Canada,

Health Canada suggests a guideline for nitrate concentration in drinking water. It sets the maximum acceptable concentration (MAC) for nitrate in drinking water as 45 mg NO_3^- /L which is equal to 10 mg NO_3^--N/L and the concentration of nitrite not to exceed 3.2 mg NO_2^-/L in cases where nitrite is measured separately from nitrate.

The United States Environmental Protection Agency (USEPA) currently sets nitrate and nitrite concentration standards in drinking water as 10 mg NO_3^--N/L and 1 mg NO_2^--N/L, respectively (USEPA, 2002). The European Community has set the maximum level of nitrate in drinking water at 11.3 mg NO_3^--N/L, a recommended level of 5.7 mg NO_3^--N/L and a stricter limit on nitrite at 0.03 mg NO_2^--N/L (Urbain et al., 1996; Kapoor and Viraraghavan, 1997). WHO (World Health Organization) established the maximum level of nitrate and nitrite concentrations in drinking water as 50 mg NO_3^-/L and 3 mg NO_2^-/L, respectively (WHO, 1998).

5. Technologies to Treat Nitrate in Groundwater

The removal of nitrate can be accomplished by physical, chemical and biological means. Physical and chemical methods include ion exchange, reverse osmosis, electrodialysis and chemical denitrification. In the following subsections, a brief summary about most commonly practiced physical nitrate removal processes are provided.

5.1 Ion Exchange

The ion exchange (IX) process can be defined as a unit process in which ions of a given species are displaced from an insoluble exchange material (i.e. the resin) by ions of a different species in solution (Metcalf and Eddy, 2003). The ion exchange mechanism involved in the removal of nitrate ions from groundwater is typically the replacement of these ions with chloride ions when the groundwater is passed through the resin. For drinking water treatment, IX is currently the predominant method for removing nitrate in the United States (Jahan, 2003).

Ion exchange is an attractive process for nitrate removal from groundwater since it offers process control, is easily automated, and is not affected by temperature in typical operating ranges (Canter, 1997). Nevertheless, it has shown two major problems. The first problem is that a resin of high selectivity for nitrates over ions that are commonly present in groundwater does not exist. In the case that sulfates are present in the water they can compete for the exchange sites on the resin. In fact, many ion exchange resins are more selective for sulfate than for nitrate (Sorg, 1980). The second problem is associated with the production of waste brines. Although ion exchange can provide immediate nitrate removal, it produces the most waste brines (regenerants) of the physical and chemical nitrate removal processes and this directly affects the operating cost (Kapoor and Viraraghavan, 1997). Several studies were conducted about the regenerant problem of ion-exchange processes for nitrate removal (Guter, 1981; Guter, 1987a; Guter, 1987b). Guter (1981) conducted a pilot-scale ion-exchange study at McFarland, California. He reported that a significant operating cost for the process was related to the use of sodium chloride as a resin regenerant. Also, the presence of sulfate in the raw water decreased the efficiency of the resin in removing nitrate because anion-

exchange resins can be selective for sulfate ions. After the pilot-study, a full scale plant was built and 6-month and 25-month operation reports were released. Although nitrate removal by the ion-exchange process is largely being considered as a process adaptable for small communities, it was found that the waste disposal problems will be the most difficult to solve. During the 1985 -1986 period, over 250 tons of salt were consumed in the nitrate removal process. The disposal of large quantity of waste salt to the environment poses serious questions about the fate these materials and their impact on the local environment (Guter, 1987b). In addition, the long-term operational problem with an IX/denitrification process is that anion exchange resins are susceptible to significant organic fouling (Jahan, 2003).

5.2 Reverse Osmosis

Reverse osmosis (RO) refers to a process whereby ionic species (e.g. nitrates in groundwater) present in water are removed by forcing the water to be transported across a semi-permeable membrane, effectively leaving the contaminants (e.g. nitrates) behind (Canter, 1997). Reverse osmosis processes can provide a high and controlled nitrate removal. The main problem associated with reverse osmosis is related to the selectivity of the membrane used for reverse osmosis. The RO membranes generally do not exhibit high selectivity for nitrates. The degree of rejection is directly related to the valency of the ions. That is the reason why the RO process works better for the removal of multivalent ions such as Mg^{2+} and Ca^{2+} and the mineral content of the water (Mateju et al., 1994). Membrane fouling is another major problem when using RO process. Due to

this fouling problem, RO requires a close monitoring and cleaning leading to increase an operating cost. Handling of brined waste produced from reverse osmosis is also a potential problem. Furthermore, it is reported that reverse osmosis requires relatively high energy and capital costs compared to ion-exchange or electrodialysis (Sorg, 1980).

5.3 Electrodialysis

Electrodialysis (ED) refers to an electrically driven unit operation in which ions are separated through semi-permeable ion-selective membranes from one solution to another under the influence of a direct current electric field.

The nitrate removal efficiency of ED is similar to RO. The ED process is limited to treating soft water. At present, nitrate removal by ED is considered an expensive process, requiring close monitoring (Sorg, 1980).

ED membranes can be susceptible to fouling by inorganics such as calcium carbonate, barium, calcium, iron and manganese oxides, colloids, microorganisms and organic chemicals (Canter, 1997). Pretreatment such as activated carbon pretreatment and/or by addition of a small amount of acid to the feed stream is required to solve these problems. Organic fouling can be reduced by periodical cleaning of the membranes with an enzyme detergent solution. The development of nitrate-selective membranes makes the ED process a more viable technology for nitrate removal from groundwater; however, the

energy demands of ED systems is high, making it more expensive when compared to ion-exchange or biological denitrification.

6. Biological Denitrification

As an alternative to these physico-chemical methods, biological denitrification has drawn more attention due to its simple procedure and high denitrification efficiency.

Biological denitrification is defined as the reduction of nitrate (NO_3^-) or nitrite (NO_2^-) to gaseous nitrogen (N_2) by denitrifying bacteria. In biological denitrification, NO_3^- or NO_2^- serves as the electron acceptor used in energy generation. Biological denitrification has a sequence of enzymatic reactions resulting in yielding the final product of gaseous nitrogen (N_2) as follows:

NO_3^- (nitrate) $\rightarrow$ NO_2^- (nitrite) $\rightarrow$ NO (nitric oxide) $\rightarrow$ N_2O (nitrous oxide) $\rightarrow$ N_2

In biological denitrification, the denitrifying bacteria can utilize either an organic (heterotrophic) or inorganic (autotrophic) carbon source. In the following sub-section, a detailed summary of heterotrophic and autotrophic denitrification is provided.

6.1 Heterotrophic Denitrification

Heterotrophic denitrification, in which an organic carbon source also serves as the electron donor, is a commonly used biological denitrification method for nitrate removal

in water and wastewater treatment. Different types of organic carbon sources can be used for heterotrophic denitrification: methanol, ethanol and acetate. A theoretical equation for heterotrophic denitrification using methanol as carbon and energy source is as follows (Lee, 1999):

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow 0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O \quad \text{(Eq. 1)}$$

From the equation above (Eq. 1), it is noted that heterotrophic denitrification provides a high yield of 0.406 g cells/g NO_3^--N. Heterotrophic denitrification systems can offer advantages such as the high specificity of denitrifying organisms for nitrate and low cost (Ergas and Ruess, 2001). However, it also has some drawbacks. Use of an organic carbon substrate can result in carryover of organic carbon to the treated water, leading to biological instability. Biological instability can cause the increased microbial growth in the drinking water distribution system which can result in the adverse effects such as increased heterotrophic and coliform plate counts, decreased hydraulic capacity due to slime growths on the walls of pipes, increased taste and odor problems, and accelerated rates of pipe corrosion (Gantzer, 1995). Furthermore, there may be a risk that the unconsumed organic compounds may also increase chlorine demand and form of trihalomethanes (THMs) and other undesirable disinfection by-products (DBP). Therefore, heterotrophic denitrification is generally not preferable for the treatment of groundwater which is usually electron donor limited (Smith, 1994).

6.2 Autotrophic Denitrification

Due to these reasons, autotrophic denitrification can be a preferable biological denitrification means over heterotrophic denitrification for groundwater treatment. In autotrophic denitrification, nitrate is reduced to nitrogen gas (N_2) by autotrophic bacteria. Carbon dioxide (CO_2) or bicarbonate (HCO_3) act as the carbon source and nitrate acts as the electron acceptor in the absence of oxygen. Autotrophic denitrifiers can use one of the following sources as their election donor: hydrogen, reduced sulfur compounds, ferrous ion and chloric compounds. Typically, reduced sulfur compounds and hydrogen are usually used for autotrophic denitrification. The problem associated with the use of reduced sulfur compounds is the evolution of sulfate. Denitrification of wastewaters containing high nitrate concentrations can result in sulfate inhibition of the process due to high concentrations of sulfate produced in treatment. This is not the case with potable water denitrification because nitrate concentrations to be treated are lower and sulfate inhibition would not occur. On the other hand, the potability of water may be reduced due to higher sulfate concentrations. Mateju et al. (1994) described that 250 mg/L of sulfate would be stoichiometrically produced when 152 mg NO_3/L is reduced. 250 mg/L of sulfate is the upper limit in most water quality standards.

6.2.1 Hydrogenotrophic Denitrification

In hydrogenotrophic denitrification, nitrate is reduced to nitrogen gas using autotrophic hydrogen oxidizing bacteria. Nitrate (NO_3^-) acts as the electron acceptor, hydrogen (H_2) as the energy source/electron donor, and carbon dioxide (CO_2) or bicarbonate (HCO_3-) as the carbon source in the absence of oxygen. The reduction reaction of nitrate to nitrogen gas using hydrogen as an electron donor is as follows (Kurt et al., 1987):

$$2NO_3^- + 2H_2 \rightarrow 2NO_2^- + 2H_2O \qquad \text{(Eq. 2)}$$

$$2NO_2^- + 3H_2 \rightarrow N_2 + 2H_2O + 2OH^- \qquad \text{(Eq. 3)}$$

Overall reaction: $2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^-$ (Eq. 4)

From the overall reaction given above (Eq. 4), 2 moles of OH^- are produced for every 2 moles of NO_3^- reduced; thus, alkaline conditions will occur leading to high pH condition and nitrite accumulation can be expected. To prevent pH increase and accumulation of nitrite, CO_2 or HCO_3^- can be added to buffer the system as well as to serve as the inorganic carbon source for cell synthesis. From the equation (Eq. 4), theoretically 0.35 mg H_2/mg NO_3^--N is required for a complete reduction of nitrate to nitrogen gas. Experimental values were 0.38 mg H_2/ mg NO_3^--N in a bench scale reactor (Kurt et al., 1987) and 0.40 mg H_2/ mg NO_3^--N at a full-scale plant in Germany (Gros et al., 1988). Ergas and Reuss (2001) developed a theoretical equation for hydrogenotrophic denitrification as follows:

$$NO_3^- + 2.86H_2 + H^+ + 0.15CO_2 \rightarrow 0.03C_5H_7O_2N + 0.49N_2 + 3.14H_2O \qquad \text{(Eq. 5)}$$

From the equation (Eq. 5), it is noted that hydrogenotrophic denitrification has a lower yield of 0.24mg VSS/mg NO_3^--N than heterotrophic denitrification (Eq. 1).

Hydrogenotrophic denitrification can offer several advantages over heterotrophic denitrification. Firstly, it eliminates the risk of carryover of organic compounds to the treated water as hydrogen is not an organic compound. Secondly, it generates less excess biomass than heterotrophic process due to the low reproduction rate. Thirdly, it is easy to remove residual hydrogen by sparging as hydrogen has a relatively low water solubility (1.62 mg/L at 20°C). Fourthly, lower cost of hydrogen compared to methanol or acetate makes hydrogenotrophic denitrification more attractive in terms of cost of the electron donor (Ergas and Reuss, 2001; Fang et al., 2002). Gantzer (1995) reported that the use of hydrogen is more than ten times less expensive with the on-site hydrogen generation than the use of methanol and acetate, based on bulk chemical costs in Minneapolis, Minnesota, U.S.A. The transportation cost may be as high as the cost of the chemical itself depending on the actual location of the site (Pierkiel, 2002). Lee (1999) also reported that hydrogen costs 3-15 times less than the common organic supplements to remove the same amount of nitrate. Lastly, hydrogenotrophic denitrification can achieve a stable and reliable process management (Gros et al., 1988).

Several attempts have been made to treat nitrate in drinking water by hydrogenotrophic denitrification in late 1980s (Dries et al., 1988; Gros et al., 1988). In earlier stages of hydrogenotrophic denitrification research, Dries et al. (1988) attempted to use hydrogenotrophic denitrifiers to remove nitrate from groundwater. They used lithotrophic denitrification for their study in which inorganic HCO_3^- ions and carbonic acid dissolved in the water were used as carbon source and H_2 gas as the reducing agent. A fixed bed reactor was constructed with polyurethane (PU) sponges as a carrier material for biomass. In their PU carrier reactor with low nitrate loaded water (15 mg NO_3^--N/L), they achieved

up to 100% nitrate removal efficiency. For contaminated water containing 15 mg NO_3^--N/L, nitrate removal rate of 0.5 g NO_3^--N/L·d was obtained at 20°C. The maximum denitrification rate reached only 0.2 g N/L·d under optimal conditions (i.e. 80% H_2 or more in the gas phase). In that case, the efficiency of nitrate removal reached 80-100% and the efficiency of the H_2 consumption reached 30-40%. However, the gas transfer efficiency of H_2 transfer only reached 50-55%. They reported that the obtained volumetric loading rate from their experiment was too low compared to the rates obtained by other denitrification systems. The problem reported from this study was the obstruction of the flow of the water and the gas in the reactor. Due to the growth of the biofilm around the cubes, the initially separated cubes tended to stick together. This invoked the formation of preferential channels of the water and gas which strongly affected the overall nitrate removal capacity. Through their study, they found the cubic PU sponges are not advisable as a carrier material for the denitrifying biomass as they may cause gas diffusion and flow-through problems. The authors also stated that their process is not directly recommendable for denitrification of high nitrate loaded waters (> 50 mg NO_3^--N/L).

Another attempt to nitrate removal in groundwater was made by Gros et al. (1988). They reported the results of full-scale hydrogenotrophic denitrification process plant of drinking water built in Monchengladbach, Germany. The process is called Denitropur. After start-up in February 1986, the Denitropur plant reached its full capacity and performance within some weeks. The plant laid out to treat ground water and produces 100 m^3/h drinking water containing about 40 mg/L of nitrate. The available ground water containing about 80 mg/L of nitrate is denitrified in the plant and then blended with

untreated groundwater. The nitrate load eliminated up to 90 kg NO_3/d. The nitrate was eliminated to a very low value as it is the case for nitrite. Nitrite was always lower than 0.1 mg NO_2/L within the whole biological reactor and became lower than 0.01 mg NO_2/L when nitrate reached the value of 1 mg NO_3/L. Their fluidized bed reactor in the pilot plant achieved less than 1 mg/L nitrate and 0.01 mg/L nitrite in effluent with less than 75 NO_3 mg/L and less than 0.02 NO_2 mg/L in influent. The 50m^3/h facility eliminated nitrate from 17 to less than 1mg/L of NO_3^--N within a hydraulic residence time of water in the reactors of about 1 hour. The nitrate removal rate was 0.25 g NO_3^--N/L·d. Other parameters including bacteriological and hygienic results in the effluent have been in accordance with the regulations of the German drinking water standards.

