



Investigating the Feasibility of a Membrane Biofilm Reactor to Achieve Low Nitrogen Levels for Water Reclamation and Reuse

WateReuse Research Foundation

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The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high-quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's subscribers, water and wastewater agencies, and other interested organizations.

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Cosponsors

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Acronyms and Abbreviations

APT	Applied Process Technology, Inc.
BOD	biochemical oxygen demand
CaCO ₃	calcium carbonate
CO ₂	carbon dioxide
COD	chemical oxygen demand
CTA	cellulose triacetate
DBPs	disinfection byproducts
DOC	dissolved organic carbon
EPA	Environmental Protection Agency
GVWWTP	Grass Valley Wastewater Treatment Plant
H ₂	hydrogen gas
HRT	hydraulic retention time
LACSD	Lake Arrowhead Community Services District
MBfR	membrane biofilm reactor
MBR	membrane bioreactor
MGD	million gallons per day
NDN	nitrification/denitrification
NO ₂	nitrogen dioxide
O&M	operations and maintenance
SMP	soluble microbial products
TDS	total dissolved solids