6.2.2 Limitations of Hydrogenotrophic Denitrification

The major limitation of hydrogenotrophic denitrification is the relatively low solubility of hydrogen gas (1.62 mg/L at 20°C). It may result in difficulty of hydrogen dissolution and possible accumulation of hydrogen gas in a confined space thus creating an explosive environment (Mansell and Schroeder, 2002). This problem can be eliminated by using bubble-less membrane gas diffusion.

Additional concerns with respect to the use of hydrogenotrophic denitrification are the relatively slow growth of the autotrophic denitrifying bacteria in comparison to heterotrophic denitrifying bacteria and the loss of particular strains of denitrifiers in the effluent which will have an impact on the process efficiency. The use of a membrane

bioreactor (MBR) can address the concern of biomass loss and can also provide additional pathogen reduction in the effluent.

The detailed review and the rationale regarding the use of the membrane gas diffusion and membrane bioreactor will be provided in the following sections.

7. Membrane gas diffusion applications in water treatment

Typically, gases required for the denitrification system are supplied to a system using conventional bubble diffusers (i.e. stone or silicone diffusers). However, bubble forming gas diffusion systems have a low gas transfer efficiency, and the cost of dissolving the required amount of gas is consequently very high. High cost of gas directly affects the overall cost of the process operation. In addition, the sparging of gas promotes the stripping of gaseous denitrification intermediates NO and NO_2. Safety issues can also arise when the hydrogen gas is used for denitrification process; as described earlier, it can carry a risk of creating an explosive atmosphere in a closed space. These are the main reasons that hydrogenotrophic denitrification systems have not been attractive to engineers. In order to take advantage of the operational and economic benefits of using hydrogen in the biological denitrification of drinking water, Gantzer (1995) suggested the following desired characteristics for a hydrogen dissolution device:

- rapid gas transfer rates and the ability to generate dissolved hydrogen concentrations approaching or exceeding solubility
- 100 % absorption efficiency to prevent the wastage of hydrogen; and

- bubble-less operation to prevent the accumulation of explosive gases in a confined space.

Using a membrane gas transfer device can resolve these concerns while meeting his suggestions (Semmens, 1991). Several studies (Ahmed and Semmens, 1992; Semmens and Gantzer, 1993; Pankhania et al., 1994) demonstrated that the membrane systems can be used to transfer hydrogen with 100% gas transfer efficiency and its bubble-less operation prevents the release and waste of hydrogen which can result in explosive conditions in closed spaces.

Bubble-less membrane gas diffusion was recently employed in the water/wastewater treatment process for bubble-free oxygenation in which pure oxygen was delivered without bubble formation (Cote, 1986). Bubble-less oxygenation can be accomplished by hollow fiber membranes with the oxygen phase on the lumen side and the wastewater on the shell side of the fibers. Hollow fibers provide a high surface area for oxygen transfer while occupying a relatively small volume within the bioreactor (Brindle et al., 1998). Ahmed and Semmens (1992) examined microporous polypropylene hollow fiber membrane modules with sealed-end design to evaluate its oxygen transfer rate. From their experiment, the process gave 100% oxygen transfer efficiency at a reasonable power input. Semmens and Gantzer (1995) used bubble-less oxygenation and achieved close to 100% oxygen transfer efficiency with the sealed-end hollow fiber membrane. However, they reported non-biological fouling and loss of performance of porous hollow fibers due to iron oxidation, absorption of free oils and greases into pores, surfactants, suspended

solids and fiber tangling. Pankhania et al. (1994) conducted a study about wastewater treatment using a hollow fiber biofilm bioreactor with bubble-less membrane aeration. They reported that the oxygen transfer efficiency of 100% was achieved in the system. Weiss et al. (1996) also reported superior gas diffusion by hollow fiber membrane and mentioned the advantages including low operating cost and relatively small system.

Two different configurations of hollow fiber membrane gas diffusers are available: flow-through and dead-end. In the flow-through configuration, the fibers are open-ended with gas transfer through the membrane wall into the bioreactor while being either exhausted to the atmosphere or recirculated. In the dead-end configuration, one end of the fibers is sealed, thus ensuring a 100% oxygen transfer efficiency.

There has been conflicting reports regarding the use of these two different configurations. Cote et al. (1988) argued that the flow-through operation is preferred over the dead-end operation. However, the flow-through configurations have shown two major drawbacks. Firstly, complete (100%) gas transfer efficiency cannot be accomplished since air or gas is vented. Secondly, the flow-through operation may result in stripping of dissolved volatile organic compounds (VOCs) from the liquid with the venting gas since VOCs can diffuse across the membrane into the air stream. In the dead-end mode, all the gas supplied to the fibers will diffuse through the membrane and into the water, and VOCs cannot be stripped from the water since no gas is vented. Therefore, dead-end membrane modules are preferred to achieve 100% of gas diffusion efficiency. The use of dead-end membranes has been demonstrated by previous studies involving membrane gas diffusion configurations. Ahmed and Semmens (1992) demonstrated that sealed-end operation results in superior performance as compared to the flow-through configuration. Pierkiel

(2002) has demonstrated that sealed-end membrane performed better than flow-through configuration by comparing the mass transfer coefficients.

It is very recent that membrane gas diffusion is applied for hydrogenotrophic denitrification. Several studies have been conducted on nitrate removal by hydrogenotrophic denitrification with gas permeable hollow fiber membranes, which were used to enhance the hydrogen delivery efficiency and limit explosion risks through the bubble-less introduction of hydrogen.

Gantzer (1995) used a hollow fiber membrane gas transfer system to deliver H_2 to hydrogenotrophic denitrifying populations in a two-stage fixed-bed reactor system. Hydrogen transfer occurred in the first stage and denitrification was carried out in a fixed bed bioreactor. Greater than 99% removal efficiency was achieved with an influent nitrate concentration of 15 mg NO_3^--N/L.

Lee and Rittmann (2000) carried out hydrogenotrophic denitrification in a single stage hollow fiber membrane bioreactor. Greater than 92% removal efficiency was achieved with an influent NO_3^--N/L concentration of 12.5 mg NO_3^--N/L. Nitrate fluxes of up to 2.2 g NO_3^--N/m^2·d were achieved. Both studies used sealed end hollow fiber membranes and reported high H_2 utilization efficiencies.

Ergas and Reuss (2001) studied a hydrogenotrophic denitrification system using attached biofilm for nitrate removal in groundwater with the aid of hollow fiber membrane gas diffusion in a flow-through mode. They achieved more than 99.3% of nitrate removal in their system with 90 mg NO_3^--N/L with more than 20 hours of HRT. However, they experienced lower denitrification rates as the biofilm got thicker and it had to be sheared in order to ensure consistent reactor performance.

Jahan et al. (2002) conducted hydrogenotrophic denitrification with two different nitrate loadings in a two-stage packed bed reactor with continuous flow. They used a microporous hollow fiber membrane with a sealed-end module design and developed a fixed biofilm on the membrane. The percent removal of nitrate was 100% and 96% at the nitrate loadings of 54.24 mg NO_3^--N/L·d (HRT of 1.75hr and influent nitrate concentration of 13.58 mg NO_3^--N/L) and 186.24 mg NO_3^--N/L·d (HRT of 10hr and influent nitrate concentration of 22.6 mg NO_3^--N/L), respectively. The reported volumetric nitrate removal rate was 0.312 kg NO_3^--N/m^3·d and the observed effluent DOC concentration was 5.7 mg/L at the steady-state of 54.24 mg NO_3^--N/L·d loading.

8. Membrane Bioreactor (MBR) Application in Water Treatment

Additional concerns regarding the use of hydrogenotrophic denitrification are the relatively slow growth of the autotrophic denitrifying bacteria in comparison to heterotrophic denitrifying bacteria and the loss of particular strains of denitrifying bacteria in the effluent which will have an impact on the process efficiency. The use of a membrane bioreactor can address these concerns and will also provide additional pathogen reduction.

The membrane bioreactor (MBR) process can be defined as a modified activated sludge process where a clarifier is replaced by a membrane unit for the separation of mixed liquor and effluent (Cicek et al., 1998b). There are several advantages associated with the MBR which make it more attractive than conventional treatment processes with a clarifier. Firstly, absolute retention of all suspended solids and most soluble compounds

within the bioreactor ensures the complete disinfection of the treated water. This results in excellent effluent quality, thus being capable of meeting stringent discharge requirements. As described previously, autotrophic microorganisms have a relatively slow growth rate. Thus, they must be well kept or recycled within the system in order to prevent their 'wash out' (Gros et al., 1988). The membrane not only retains all biomass but also prevents the escape of exocellular enzymes and soluble oxidants creating a more active biological mixture (Cicek et al., 1999b). Moreover, the possibility of retaining all bacteria and viruses can eliminate further disinfection process and the hazards related to disinfection by-products (DBP) (Cicek et al., 1998a).

Secondly, MBRs can be operated at very high sludge ages without having the obstacle of settling, allowing for high biomass concentrations in the bioreactor. In a conventional activated sludge process, biodegradation occurs in a bioreactor, followed by a secondary clarifier to separate treated water from the biomass. Therefore, the quality of the final effluent is strongly dependent on the settling characteristics of the sludge. Engelhardt et al. (1998) reported that the biomass concentration in the bioreactor before a clarifier should be between 3 to 5 g MLSS/L to achieve a successful separation. Accordingly, close control of the activated sludge process, large volume sedimentation tanks and sometimes further treatment are required to ensure a good solid-liquid separation and effluent quality.

Thirdly, the absence of a clarifier in MBR system can prevent the loss of sensitive, slow-growing species such as nitrifying and denitrifying bacteria (Cicek et al., 2001). It also results in more compact systems than conventional processes leading to significant

reduction of reactor volumes and plant footprint. This also makes MBRs desirable for water recycling applications and retrofitting existing water/wastewater treatment plants. Several researchers have conducted denitrification studies of drinking water with MBRs. Delanghe et al. (1994) worked on heterotrophic denitrification on a pilot plant and achieved constant 99% of nitrate removal by using two external UF membranes. Nuhoglu et al. (2002) also conducted drinking water denitrification with MF membrane. They achieved up to 98.5% of nitrate removal efficiency in their MBR system with an ethanol based heterotrophic denitrification system.

10. Hydrogenotrophic Denitrification in Suspended Growth Reactors

All of the previous hydrogenotrophic denitrification system studies were attached growth systems due to the relatively slow growth of autotrophic denitrifiers (Ergas and Reuss, 2001; Falk, 2002; Pierkiel, 2002). Nevertheless, attached growth systems have shown several problems. These problems are usually associated with the biofilm thickness: the difficulty of biofilm control, limited mass transfer and decreasing biomass activity due to thick biofilm formation (Brindle and Stephenson, 1996; Freitas dos Santos et al., 1997). Brindle and Stephenson (1996) reported the drawbacks of attached growth systems. They observed that excess biofilm accumulation can lead to limited transport of oxygen and other nutrients, plugging of membrane fibers, a decrease in biomass activity, metabolite accumulation within the biofilm, and the channeling of flow in the bioreactor such that steady-state conditions may not be maintained. In their experiment, occasional membrane washing, air scouring and high-rate recirculation of wastewater to achieve high shear

velocities have all been employed to control biomass accumulation and to operate the system at maximum efficiency.

Falk (2002) reported during his research, if the biofilm grows too thick, mass transfer limitations occur with the electron donor and/or the electron acceptor. Thick biofilms exhibit decreased biomass activity, the plugging of membrane fibers, and/or metabolite accumulation. When mass transfer limitations ensue, the denitrification rates decrease with the additional sloughing of excess biomass from the biofilm. He concluded that controlling the thickness and/or density of a biofilm for drinking water is a serious concern for hydrogenotrophic denitrification.

To address these concerns regarding the use of attached growth system, a suspended growth process was employed in the present study, marking its first time that such systems for the hydrogenotrophic denitrification was studied in an MBR.

11. Objectives of the Research

With the background provided above, the following research objectives were developed. The main objective of this research was to examine the technical feasibility of a novel membrane process involving the hydrogenotrophic denitrification of groundwater in a suspended growth system. The specific objectives were as follows:

- To investigate the optimum operating conditions for hydrogenotrophic denitrificaiton in suspended growth MBR system

- To investigate of the efficiency of the hybrid hydrogenotrophic denitrification system at increased nitrate loading rates with the aim to define maximum nitrate/nitrite removal capacity
- To examine the operational bottlenecks such as effectiveness of H_2 delivery and membrane fouling.

MATERIALS AND METHODS

1. Source of Denitrifying Cultures

Batch cultures were enriched with non-nitrifying mixed liquor prior to the MBR experiment in order to seed them into the MBR. Non-nitrifying mixed liquor was obtained from North End Pollution Control Centre (NEWPCC) in Winnipeg, Manitoba, Canada. Hydrogenotrophic denitrifying biomass was then developed in a batch reactor at ambient temperature under anoxic conditions in order to inoculate them into the MBR. The batch reactor was fed synthetic groundwater, with the composition presented in Table 1. All the chemicals were obtained from Fisher Scientific.

Table 1. Composition of the synthetic groundwater for the batch reactor

Chemical	Concentration (mg/L)
Dibasic potassium phosphate (K_2HPO_4)	1100
Monobasic potassium phosphate (KH_2PO_4)	900
Sodium bicarbonate ($NaHCO_3$)	80
Calcium chloride ($CaCl_2 \cdot 2\ H_2O$)	30
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	20.5
Ferrous sulfate ($FeSO_4 \cdot 7H_2O$)	7.5
Sodium nitrate ($NaNO_3$)	500

The batch reactor consisted of the reactor vessel with the total volume of 20L, mixer for mixed liquor agitation and the hydrogen gas cylinder to supply hydrogen gas to the reactor. A stone, coarse bubble gas diffuser was employed for hydrogen gas diffusion in the reactor. The headspace residual gas was vented to open atmosphere.

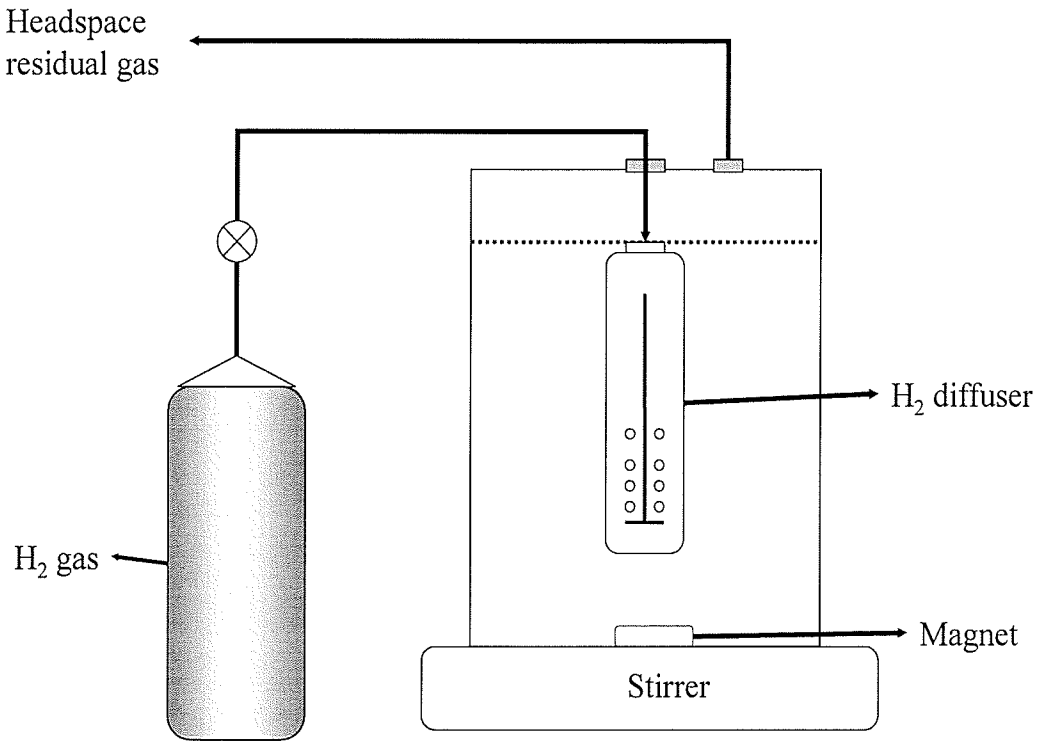


Figure 1. Schematic diagram of laboratory scale seed batch reactor

DO (dissolved oxygen) concentrations and nitrate concentration in the effluent were measured to ensure the reactor condition and the biomass performance, respectively. The solids retention time (SRT) of 20 days was maintained for the batch reactor by wasting one-twentieth of mixed liquor daily. Feeding occurred once per day after a 1 hour settling period of biomass and a 0.25 h drawing period of 15L liquid. The schematic of the seed batch reactor is presented in Figure 1.

2. Membrane Bioreactor

2.1 Gas Diffusion Membrane Module Design

Celgard® X30-240 microporous hollow fiber polypropylene gas permeable membrane fibers were used for the manufacturing of a hydrogen gas diffuser to be used in this study. Celgard® X30-240 microporous hollow fibers are thin-walled, opaque, polypropylene fibers with a nominal internal diameter of 240 microns. Other characteristics and the properties of the Celgard® X30-240 fibers are summarized in Table 2.

Table 2. Characteristics of Celgard® X30-240 microporous hollow fibers

Product Characteristics	Typical Values
Porosity, (nominal)	40%
Pore Dimensions	0.04 x 0.10 μm
Effective Pore Size	0.04 μm
Burst Strength (min)	220 psi (15.5 kg/cm^2)
Internal Diameter (nominal)	240 μm
Wall Thickness (nominal)	30 μm
Outer Diameter (nominal)	300 μm

The Celgard® membrane module design was based on the hydrogen gas flux equation (Eq.6) in which maximum nitrate loading to the system was assumed to be 1.4 g/d.

$$N = KA(C^* - C_L) \qquad \text{(Eq. 6)}$$

where N is hydrogen flux ($g \cdot s^{-1}$); K is the overall hydrogen mass transfer coefficient ($m \cdot s^{-1}$); A is the surface area (m^2); C* is the water phase hydrogen saturation concentration ($g \cdot l^{-1}$); and C_L is the dissolved hydrogen concentration in the liquid phase ($g \cdot l^{-1}$). Hydrogen saturation concentration was determined to be 1.62 mg/L by Henry's law at 20 °C.

With the total membrane surface area requirement of 0.00556 m^2, outer diameter of 0.3 mm and 40 % of porosity of fiber, a total of 94 fibers, each 16 cm in length, were required for the module in order to transfer sufficient hydrogen to the bioreactor by the following equation (Eq. 7).

$$n \times 2 \times 3.14 \times 0.15 \times 0.001 = 0.00556 / 0.4 \qquad \text{(Eq. 7)}$$

n = number of fibers required for the membrane module = 94

2.2 Membrane Bioreactor (MBR) Design and Operation

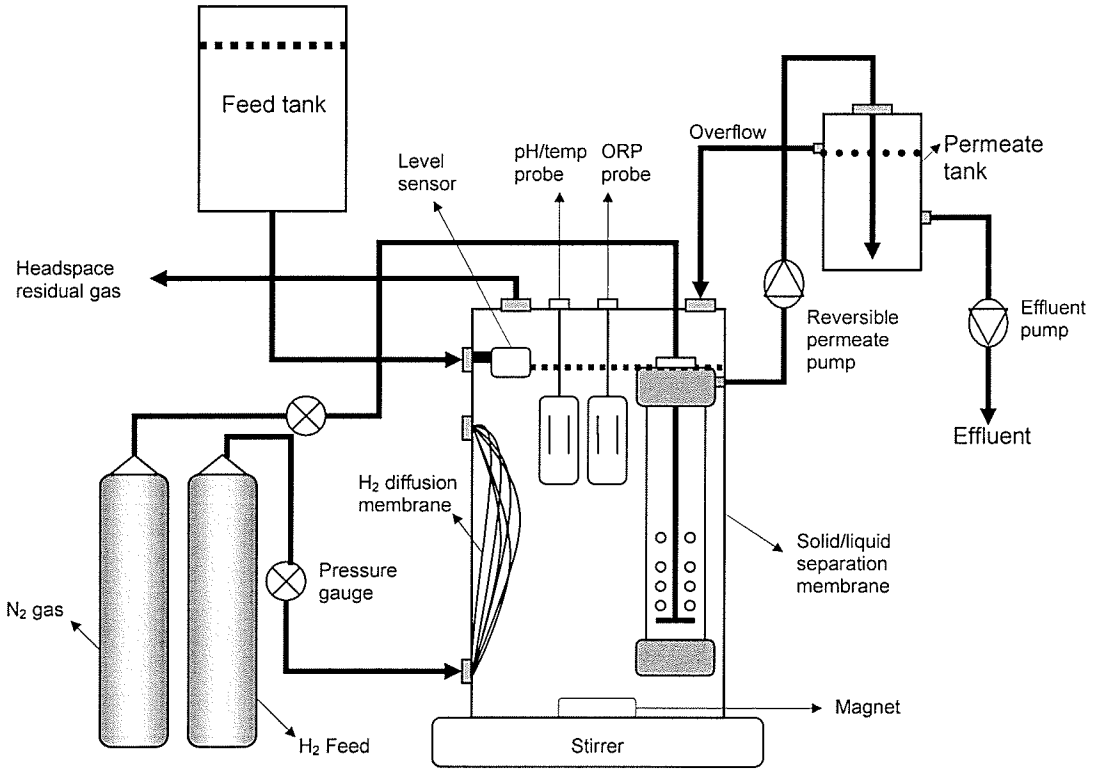
Figure 2 presents a system configuration of the laboratory scale membrane bioreactor (MBR) utilized in this research. The bioreactor was constructed using a cylindrical Plexiglas vessel with a total volume of 9.57L. The reactor had dimensions of 30.47 cm height and 20 cm outer diameter. Of the total volume, 7L of the reactor was occupied by the mixed liquor and 2.57L by headspace.

The reactor was inoculated with hydrogenotrophic (autotrophic) denitrifying biomass developed from the seed batch reactor. Two vertically oriented hollow fiber membrane modules were submerged in the bioreactor. The first membrane was a module

constructed by the researchers for this research using 94, 16cm Celgard® X30-240 microporous hollow fibers. The module was constructed as a dead-end hydrogen delivery unit by sealing one end of the hollow fiber bundle. The second membrane, a ZeeWeed®-1 (ZW-1) water filtration module, made available for this research by Zenon Environmental Inc., was used for solid/liquid separation. This membrane has a nominal pore size of 0.04 μm and the nominal membrane surface area of 0.047 m^2 with a recommended pump capacity of up to 150 mL/min. It also has a maximum operating temperature of 40°C and operating pH ranging 5 to 9. Industrial grade hydrogen gas (Welders Supplies, Winnipeg) was supplied to the system through the hollow membrane diffuser. Gas regulator and the flow meter were connected to the gas cylinder and used to monitor hydrogen gas flow to the MBR. Industrial grade nitrogen gas was also employed to vent residual dissolved oxygen (DO) within the reactor and facilitate scouring of the membrane surface. Excess headspace residual gas was directed to the open atmosphere.

Automatic feeding was provided by a float valve by gravity from the feed tank which was placed above the bioreactor. The permeate flow from the hollow fiber module was pumped by a reversible permeate micropump (Micropump model G18, Micropump Inc.) This micropump was controlled by a data acquisition system (Agilent Technologies, Palo Alto, CA), and a computer. Biomass agitation in the reactor was provided by a magnetic stirrer. The effluent was then collected in a 3L closed cylindrical permeate tank. Overflow from the permeate tank was returned to the bioreactor. Finally, the water was withdrawn from the permeate tank by a peristaltic pump for final discharge. Effluent flow rates and hydraulic retention time (HRT) of the system were measured and maintained at

constant levels by controlling this peristaltic pump. Level sensor was also employed to avoid overflow from the reactor. On-line ORP and pH/temperature probes were also submerged in the system. A pH controller (OAKTON Instruments, Alpha 100 Series 1/8 DIN) was used to control pH when pH exceeded 9 in the last stage of the experiment. Mixed liquor pH, ORP and temperature were continuously monitored on a data logger and effluent flow rates were closely monitored. Mixed liquor total and volatile suspended solid (TSS, VSS), effluent nitrate and nitrite, chemical oxygen demand (COD) and dissolved organic carbon (DOC) were measured once a week.



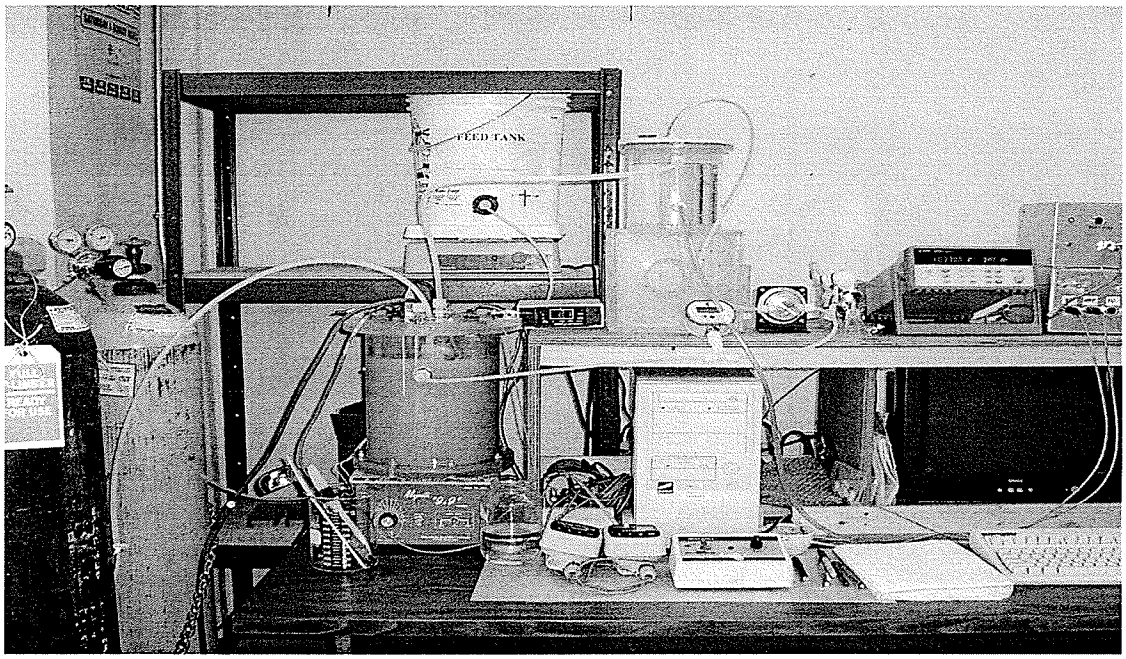


Figure 2. Schematic diagram and picture of laboratory scale bioreactor

2.3 Growth Medium

The bioreactor was operated in continuous mode with synthetic nitrate contaminated groundwater as feed. The synthetic groundwater was composed of the same chemicals which were used for the seed batch reactor synthetic groundwater except different concentrations of sodium nitrate ($NaNO_3$) as per nitrate loading and sodium bicarbonate ($NaHCO_3$) concentrations in the later stages of the experiment. The composition of the synthetic water used for this MBR is presented in Table 3.

Table 3. Composition of the synthetic groundwater

Chemical	Concentration (mg/L)
Dibasic potassium phosphate (K_2HPO_4)	1100
Monobasic potassium phosphate (KH_2PO_4)	900
Sodium bicarbonate ($NaHCO_3$)	80 (first three stages) 240 (during parts of the 4th stage) various per nitrate loadings
Calcium chloride ($CaCl_2 \cdot 2\ H_2O$)	30
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	20.5
Ferrous ion ($FeSO_4 \cdot 7H_2O$)	7.5
Sodium nitrate ($NaNO_3$)	Various per nitrate loading (72.7 – 1793)

2.4 Operating Conditions

Various nitrate loading rates were examined at an SRT of 20 days and at room temperature. SRT was controlled by wasting 1/20 of mixed liquor from the reactor once per day. Operating conditions of the MBR system is summarized in Table 4.

Table 4. Operating conditions of the MBR system

Stage	Time (day)	Influent NO_3^--N (mg/L)	HRT (hr)	Nitrate loading (NO_3^--N mg/L·d)
1	1-30	12	12	24
2	31- 119	24	12	48
3	120 – 163	48	12	96
4	164 – 330	72	9	192
5	331 - 420	288	18	384

2.5 Membrane Cleaning Regimes

Both physical and chemical means of cleaning were applied to membranes in order to ensure their performance. Automatic backwashing was employed for 30 seconds out of every 600 seconds to clean the ZW-1 membrane. Both membranes were brushed twice a day to remove attached biomass on the surface of the membranes. Chemical cleaning procedures of membranes followed the manufacturers' recommendations. ZW-1 membrane were cleaned using sodium hypochlorite (NaOCl) every two weeks. The ZW-1 module was soaked in 200 ppm NaOCl at room temperature for a minimum 5 hours and was then rinsed with clean water before use. In the later stages of the operation, more frequent and aggressive cleaning was applied to ZW-1 membrane as its performance declined. The membrane hydrogen diffuser was cleaned using a 5% solution of sodium hydroxide (NaOH) and deionized water every three weeks. When inorganic fouling was observed, an additional soak in citric acid (5mg/L) solution for a minimum of 5 hours was performed. The module was rinsed well with clean water between and after each step.

3. Analytical Methods

Nitrate (NO_3^-) and nitrite (NO_2^-) concentrations were measured by the automated cadmium reduction method (4500-NO_3^--F) (*Standard Methods*, 1995). Total suspended solids (TSS) and volatile suspended solids (VSS) were measured according to methods 2540 D and 2540 E (*Standard Methods*, 1995), respectively. Temperature, pH and ORP were determined using a flat surface electrode pH/ORP meter (OMEGA, USA). Chemical oxygen demand (COD) samples were analyzed using the Hach Digestions Vials (ultra low range 0-40 COD mg/L) and the Hach spectrophotometer (Hach, USA). Dissolved organic carbon (DOC) concentration was determined by Phoenix 8000 carbon analyzer (*Standard Methods*, 1995; 5310 C).

RESULTS AND DISCUSSION

Some 40 days after start-up, stable operation and consistent denitrification performance was achieved in the system. The system was operated continuously for about 420 days in five stages with nitrate loadings of 24, 48, 96, 192 and 384 NO_3^--N mg/L·d. Nitrate loading was increased when the system reached steady-state in each stage. The second stage was longer in duration than the other stages due to mechanical problems which occurred at the days of 74 and 75 during the experiment. Also, the fourth stage was longer than other stages due to the temporary unavailability of sample analysis.

1 Membrane Bioreactor Performance

1.1 Nitrate removal

Influent and effluent nitrate concentrations throughout the course of the experiment are shown in Figure 3.

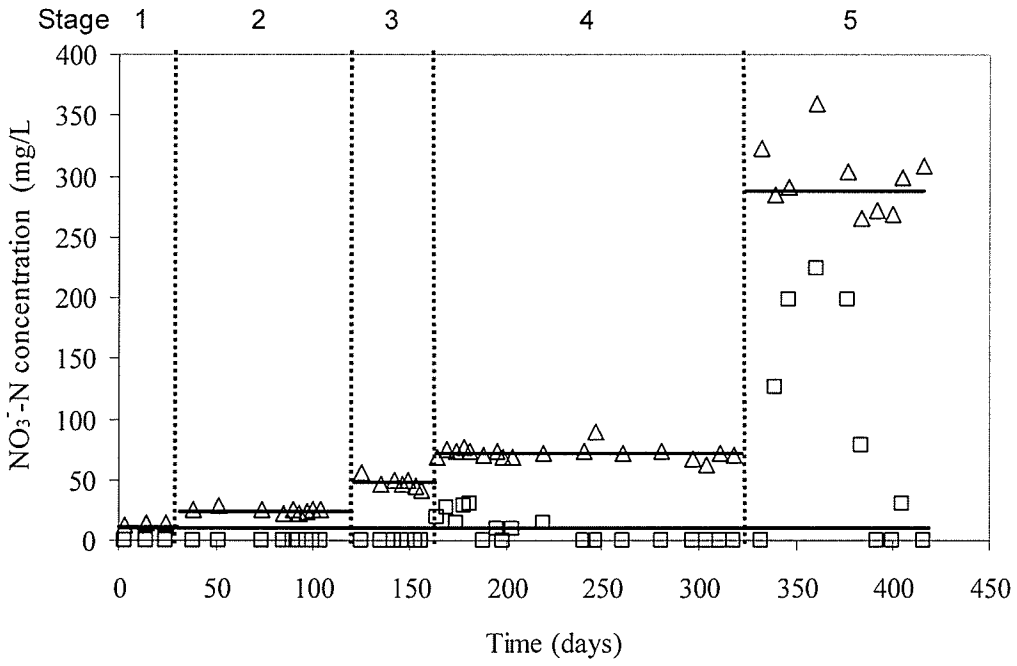


Figure 3. Nitrate removal efficiency of the system: Influent NO_3^- - measured (△); Influent NO_3^--N theoretical (—); Effluent NO_3^--N (□)

Complete (100%) nitrate and nitrite removal was achieved for nitrate loading rates with 24, 48, and 96 NO_3^--N mg/L·d as shown in Figure 3.

The result from the first stage is comparable with one obtained by Lee and Rittmann (2001) where a dead-end hollow fiber membrane was used in an attached biofilm system for the denitrification of the synthetic groundwater. With the influent nitrate concentration of 12.5 mg NO_3^--N/L, they achieved less than 1 mg NO_3^--N/L in the effluent without any nitrite accumulation. The nitrate removal efficiency results from second and fourth stages are comparable with those obtained from a work by Jahan et al. (2002), where a fixed bed hydrogenotrophic denitrification reactor with sealed end hollow fiber membrane gas diffuser was used. 100 and 87.1% of nitrate removal efficiency were achieved at the nitrate loadings of 54.24 and 186.24 NO_3^--N mg/L·d, respectively.

The results of the present work also showed similar nitrate removal efficiency with a previous hydrogenotrophic denitrification system using an attached biofilm. Greater than 99.3% of nitrate removal was obtained by Ergas and Reuss (2001) in their system with 90 NO_3^--N mg/L with more than 20 hours of HRT. For their work, it should be noted that they used a flow-through membrane which was found to have less than 40% hydrogen utilization efficiency during their experiment.

The present hydrogenotrophic denitrification system showed a superior performance than the one by Falk (2002). He used a dead-end hollow fiber membrane bioreactor with the aid of biofilm on the membrane surface to treat nitrate. In his system, effluent NO_3^--N concentration of 28 NO_3^--N mg/L was obtained with influent NO_3^--N concentration of 76

mg/L. This is much higher than the recommended MAC (maximum acceptable concentration) of 10 mg/L and the nitrate removal efficiency reached only 63%.

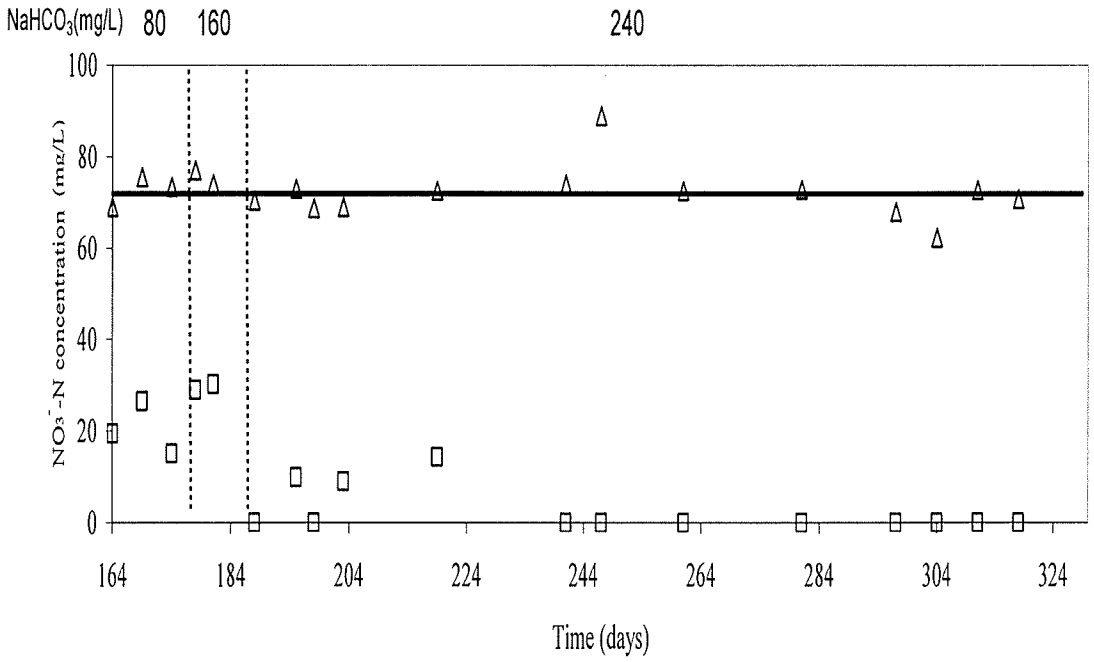


Figure 4. Nitrate removal efficiency during the fourth stage: Influent NO_3^- - N measured (△); Influent NO_3^- -N theoretical (—); Effluent NO_3^--N (△)

As shown in Figure 4, the last two stages of the experiment have shown a distinctive difference from the previous three stages in terms of nitrate removal performance. During the first three stages, hydraulic retention time (HRT) of 12 hours was maintained. However, it was reduced to 9 hours at the fourth stage to further challenge the system as no residual nitrate/nitrite was observed in the effluent in the previous three stages. As soon as the nitrate loading was raised to 192 NO_3^--N mg/L·d, residual nitrate concentrations were observed consistently. For this decreasing nitrate removal efficiency

in the fourth stage, it was thought that either hydrogen or inorganic carbon source was responsible. Hydrogen was ruled out as a cause since no nitrite was detected in the effluent meaning sufficient hydrogen has been provided to the system. Thus, the concentration of sodium bicarbonate ($NaHCO_3$), which serves as a carbon source for this hydrogenotrophic denitrification system, was raised to prevent carbon limitation. Lower nitrate removal efficiency was observed during the first 20 days of the fourth stage with the nitrate loading of 192 NO_3^--N mg/L·d when 80 and 160 mg/L of $NaHCO_3$ was provided to the system; nitrate removal efficiency decreased down to 59.2% and no nitrite was detected. As shown in Figure 4, no particular improvement was observed after increasing $NaHCO_3$ concentration to 160 mg/L from 80 mg/L in the third week of the fourth stage. Then $NaHCO_3$ concentration was increased to 240 mg/L in the feed. As soon as 240 mg/L of $NaHCO_3$ was applied to the system, nitrate removal was significantly enhanced without any nitrite in the effluent. Nevertheless, the removal efficiency rate has been fluctuating since then, most likely due to occasional mechanical problems including insufficient agitation and pH controller failure. Also, nitrate removal efficiency decrease in the fourth stage was observed when the temperature dropped below15 °C for some days. Nitrite accumulation was expected in the fourth stage when complete denitrification was not achieved. However, no nitrite accumulation was observed even when 10-25% of incoming nitrate was not treated.

In the last stage of the experiment, the system showed a similar trend to the fourth stage. For the last stage, high nitrate loading of 384 NO_3^--N mg/L·d was applied to the system to see the maximum capacity of this hydrogenotrophic denitrification system.

When high nitrate loading of 384 NO_3^--N mg/L·d was applied to the system, nitrate removal efficiency decreased significantly to 59% as seen in Figure 5. In order to enhance the removal efficiency, the same strategy was employed: the concentration of sodium bicarbonate was increased to 360 mg/L in the feed. However, as shown in Figure 5, no improvement was observed. Then $NaHCO_3$ concentration in the feed was increased to 480 mg/L. Residual nitrate concentration still remained higher than MAC of 10 mg/L. Failing to meet the goal, 720 mg/L of $NaHCO_3$ was then used for the feed. As soon as 720 mg/L was applied to the system, nitrate removal efficiency was improved to 100% and the effluent nitrate concentration was lower than 10 m g NO_3^--N/L. Since then, an average 90% of nitrate removal efficiency was achieved in the last stage.

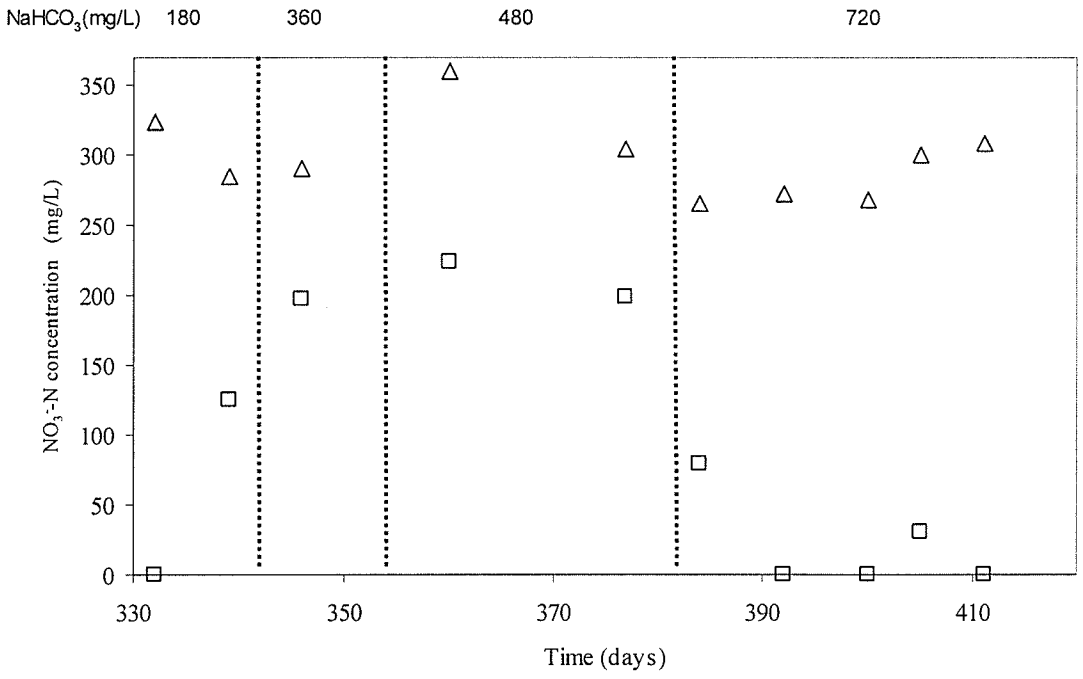


Figure 5. Nitrate removal efficiency during the fifth stage: Influent NO_3^- - N measured (△) and effluent NO_3^--N (□)

Through the fourth and fifth stage of the experiment, one important finding has been made: the inorganic carbon source can affect the nitrate removal efficiency of the hydrogenotrophic denitrification system. At the beginning of the experiment, the sodium bicarbonate concentration, which serves as an inorganic carbon source for hydrogenotrophic microorganisms, was only 80 mg/L. This is very low compared to the one used for Falk (2002)'s research. Theoretical amount of inorganic carbon required to treat nitrate is found from the following equation.

$$NO_3^- + 2.86H_2 + H^+ + 0.15CO_2 \rightarrow 0.03C_5H_7O_2N + 0.49N_2 + 3.14H_2O \qquad \text{(Eq. 8)}$$

From the equation above (Eq. 8), it is noted that 0.15 mol of CO_2 is required to treat 1 mole of NO_3^-. On a mass basis, 1 mg/L of NO_3^--N requires 0.9 mg/L of $NaHCO_3$. In Falk (2002)'s work, he used 722 mg/L of sodium bicarbonate ($NaHCO_3$) to treat 60 mg NO_3-N/L which is approximately 13 times the required amount. The inorganic carbon concentrations used for the experiments described above are relatively higher than one used for the present study. As explained earlier, 720 mg/L of $NaHCO_3$ was used to treat 288 mg NO_3^--N/L for the present work. In both the fourth and fifth stages of the experiment, theoretical ratio of 0.9 mg of $NaHCO_3$ per mg of NO_3^--N was not sufficient to provide 100% denitrification. In the fourth stage, 160 mg of $NaHCO_3$ for 72 mg NO_3^--N representing a 2.22 ratio was still no sufficient for complete NO_3 removal. Only when a ratio of 3.33 (240 mg $NaHCO_3$ per 72 mg NO_3^--N) was reached complete denitrification was achieved. For the fifth stage, a ratio of 2.5 (720 mg $NaHCO_3$ per 288

mg NO_3^--N) was sufficient for full denitrification. Therefore, a significantly higher than stoichiometically suggested $NaHCO_3$ concentration is necessary, most probably due to mass transfer limitation and CO_2 loss via headspace. However, a $NaHCO_3$ to NO_3^--N, 3 to 1, should be a maximum for mass ratio of design purposes as more carbonate would be excessive. As well known, the amount of chemicals used for biological denitrification directly affects the overall cost of plant operation. Therefore, it is important to use proper amount of chemicals required to treat the target loading.

In the fourth and the last stage of the experiment, residual nitrite was observed in the effluent as shown in Figure 6. The accumulation of nitrite might occur if there is not sufficient hydrogen available for the biomass. It can also occur when incomplete denitrification happens in the reactor. By this observation, it can be noticed that sufficient hydrogen was provided to the system in all five stages.

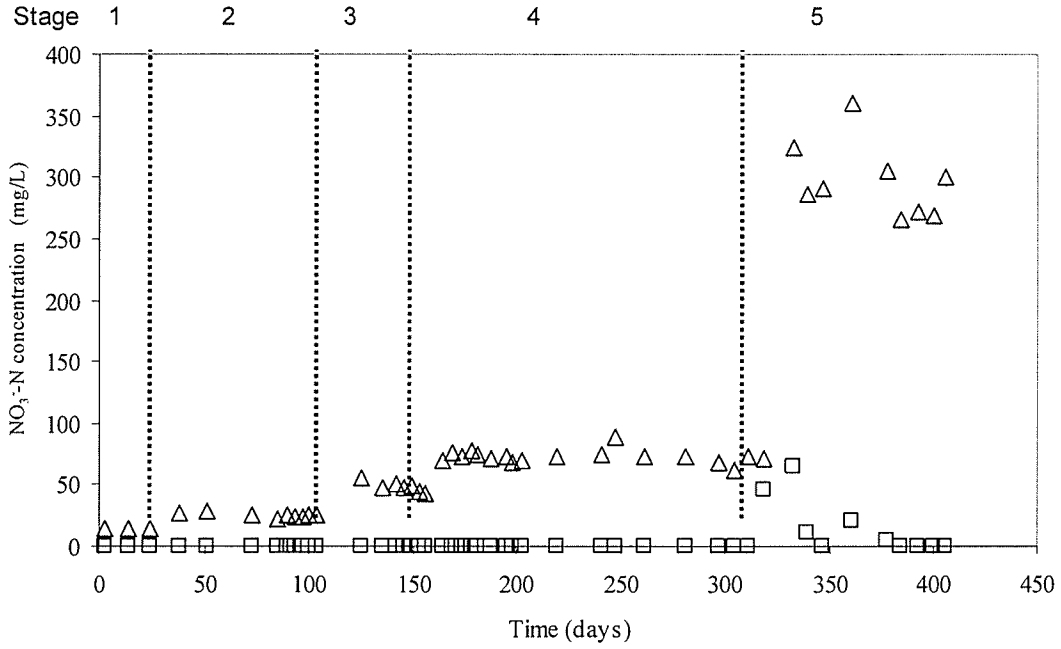


Figure 6. Nitrate removal efficiency during the fifth stage: Influent NO_3^- - N measured (△) and effluent NO_3^--N (□)

As mentioned previously, both Ergas and Reuss (2001) and Falk (2002) used an attached biofilm system for their hydrogenotrophic denitrification systems. During their experiment, they experienced lower denitrification rates as the biofilm became thicker and the thick biofilm had to be sheared in order to ensure consistent reactor performance. Falk (2002) reported that denitrification rate was constantly changing as the biomass grew thicker. He explained that the biomass can grow too thick limiting the mass transfer of the carbon source and electron acceptor, decrease biomass activity, cause the membrane fiber plugging, and/or accumulates metabolites. For his system, routine shearing of the biofilm was done every two to three weeks to control the growth of biomass. With time, the shearing increased the denitrification rate; however, the

frequency of shearing needs closer monitoring. Ergas and Reuss (2001) also experienced the similar problem while operating their system. Decreased system performance was observed in their bioreactors after the development of a thick biofilm. They observed that the NO_3^--N concentration in the effluent significantly increased when a thick film was developed on the outer fibers of the membrane module. In order to maintain film thickness at an optimum level, several operational strategies including shearing the biomass were used. In the present study, this problem was not of concern as a suspended growth system was utilized in the system.

The nitrate utilization rate (NUR) of the biomass was investigated in batch mode for each stage at steady-state. It was determined by using conventional Monod equation.

Nitrate utilization rates of 30.6 and 23.4 mg NO_3^--N/L·d were achieved in the first and second stage, respectively. Low NUR of 23.4 mg NO_3^--N/L·d in the second stage in comparison to NUR from the first stage was expected as the test was conducted at ambient temperatures approximately 5 °C lower than the first stage. In the third stage, 37.7 mg NO_3^--N/L·d of NUR was obtained. These denitrification rate results are lower than those reported in a previous hydrogenotrophic denitrification study. Ergas and Reuss (2001) reported an average nitrate utilization rate of 59 mg NO_3^--N/L·d with the influent nitrate concentrations of 65 to 72 mg NO_3^--N/L. Pierkiel (2002) obtained 1.0 mg NO_3^--N/mg VSS·d of NUR from a batch hydrogenotrophic denitrification system. With the unit of mg NO_3^--N/mg VSS·d, the first three stages gave 0.18, 0.17 and 0.19 mg NO_3^--N/mg VSS·d, respectively.

NUR tests in the present work were performed at temperatures similar to ones in real groundwater which is likely to be between 10 and 16°C. Considering that most of previous studies regarding denitrification were performed at 20°C and higher, lower nitrate utilization rates from the present study were partially attributed to the relatively suppressed operating temperature. Another reason would be the NO_3 limited environment in the bioreactor during stages 1, 2 and 3 which could result in a less active biomass in terms of denitrification.

No further comparisons of NUR results with other previous hydrogenotrophic denitrification studies were made since most of the previous works employed attached biofilm system and NUR is reported as g nitrate per membrane surface area (m^2) per day.

Table 5. NUR results from the steady-state of each stage

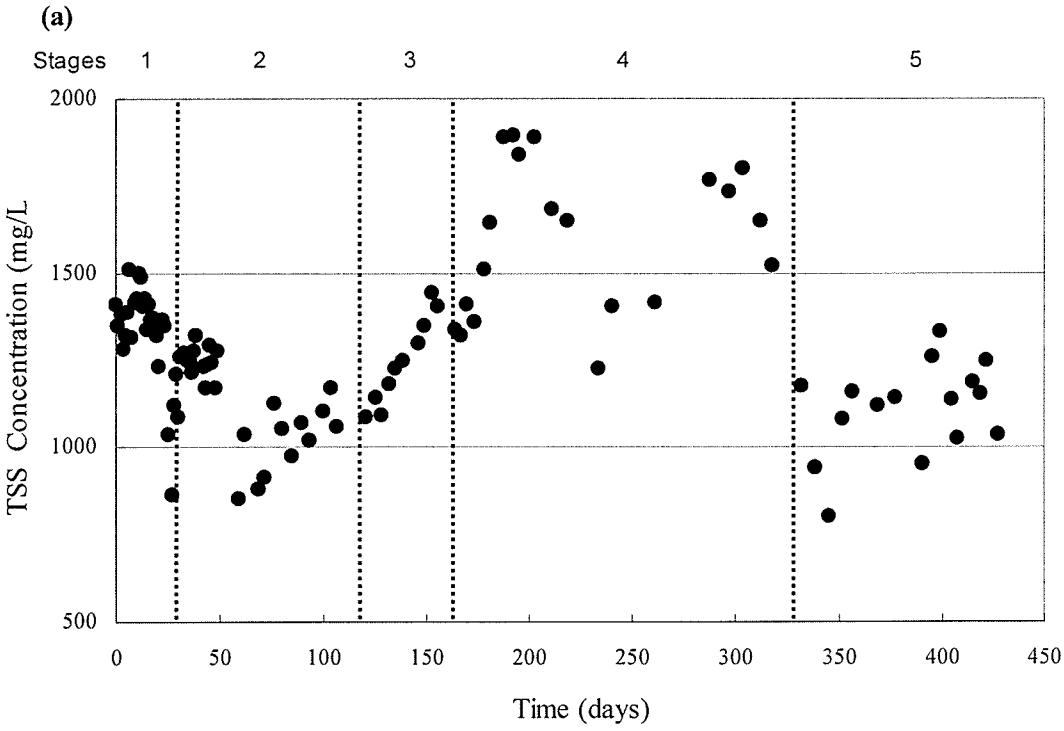
Stage	NUR (g NO_3^--N/m^3/d)
1	30.5
2	23.4
3	37.7
4	184.2

The NUR from the fourth stage showed a significant difference from those obtained from the previous stages. As discussed earlier, NURs from the first three stages showed 30.6, 23.4 and 37.7 mg NO_3^--N/L·d. However, the NUR was determined to be of 184.2 mg NO_3^--N/L·d when the system was operated with 192 NO_3^--N mg/L·d in the fourth stage. Two factors are considered to contribute to this unexpectedly high NUR rate from the fourth stage. Firstly, the initial biomass seed to the reactor originated from an

environment where excess nitrate was available. During the first three stages of operation the biomass was under severe nitrate limiting conditions, presumably resulting in reduced metabolic rates and an existence geared towards maintenance. When excess nitrate was finally available during the fourth stage, a significant switch in metabolism occurred resulting in aggressive denitrification and subsequent biomass growth. The return to high nitrate loadings could have triggered the transformation from maintenance-based to growth and consumption driven metabolism. Another factor for elevated NUR could be increasing reactor temperature. Until the third stage, where ambient temperature was relatively low (below 15°C), the reactor temperature gradually increased in the fourth stage to about 20°C as it approached the summer. The warmer temperature will further boost denitrification reaction in the reactor.

1.2 Observations of Biomass

Figure 7 illustrates the variations of total and volatile suspended solids (TSS and VSS) concentrations throughout the experiment. As shown in Figure 4, mixed liquor suspended solids concentration remained relatively stable during the testing, and did not exhibit a strong correlation to nitrate loading rates during the first three stages. However, when the nitrate loading reached to 192 NO_3^--N mg/L·d, TSS and VSS concentrations showed a gradual increasing trend. In the last stage of the experiment with the 384 NO_3^--N mg/L·d, VSS concentration once again showed an increasing trend. Then it stabilized after reaching 490 mg/L. The availability of excess nitrate in the fourth and the last stage resulted in gradual biomass growth.


(a)
Stages 1 2 3 4 5
2000
1500
1000
500
TSS Concentration (mg/L
0 50 100 150 200 250 300 350 400 450
Time (days)

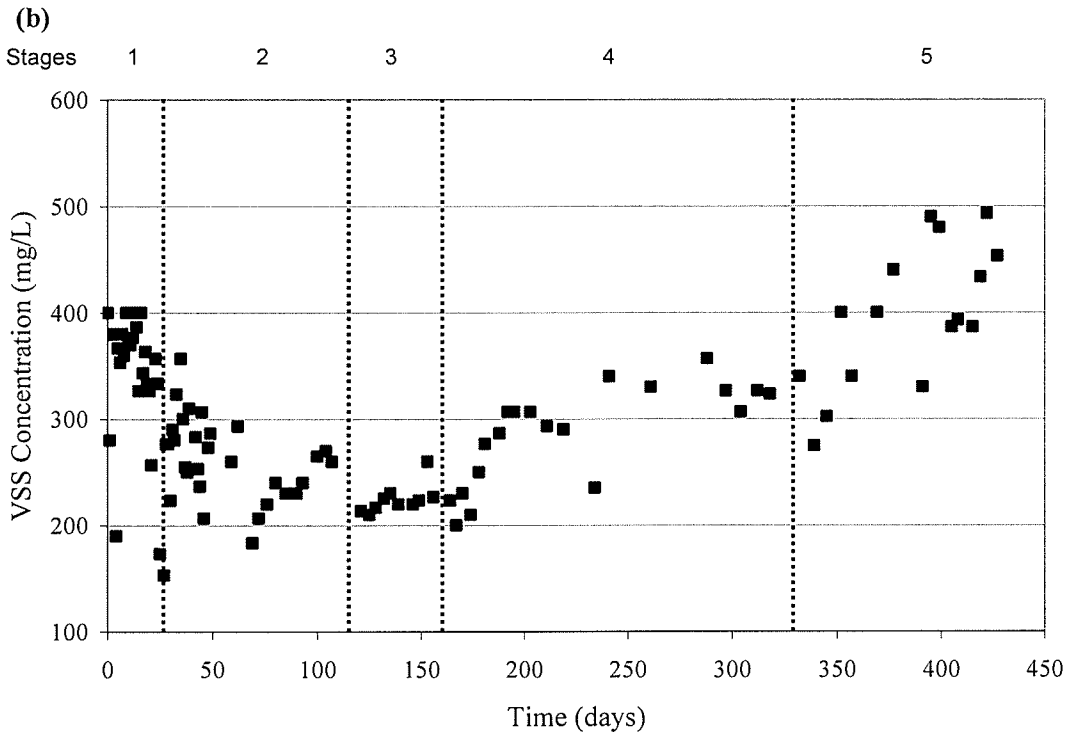


Figure 7. Variations of mixed liquor concentrations: (a) Total suspended solids (TSS); (b) Volatile suspended solids (VSS)

There was some loss of biomass during the batch NUR tests. While switching continuous mode to batch mode for the NUR test, some portion of biomass was lost due to the poor settleability of biomass. However, following the NUR tests VSS concentration increased slowly and soon remained stable. It is also noted that a portion of VSS in TSS (percent VSS in TSS) decreased as the nitrate loading increased. This is most likely due to the precipitation of inorganic complexes formed between nitrate and feed constituents including magnesium (Mg), calcium (Ca), and iron (Fe). However, opposite trend was observed in the last stage; its portion showed an increasing trend. This can be explained

by the presence of higher concentration of VSS in the reactor during the last stage. As more biomass present in the reactor they may have consumed more inorganics in the feed for their growth and maintenance. As a result, less precipitation of inorganics may have happened than the previous stages.

The change in the color of mixed liquor was an interesting indication of nitrate exhaustion. The seed biomass, which was cultivated under very high nitrate concentration (500 mg NO_3^--N/L), was brownish in color. When operating under nitrate-limiting conditions in the first three stages, the mixed liquor in the MBR turned dark grey and the color changed gradually back to light brown as the nitrate loading increased. This is most likely due to the action of sulfate and iron reducing bacteria which proliferated under nitrate limiting conditions. During the last two stages of testing, where excess nitrate is available, the general appearance of the mixed liquor was very similar to the seed population. This observation is expected to serve a good visual indication of biomass condition of biomass in the reactor.

Complete VSS retention was achieved in the system during testing (Table 6). This indicates that by utilizing an MBR rather than a conventional system with a clarifier the loss of active denitrifiers can be prevented. Effluent TSS concentrations (Table 6) were higher than previously published results where attached growth systems were used for hydrogenotrophic denitrification (Eras and Reuss, 2001). This result was unexpected as the solid/liquid separation membrane was designed to provide a barrier for suspended solids. One possible source of TSS might be connecting pipes following the membrane filter, where reformation of inorganic particles could occur in very low-flow (no mixing) environments. TSS and VSS analysis methods can also be a probable cause as the

effluent TSS/VSS concentration might be at or below the detection limit. Despite extensive investigation the exact source for effluent TSS could not be established.

1.3 Observations of Operating Parameters

Figures 8 shows the variations in temperature, oxidation reduction potential (ORP) and pH. The reactor temperature varied from 11.6 to 21.9°C throughout the experiment due to the fluctuations in room temperature. During the first stage, the temperature was relatively stable at 17.0±1.3°C. The temperature dropped down to 12.5°C at one point during the second stage due to changes in ambient conditions. The sudden drops in temperature affected denitrification conditions as sharp increases were observed in ORP. In the fourth stage, relatively warmer temperature was maintained as it was summer time. This most likely led to faster DO exhaustion and denitrification reaction. In the last stage, it showed a decreasing trend as the season was approaching winter ambient temperature was dropping. Overall, the impacts of temperature variations were short-lived and stable ORP conditions were generally observed.

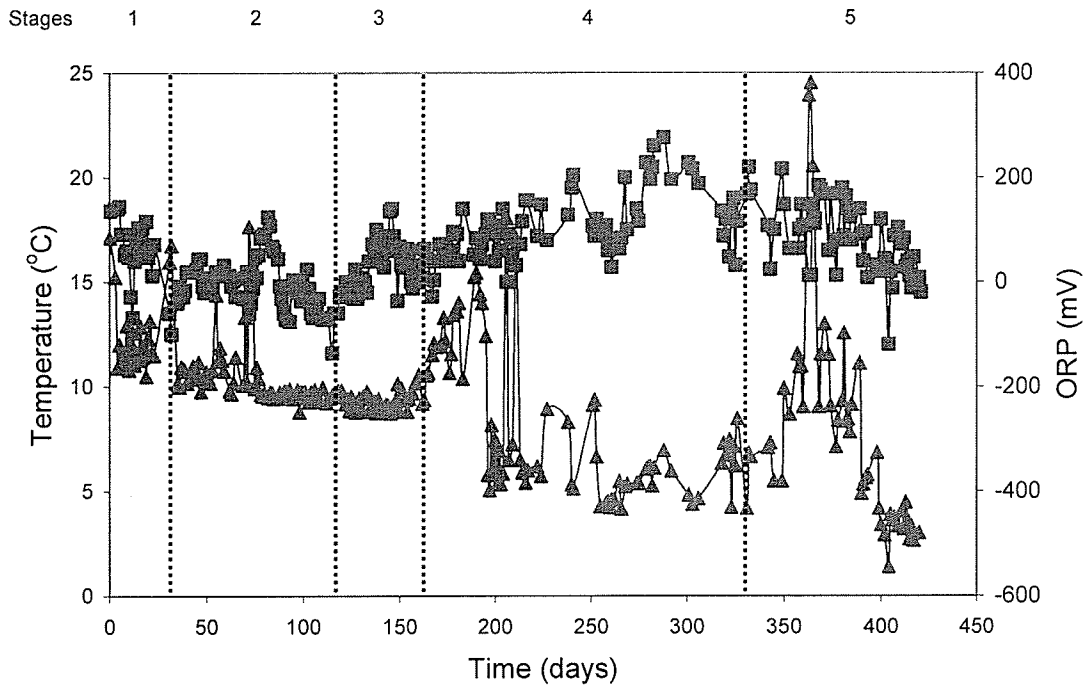


Figure 8. Variations in ORP and temperature: ORP (△) and temperature (□)

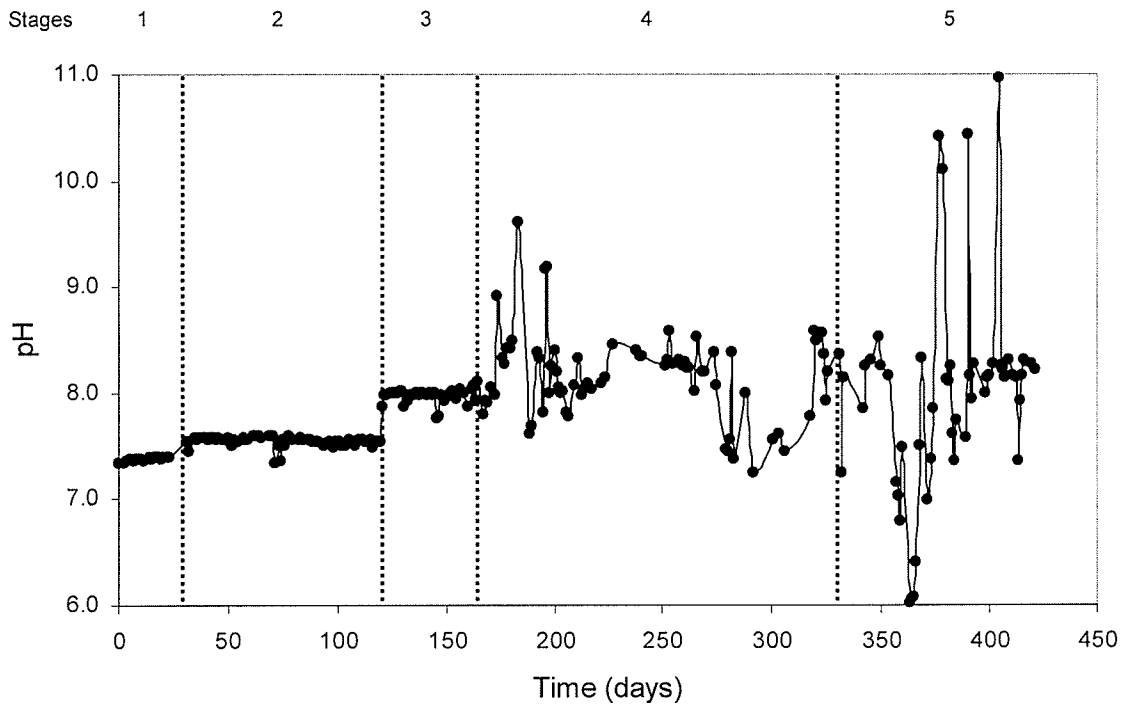


Figure 9. Variations pH during the experiment

A distinctive change in pH values was observed throughout the experiment. In the first stage, the initial pH was 7.34 and it gradually increased up to 7.40. An increase in pH was observed as nitrate loadings increased, reaching up to 7.59 in the second stage and 8.01 in the third stage. During the initial period of the fourth stage, pH did not change, presumably due to lack of additional denitrification, which was supported by the observation of residual nitrate in the reactor. However, pH increased sharply up to 9.0 when $NaHCO_3$ was increased up to 240 mg/L representing active denitrification occurrence in the system. Since the optimum pH for denitrification ranges from 7.5 to 8, pH was maintained at about 8 by using a pH controller. However, during the time pH

controller was used for the experiment pH was not very stable. From day 363 to 366, pH controller was out of order and it resulted in overdosing of pH buffer solution to the reactor. This caused lower pH in the reactor and most likely increased ORP condition. However, pH and ORP values returned to normal as soon as the controller was fixed. Since the pH controller was used for the system, pH was maintained at around 8 except times when the pH controller did not work properly.

ORP decreased quickly from 85 mV at the initial start of the first stage to -164 mV after 4 days and it was at -120±61 mV during the rest of the first stage. Short term fluctuations in ORP and pH were observed during a mechanical failure at days 74 and 75 of operation, but the system re-established steady state fairly quickly. During the fourth stage of operation, when nitrate loading rate reached 192 NO_3^--N mg/L·d, higher ORP values were observed due to incomplete denitrification and the presence of residual nitrate in the reactor. ORP showed a slightly different trend from pH in the fourth stage when higher $NaHCO_3$ concentration was applied; while pH increased drastically as soon as $NaHCO_3$ concentration increased, ORP did not show a significant change for the next five days. However, it started to decrease from the 6^{th} day after $NaHCO_3$ concentration increase and was stable except the times when there was an interruption in mixing. In the last stage of the experiment, ORP increased again possibly due to the presence of the residual nitrate in the reactor. It showed a fluctuation during the initial period of the last stage. When the reactor had a mechanical failure with pH controller, ORP values increased significantly reaching higher than zero. It soon recovered to negative values when the pH controller came back to normal operation.

As seen in Figure 8, ORP values in the last stage were maintained higher than the fourth stage when relatively high residual nitrate concentration were consistently observed in the effluent. However, it decreased when full nitrate removal activity started to occur with the aid of higher $NaHCO_3$ concentration in the feed. After that, it got stabilized and ranged around -400 mV until the end of the experiment.

Overall, on-line ORP and pH measurements served as good indicators for the health of the denitrification process in this system.

1.4 Dissolved organic carbon (DOC) results

Throughout the experiment, the dissolved organic carbon (DOC) concentration did not exhibit a particular trend as shown in Figure 10. The average residual DOC in the effluent was 7.9, 7.6, 8.1, 8.2 and 8.3 mg/L in each stage, respectively (Table 6). Interesting comparison can be made from DOC results from the present work and the previous works. These results were comparable with those from Lee and Rittmann (2000) and Haugen et al. (2002), but lower than those presented by Ergas and Reuss (2001). Increase of DOC in hydrogenotrophic denitrification has been reported by both Lee and Rittmann (2000) and Ergas and Reuss (2001). In Ergas and Reuss (2001)'s work, a large increase of DOC in the effluent from 11 to 31 mg/L was observed. They speculated that this high DOC concentration may be due to the presence of SOC (soluble organic carbon) in the effluent. In Falk's work (2002), he observed relatively low DOC concentration in the effluent of 2.7 mg/L. However, no clear explanation was provided why relatively low DOC

concentration was obtained in the effluent compared to ones observed from other previous hydrogenotrophic studies.

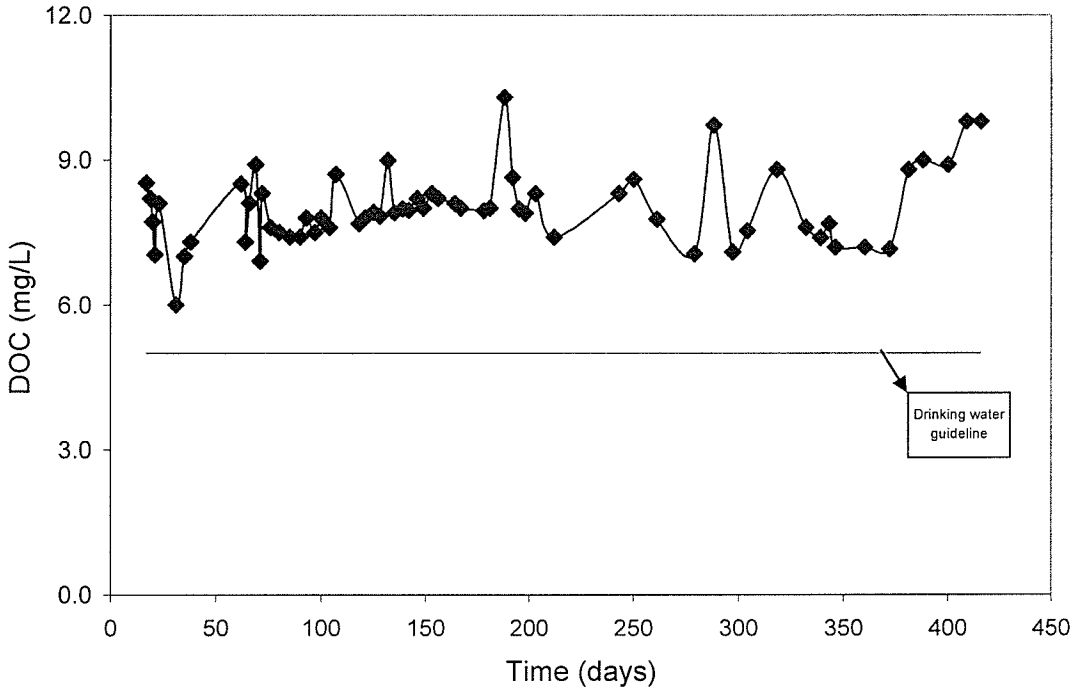


Figure 10. Variations of effluent DOC concentration during the experiment

Lower effluent DOC in the present study was expected as the membrane filter was responsible for trapping some DOC on the membrane surface. The possible sources of this effluent organic matter are cell components and soluble microbial products (SMP). Other source can be volatile fatty acids (VFA) produced by acetogenic bacteria in the biomass population. Since the biomass population is not solely autotrophic, other heterotrophic organisms can be digested in low ORP conditions producing VFA.

However, Rezania et al. (2004) reported that no activity of acetogenic bacteria was observed within the hydrogenotrophic culture with which he used for his hydrogenotrophic denitrification study. They concluded that the source of organic matter for reduction of nitrite to nitrogen gas did not originate from acetogens.

Biofilm formed on the surface of the membrane can be another source for DOC. In this case, exocellular polymeric substances (EPS) which are produced by the micro-organisms in the biofilm to promote attachment could be released to the solution.

As these levels of DOC were detected in the effluent, additional removal of DOC will be necessary to comply with drinking water regulations.

1.5 Chemical oxygen demand (COD) results

Soluble chemical oxygen demand (SCOD) concentration did not show a particular trend or relationship with nitrate loading. As presented in Table 6, relatively high concentrations of COD were detected in the effluent and average COD in the effluent were 14.0, 9.8 and 14.6 mg/L in the last three stages, respectively.

As well known, COD is defined as the oxygen demand for the organic matter to be oxidized (de Silva et al, 1998). A general oxidation reaction of biomass provides its theoretical relationship to COD is as follows:

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \qquad \text{(Eq. 9)}$$

From Eq. 9, five moles of oxygen with a mass of 160g are required to oxidize one mole biomass, yielding a theoretical COD/VSS ratio of 1.42 mg COD/mg VSS. Based on the theoretical COD/VSS ratio and the effluent VSS observed during the experiment, very low COD values could have been expected from effluent COD samples. However, a conflicting expectation was made due to the effluent DOC results. As mentioned earlier, high DOC concentrations were observed in the effluent throughout the study. COD values in the effluent indicate the presence of organic matter in the effluent. Relatively high effluent COD results are expected throughout the experiment since the presence of organic matter is already proven by the high DOC values in the effluent. As shown in Table 6, the expectation was in accordance with the effluent COD results.

Since no results from previous hydrogenotrophic studies are available, no comparison was made with the COD results from the present study.

Microbial products which contribute effluent DOC values can also contribute COD values as they are products from biomass. As tubings between the bioreactor and the effluent reservoir were suspected to be responsible for the COD values in the effluent, all the tubings and other connecting pipes were cleaned. However, no decrease was observed in the effluent COD concentrations after cleaning. Since the VSS concentration in the effluent was always under detectable limit throughout the experiment, microbial products such as SMP are considered to be responsible for the COD values.

2. Operational problems – membrane fouling

Throughout the experiment, several operational problems were observed. The main problem associated with the operation of this system was the fouling of the water filtration membrane (ZW-1 membrane). ZW-1 membrane was originally designed for aerobic bioreactors to have the hole located in the bottom of the axis of the membrane for air supply. However, N_2 gas was introduced through the hole instead of air in order to make the reactor an anaerobic condition and to scour the membrane. It was observed that the fouling especially occurs when insufficient or no nitrogen gas is supplied to the membrane for scouring.

After the reactor was operated for four stages, it was observed that the membrane can be severely fouled without N_2 gas introduction to the system. In order to determine the effect of N_2 gas supply to the water filtration membrane performance, a simple experiment was conducted under two different conditions; firstly, when sufficient N_2 is continuously provided to the membrane and secondly when no N_2 gas introduced to the membrane.

For this experiment, new ZW-1 membrane was employed and its initial flow and TMP (trans-membrane pressure) variations were measured on a various micropump speed. After some time of using this membrane, chemical cleaning was done with NaOCl according to the product manual. Then TMP and flow were evaluated after first and third chemical cleaning.

N_2 gas was introduced to the membrane through the hole located in the bottom of the axis of the membrane, and TMP and the flow were measured. Then N_2 gas supply was stopped for one day in order to see how TMP and flow change due to the lack of N_2 gas introduction. The experiments were repeated three times under identical conditions. Variations of TMP and flow are depicted in Figure 11.

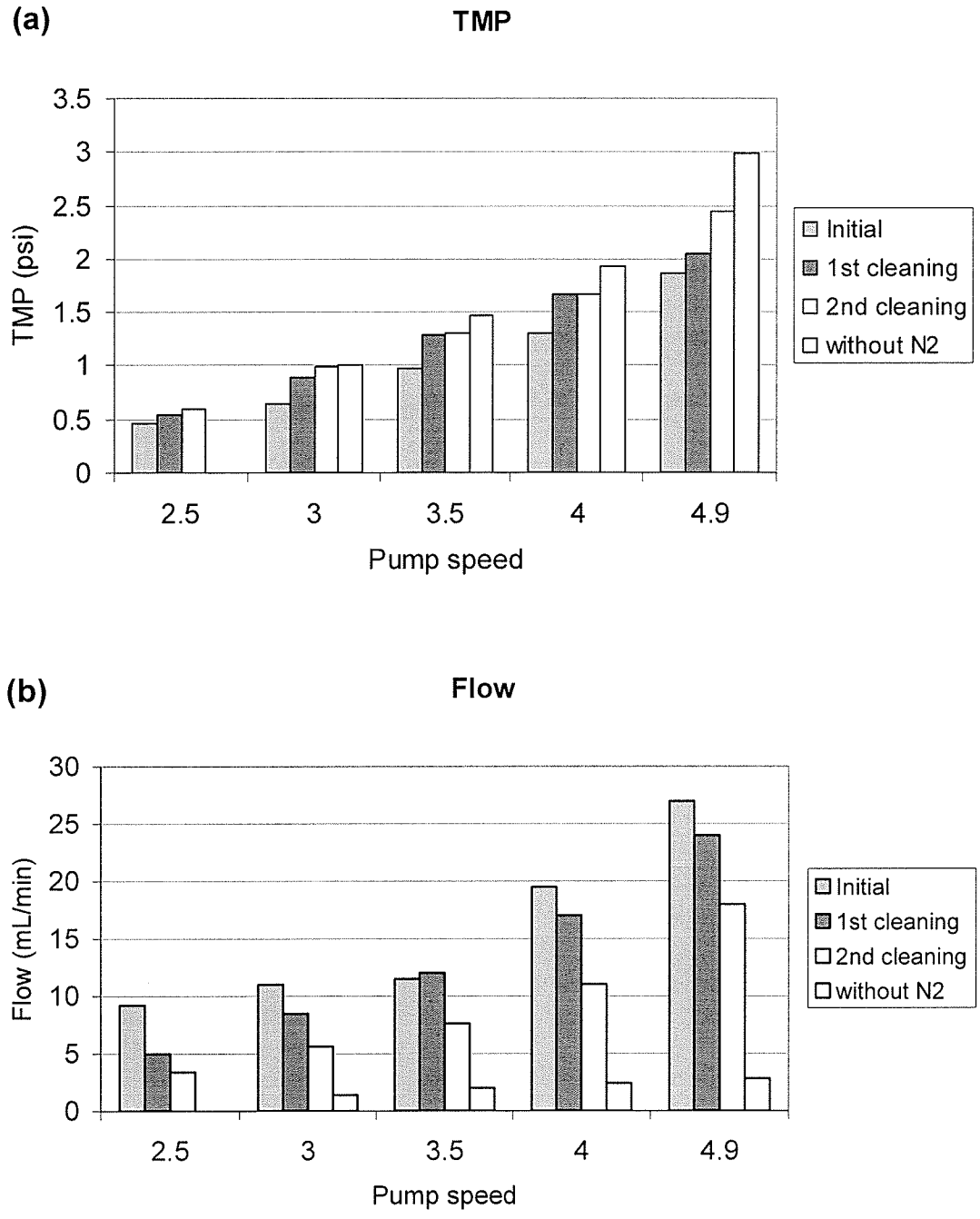


Figure 11. Variations of TMP (a) and flow (b) on the cleaning and N_2 gas supply

As presented in Figure 11, when sufficient N_2 gas was supplied to the system during the first day of the experiment, TMP did not increase and flow showed a small change on micropump speed after 1st and 2nd chemical cleaning. However, TMP significantly increased when no N_2 gas was provided to the membrane. Also, flow through the micropump decreased drastically without N_2 gas introduction showing the maximum decrease of 90%. This is thought to be most likely due to the membrane fouling.

This result suggests that N_2 gas introduction can prevent the fouling of the water filtration membrane. However, the use of N_2 gas for the prevention of membrane fouling has three major drawbacks. Firstly, the cost of N_2 gas will raise the overall operation cost. For example, one full N_2 gas cylinder was used every four days for a sufficient N_2 gas supply to the membrane for this research. Secondly, vigorous N_2 gas introduction might strip some H_2 gas in the reactor resulting in lower H_2 dissolution in the reactor. Lastly, N_2 gas introduction might lower the reactor temperature and can have an impact on the biomass activity and thus the system efficiency.

Three suggestions can be made to address these problems associated with the membrane fouling. Through this simple experiment, it is suggested that using an external water filtration membrane might work better for this system as it uses cross-flow to limit fouling. Another suggestion can be the use of a conventional sedimentation tank instead of water filtration membrane unit. In order to use a settling basin, it is required to check the settleability of the sludge in the reactor. In the present study, the VSS concentration is relatively low compared to one from general heterotrophic denitrification and the poor settleability was observed during the NUR tests.

The last suggestion is to introduce CO_2 in place of N_2 to the system via the membrane module. The CO_2 could replace the carbonate added in solid form to the incoming water and also serve as a scouring agent. However, the drop in pH resulting from CO_2 addition needs to be counted to maintain high denitrification activity.

Table 6. Important performance parameters during five stages

Stage	1	2	3	4	5
Days of operation	1-30	31- 119	120 – 163	164 – 330	331 - 420
Nitrate loading (NO_3^--N mg/L·d)	24	48	96	192	384
Influent NO_3^--N (mg/L)	13.6±0.1	25.0±1.8	48.0±4.4	72.0±6.0	288.0±20.0
Reactor temperature (°C)	17.0±1.3	15.0±1.2	16.0±1.1	15.5±0.8	17.1±1.7
pH	7.40±0.02	7.54±0.04	8.00±0.09	7.93±0.12	8.0±0.96
ORP (mV)	-120±61	-180±71	-230±17	-300±145	-300±204
Effluent NO_3^--N (mg/L)	0	0	0	7.0±6.4	2.6±5.0
Effluent NO_2^--N (mg/L)	n/d*	n/d	n/d	n/d	n/d
Nitrate removal efficiency (%)	100	100	100	97.0±7.0	97.0±5.15
Nitrate utilization rate (mg NO_3^--N /L·d)	30.6	23.4	37.7	184.2	n/a
Total suspended solids in the reactor (mg/L)	1300±146	1100±135	1200±126	1500±267	1100±134
Volatile suspended solids in the reactor (mg/L)	330±72	260±40	230±20	280±49	400±67
Effluent total suspended solids (mg/L)	n/a**	n/a	10.0±3.0	9.0±1.3	n/a
Effluent volatile suspended solids (mg/L)	n/a	n/a	bdl***	bdl	bdl
Effluent DOC (mg/L)	7.9±0.5	7.6±0.7	8.1±0.3	8.2±0.8	8.3±1.1

Effluent COD (mg/L)	n/a	n/a	14.0±1.3	10.0.±5.5	15.0±7.0

* not detected ** not available *** below detection limit

CONCLUSIONS

The aim of this research was to design and evaluate a suspended growth hydrogenotrophic denitrification system incorporating hollow fiber membranes for both cell retention and hydrogen gas diffusion for nitrate contaminated ground water treatment. Furthermore, the effects of inorganic carbon source on the biomass and gas scouring on the operation water of the filtration were examined. Important observations and conclusions obtained from this investigation are as follows:

- Five nitrate loadings of 24, 48, 96, 192 and 384 NO_3^--N mg/L·d were applied to the system. Nitrate was completely removed and no nitrite was detected in the first three nitrate loadings. In both fourth and fifth stages with 192 and 384 NO_3^--N mg/L·d, 97% of nitrate removal was achieved without any accumulation of nitrite when sufficient inorganic carbon source was supplied to the system.
- As the nitrate loading was increased, pH increased due to increased denitrification and release of OH^- ions. When nitrate loading rates were raised to192 NO_3^--N mg/L·d, pH decreased and ORP increased most likely due to incomplete denitrification and the residual nitrate in the reactor. However, pH started to increase and ORP to decrease when sufficient amount of $NaHCO_3$ which served as an inorganic carbon source for the hydrogentrophic denitrifiers was provided to the system. Throughout the study, on-line ORP and pH measurements served as good indicators of denitrification and general performance of the system.

- Nitrate utilization rates (NUR) of 30.6, 23.4, 37.7 and 184.2 mg NO_3^--N/L·d were obtained in the system with 24, 48, 96 and 192 NO_3^--N mg/L·d, respectively. High NUR from the fourth stage is considered to be due to a significant metabolic enhancement in biomass and higher operating temperature.
- The source of inorganic carbon plays an important role in the denitirification reaction and sufficient carbon source should be provided to the system to ensure system performance. Higher ratios than stoichiometric ratios of $NaHCO_3$ are required for complete denitrification.
- Average dissolved organic carbon (DOC) concentrations of approximately 8 mg/L and soluble chemical oxygen demand (COD) of 14.1 mg/L observed in the effluent, which will necessitate post-treatment. It was speculated that the DOC and COD originated from soluble microbial products (SMP).
- Water filtration membrane showed severe fouling problem without N_2 gas scouring. Due the cost of N_2 gas, it is not recommended to use N_2 continuously to prevent fouling. It is suggested that an external membrane unit is used or CO_2 gas utilized as a scouring agent. In this case, the control of pH is necessary when CO_2 is introduced in gaseous form.

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APPENDIX

1. Raw data from the experiment

Table 1. Feed nitrate concentrations and effluent nitrate/nitrite concentrations

Time (days)	Feed NO_3 (m g NO_3^--N/L)	Effluent NO_3 (m g NO_3^--N/L)	Effluent NO_2 (m g NO_3^--N/L)
3	13.5	0.0	0.0
14	13.7	0.0	0.0
24	13.7	0.0	0.0
38	26.2	0.0	0.0
51	28.4	0.0	0.0
73	24.9	0.0	0.0
85	22.0	0.0	0.0
90	25.1	0.0	0.0
93	23.1	0.0	0.0
97	24.2	0.0	0.0
100	25.5	0.0	0.0
104	25.0	0.0	0.0
125	55.8	0.0	0.0
135	46.8	0.0	0.0
142	50.4	0.0	0.0
146	47.1	0.0	0.0
149	49.2	0.0	0.0
153	45.0	0.0	0.0
156	42.0	0.0	0.0
164	69.0	19.5	0.0
169	75.5	26.5	0.0
174	73.4	15.1	0.0
178	77.0	29.0	0.0
181	74.0	30.0	0.0
188	70.4	0.0	0.0
195	73.0	9.9	0.0
198	68.7	0.0	0.0
203	69.0	9.0	0.0
219	72.5	14.3	0.0
241	74.0	0.0	0.0
247	88.9	0.0	0.0
261	72.5	0.0	0.0

281	72.9	0.0	0.0
297	67.9	0.0	0.0
304	62.4	0.0	0.0
311	72.8	0.0	0.0
318	70.8	0.0	0.0
332	323.7	0.0	45.5
339	285.5	125.8	64.2
346	290.7	198.1	10.8
360	359.9	224.6	0.0
377	304.7	198.3	20.4
384	265.2	78.7	4.9
392	272.2	0.0	0.0
400	268.2	0.0	0.0
405	300.0	30.9	0.0
416	308.6	0.0	0.0

Table 2. ORP, pH and temperature in the reactor

Time (days)	pH	Temperature (°C)	ORP (mV)
0	7.34	18.0	85
3	7.34	18.5	10
4	7.36	18.5	-164
5	7.37	18.6	-120
6	7.37	17.3	-161
7	7.36	17.3	-140
8	7.37	16.3	-150
9	7.37	16.5	-83
10	7.37	16.2	-168
11	7.38	14.3	-116
12	7.36	13.3	-97
13	7.38	16.0	-158
14	7.39	17.0	-134
15	7.37	17.6	-149
16	7.40	16.3	-85
17	7.39	17.6	-144
18	7.39	16.7	-121
19	7.39	17.9	-180

20	7.37	16.2	-107
21	7.39	16.6	-74
22	7.39	15.3	-134
23	7.40	16.8	-140
31	7.54	13.5	39
32	7.44	12.5	70
35	7.57	14.0	-194
36	7.55	14.8	-200
37	7.57	14.6	-162
38	7.57	14.3	-165
39	7.57	14.6	-170
40	7.58	15.5	-193
41	7.56	15.5	-183
42	7.58	15.5	-185
43	7.58	15.5	-161
44	7.58	15.5	-164
45	7.56	15.6	-178
46	7.58	16.1	-153
47	7.55	16.1	-210
48	7.56	14.8	-186
49	7.55	14.5	-188
50	7.58	15.1	-172
51	7.54	15.2	-183
52	7.51	14.7	-193
53	7.55	14.7	-169
55	7.53	15.5	-24
56	7.56	15.3	-151
57	7.58	15.3	-126
58	7.56	15.3	-149
59	7.56	15.8	-170
62	7.59	15.3	-208
63	7.59	14.8	-214
64	7.59	15.1	-193
65	7.58	14.3	-144
69	7.60	14.2	-197
70	7.59	15.2	-67
71	7.59	15.5	-194
72	7.33	13.5	106

73	7.51	14.0	-9
74	7.36	14.7	31
75	7.56	16.2	-203
76	7.51	15.2	-163
77	7.56	16.3	-184
78	7.59	17.1	-215
79	7.57	17.2	-218
80	7.55	17.3	-213
82	7.56	18.1	-221
83	7.57	17.7	-211
84	7.56	16.7	-213
85	7.56	16.5	-223
87	7.56	16.1	-222
88	7.55	14.8	-211
89	7.54	14.2	-216
90	7.54	13.5	-209
91	7.54	13.2	-210
93	7.52	13.1	-205
94	7.51	14.7	-217
95	7.52	15.1	-223
97	7.54	14.5	-207
98	7.49	15.1	-249
99	7.54	14.1	-211
100	7.52	14.6	-211
101	7.54	14.7	-210
102	7.51	15.6	-220
103	7.52	14.7	-229
104	7.51	13.5	-211
105	7.52	13.3	-223
106	7.55	13.5	-206
107	7.54	13.7	-228
108	7.51	14.2	-223
110	7.55	13.2	-202
112	7.55	13.3	-231
113	7.54	13.2	-222
115	7.56	11.6	-217
116	7.49	13.5	-214
118	7.54	13.5	-208

119	7.54	14.3	-213
120	7.54	14.5	-208
121	7.86	14.5	-219
122	7.97	15.0	-233
123	7.98	14.8	-224
124	8.00	14.7	-246
125	8.00	14.7	-219
126	7.99	14.2	-225
127	8.00	15.6	-249
128	8.00	14.2	-230
129	8.01	15.2	-222
130	8.01	15.2	-241
131	7.87	15.1	-219
132	7.93	15.0	-218
133	7.97	14.5	-210
134	7.97	16.0	-248
135	7.98	16.0	-222
136	7.99	16.8	-233
137	7.99	16.7	-229
138	7.98	17.5	-250
139	7.99	16.2	-224
140	7.99	16.3	-239
141	7.98	16.3	-239
142	8.00	15.7	-247
143	8.00	16.7	-235
144	7.97	17.2	-236
145	7.99	18.4	-251
146	7.76	18.5	-245
147	7.77	17.2	-233
148	7.97	16.5	-228
149	7.93	14.1	-195
150	7.96	16.7	-248
151	7.97	15.8	-203
153	8.01	15.7	-225
154	7.99	16.6	-248
155	7.94	16.5	-223
156	8.00	15.0	-212
157	8.03	14.7	-213

158	8.00	15.8	-193
160	7.87	15.0	-178
162	8.03	15.2	-233
163	8.07	16.6	-226
164	7.92	16.1	-178
165	8.10	16.0	-174
167	7.80	14.3	-139
168	7.93	15.1	-117
169	7.91	16.0	-124
171	8.06	16.8	-123
173	7.98	16.1	-68
174	8.91	16.7	-112
176	8.33	16.0	-174
177	8.27	16.5	-138
178	8.41	17.4	-63
180	8.41	17.3	-56
181	8.52	16.0	-40
183	9.61	18.5	-184.6
189	7.62	16.3	10
190	7.69	17.1	18
192	8.38	16.1	-23
193	8.33	16.8	-40
195	7.82	17.3	-103
196	9.17	18.0	-369.3
197	9.18	18.0	-398.3
198	8.00	17.5	-273.3
199	8.25	17.3	-367.3
200	8.41	16.0	-302.3
201	8.20	17.7	-387.3
202	8.05	16.5	-322.3
203	8.00	17.5	-386.3
204	8.01	18.5	-366.3
206	7.81	15.0	122.7
207	7.78	17.3	-340.3
209	8.07	16.3	-310.3
211	8.33	15.8	83.7
213	7.98	16.8	-340.3
214	8.03	17.9	-364.3

216	8.08	18.9	-384.3
217	8.04	18.9	-360.3
222	8.09	17.2	-352.3
224	8.14	18.7	-371.3
227	8.45	17.0	-243.3
238	8.40	18.2	-268.3
240	8.34	19.5	-387.3
241	8.34	20.1	-395.3
251	8.25	17.7	-235.3
252	8.30	17.2	-225.3
253	8.59	18.0	-334.3
255	8.28	17.7	-429.3
258	8.30	17.7	-423.3
259	8.26	16.5	-420.3
260	8.29	17.0	-430.3
261	8.24	15.7	-416.3
262	8.24	16.8	-416.3
265	8.01	16.6	-381.3
266	8.52	17.1	-433.3
268	8.19	20.0	-391.3
269	8.21	17.5	-386.3
274	8.38	18.5	-385.3
275	8.07	17.9	-383.3
279	7.46	20.7	-357.3
280	7.45	20.7	-354.3
281	7.55	19.9	-353.3
282	8.38	20.5	-390.3
283	7.38	21.5	-355.3
288	8.00	21.9	-322.3
292	7.24	19.9	-361.3
301	7.56	20.7	-407.3
303	7.62	20.4	-425.3
306	7.45	19.7	-414.3
318	7.78	18.4	-346.3
319	8.59	17.2	-308.3
320	8.49	18.0	-331.3
322	8.56	16.2	-302.3
323	8.57	18.4	-430.3

324	8.36	19.0	-313.3
325	7.93	15.8	-351.3
326	8.21	17.9	-261.3
331	8.37	19.2	-432.3
332	7.25	20.5	-328.3
333	8.14	19.4	-333.3
342	7.85	17.7	-316.3
343	8.25	15.6	-307.3
345	8.30	17.5	-380.3
349	8.52	20.4	-380.3
350	8.26	18.7	-203.3
353	8.16	16.6	-252.3
357	7.15	16.6	-137.3
358	7.02	17.5	-161.3
359	6.79	18.7	-160.3
360	7.48	17.7	-238.3
363	6.02	15.3	357.7
364	6.06	15.3	381.7
365	6.08	18.7	222.7
366	6.41	18.0	112.7
368	7.51	19.6	-238.3
369	8.32	19.4	-137.3
371	6.98	19.2	-80.3
373	7.38	16.5	-138.3
374	7.85	19.2	-236.3
377	10.42	15.3	-315.3
378	10.11	17.0	-264.3
380	8.12	19.5	-226.3
381	8.1	17.2	-97.3
382	8.26	19.1	-266.3
383	7.62	18.5	-262.3
384	7.35	18.1	-286.3
385	7.74	17.0	-234.3
389	7.57	18.5	-155.3
390	10.44	17.3	-404.3
391	8.17	16.0	-386.3
392	7.94	17.4	-374.3
393	8.28	15.2	-369.3

398	7.99	15.8	-326.3
399	8.14	15.5	-432
400	8.17	18.0	-464
402	8.27	16.1	-484
404	10.97	12.0	-544
405	8.26	15.5	-444
406	8.21	14.7	-454
407	8.15	17.2	-450
409	8.31	17.6	-466
411	8.16	16.8	-436
412	8.15	17.1	-472
413	7.35	15.7	-421
414	7.93	16.0	-455
415	8.17	15.3	-491
416	8.31	14.7	-467
417	8.29	16.2	-494
420	8.27	15.2	-479
421	8.21	14.5	-460

Table 3. Effluent TSS and VSS concentrations

Time (days)	TSS (mg/L)	VSS (mg/L)
0	1407	400
1	1347	280
3	1380	380
4	1280	190
5	1320	367
6	1387	353
7	1507	380
8	1313	360
9	1413	400
10	1423	373
11	1497	370
12	1487	377
13	1403	400
14	1427	387
15	1337	327

16	1410	400
17	1367	343
18	1370	363
19	1333	333
20	1320	327
21	1230	257
23	1363	357
24	1347	333
25	1037	173
27	863	153
28	1117	277
29	1207	277
30	1083	223
31	1260	290
32	1257	280
33	1270	323
35	1250	357
36	1247	300
37	1215	255
38	1277	250
39	1320	310
42	1230	283
43	1167	253
44	1233	237
45	1293	307
46	1243	207
48	1170	273
49	1273	287
59	853	260
62	1033	293
69	877	183
72	913	207
76	1127	220
80	1050	240
85	977	230
90	1067	230
93	1020	240
100	1105	265

104	1167	270
107	1057	260
121	1083	213
125	1143	210
128	1090	217
132	1180	225
135	1223	230
139	1250	220
146	1300	220
149	1350	223
153	1440	260
156	1403	227
164	1337	223
167	1320	200
170	1407	230
174	1360	210
178	1510	250
181	1643	277
188	1887	287
192	1897	307
195	1840	307
203	1890	307
211	1683	293
219	1650	290
234	1225	235
241	1405	340
261	1415	330
288	1763	357
297	1730	327
304	1800	307
312	1650	327
318	1520	323
332	1173	340
339	940	275
345	802	302
352	1080	400
357	1160	340
369	1120	400

377	1140	440
391	950	330
395	1260	490
399	1330	480
405	1133	387
408	1027	393
415	1187	387
419	1153	433
422	1247	493
427	1033	453

Table 4. Effluent COD concentrations

Time (days)	Effluent COD (mg/L)
142	16.1
147	13.9
149	14.2
153	12.5
156	13.5
164	14.8
167	18.7
170	16.1
188	17.2
192	16.1
195	14.0
198	16.5
203	5.6
212	6.2
219	8.7
234	5.3
241	5.9
247	4.2
261	2.7
279	6.4
288	6.7
297	1.3
318	11.3

332	12.3
340	12.3
346	30.5
409	15.9
353	10.6
360	15.1
372	12.4
381	17.9
400	2.8
409	16.6

Table 5. Effluent DOC concentrations

Time (days)	DOC (mg/L)
17	8.5
19	8.2
20	7.7
21	7.0
23	8.1
31	6.0
35	7.0
38	7.3
62	8.5
64	7.3
66	8.1
69	8.9
71	6.9
72	8.3
76	7.6
80	7.5
85	7.4
90	7.4
93	7.8
97	7.5
100	7.8
104	7.6
107	8.7

118	7.7
121	7.8
125	7.9
128	7.8
132	9.0
135	7.9
139	8.0
142	8.0
146	8.2
149	8.0
153	8.3
156	8.2
164	8.1
167	8.0
178	7.95
181	8.0
188	10.3
192	8.6
195	7.9
198	7.9
203	8.3
212	7.4
243	8.3
250	8.6
261	7.8
279	7.1
288	9.7
297	7.1
304	7.5
318	8.8
332	7.6
339	7.4
343	7.7
346	7.2
360	7.2
372	7.2
381	8.8
388	9.0

400	8.9
409	9.8
416	9.8

2. MBR equipments and components

Table 6. Equipment and components for MBR

Part	Catalogue Number	Description	Manufacturer
pH (with Temp display)	PHTX-271-1	PH/ORP Transmitter	OMEGA Engineering Inc. Stamford, Connecticut
	PH-2720-PA	Preamplifier for PHTX-8710	
	PHE-3271	Flat surface pH electrode	
	FP90UM	Universal NPT mount	
ORP	PHTX-271-1	PH/ORP Transmitter	
	PH-2720-PA	Preamplifier for PHTX-8710	
	ORE-2715	Flat surface ORP electrode	
	FP90UM	Universal NPT mount	
Pressure gauge	EW-68925-02	Battery powered gauges	LABCOR
Micropump	GA-X21-JFSG	Micropump model G18	Micropump Inc. Vancouver, BC
Data logging system	34970A	Data acquisition unit	Agilent Technologies, Palo Alto, CA
Hollow fibre membrane	X30-240	Celgard® Microporous hollow fiber membrane	Celgard Inc. Charlotte, NC
Hollow fibre membrane	(ZW-1)	ZeeWeed-1 bench test unit	ZENON Environmental System Inc. Oakville, Ontario
Peristaltic pump	7553-20	Masterflex®	Cole-Parmer, Vernon Hills, IL
Peristaltic pump speed controller	7553-70	Masterflex®	Cole-Parmer, Vernon Hills, IL
Peristaltic pump tubing	6404-14	Tygon®	Tygon, Akron, OH
pH controller		Oakton pH/ORP controller	Oakton Instruments, Vernon Hills, IL
pH controller speed controller	7553-70	Masterflex®	Cole-Parmer, Vernon Hills, IL

3. Calculation of the number of fivers required for hydrogen delivery membrane module (done by Babak Rezania)

Head space volume = 2.57 liter
Total reactor volume = 9.57 liter
Concentration of nitrate in the influent = 100mg/L
HRT = 12 hr
Temperature = 20 °C
Dissolved oxygen concentration in influent = 2 mg/L
Membrane length = 16cm

1) Maximum nitrate loading to the system $= \frac{100mg/L \times 7L}{12hr} = 58.33mg/hr = 1.4\ g/\ day$

$0.33\ NO_3^- + H_2 + 0.08\ CO_2 + 0.3\ H^+ \rightarrow 0.015\ C_5H_7O_2N + 0.16\ N_2 + 1.11\ H_2O$

$0.33\ NO_3^- \longrightarrow H_2$
20.46 2

1.4 X1 = Hydrogen consumption rate = 0.1368 g/day

DO loading rate $= \frac{2mg/L \times 7L \times 24\ hr}{1000 \times 1day} = 0.028$ g/day

$1/2\ O_2 + H_2 \longrightarrow H_2O$

16 2

0.028 X2 = 0.0035 g/day

Total hydrogen consumption = 0.1368+0.0035 = 0.1403 g/day, considering safety factor of 10

Hydrogen delivery rate = 14.03x 10 = 1.403 g/day

2) Membrane module design:

Hydrogen transfer rate = KA (C* - CL)

CL is dissolved gas concentration (g/L)

C* is the hydrogen saturation concentration (g/L)

K is the overall mass transfer coefficient (m/s)

A is the surface area of the membrane (m^2)

3) Calculation of hydrogen saturation concentration

H (Henry's law constant) for hydrogen at 20 °C = 68,300 atm

Pg = H Xg
Pg = partial pressure of hydrogen
Xg = mole fraction of hydrogen in water

$1 = 68300\ Xg \longrightarrow Xg = 1.46 \times 10^{-5} = \frac{ng}{ng + nw}$

One liter of water = 55.6 mole = nw
ng = 8.11×10^{-4} mole/L
C* = 2 g/mole x 8.11×10^{-4} mole/L = 1.62 mg/L

4) Calculation of mass transfer coefficient

$$Sh = 0.730\ Re^{0.379}\ Sc^{0.33} \qquad (1)$$

$Sh = K\ d/D$
$Sc = \nu/D$

$$Re = v\ d/\ \nu$$

K is mass transfer coefficient (m/s)
D is diffusion coefficient of hydrogen in water = $4x\ 10^{-5}\ cm^2/s$
ν is the velocity of water across the membrane
ν is kinematic viscosity of water = $1.007 \times 10^{-6} m^2/s$
de is the out side diameter of membrane fibers = 300 μm

5) Calculation of Reynolds number (in mixing)

$$Re = \frac{D^2 n \rho}{\mu}$$

D = diameter of impeller = 5cm
n = rotational speed (r/s) = 180 r/min = 3 r/sec
ρ = mass density of fluid (kg/m3) = 1000 kg/m3
μ = dynamics viscosity of water = 1.002×10^{-3} N.s/m^2

$$Re = \frac{(9 \times 10^{-4}) x\ 3x\ 1000}{1.002 \times 10^{-3}} = 7485$$

6) Calculation of gas transfer coefficient
$Sc = \nu/D$

$$Sc = \frac{1.007 \times 10^{-6} m^2/s}{4x\ 10^{-5}\ cm^2/s} = 251.75$$

$Sh = 0.730\ Re^{0.379}\ Sc^{0.33}$
$Sh = 0.730(7485)^{0.379} \times (251.75)^{0.33} = 133.08 = K\ d/D$

$$K = \frac{133.08 \times 4 \times 10^{-9} m^2/s}{300 \times 10^{-6} m} = 1.77 \times 10^{-3}\ m/s$$

7) Calculation of maximum hydrogen transfer rate and membrane surface area

Hydrogen transfer rate = KA (C* - CL)

We can assume that CL is zero in high Reynolds number

$1.403\ g/day = 1.77 \times 10^{-3}\ m/s\ A \times 1.62\ mg/L$
$A = 0.00556\ m^2$ = membrane surface area

8) Calculation of hydrogen flow rate

PV=nRT
n= 4.436/2
P=1 atm
T=293 K
R= 0.08206 Atmosphere, liter/g-mole, Deg K

1x V= 1.403/2 x 0.08206 x 293 ⟶ V=16.86 liter ⟶ Hydrogen flow rate=16.86 liter/day

9) Calculation of fibre numbers

Total surface area= $0.00556\ m^2$
Outside diameter of fibres = 0.3mm
Fibre length= 16 cm
Porosity of fibres = 40%
N x 2x 3.14 x 0.15 x 0.001 = 0.00556/0.4
N= the number of fibres = 94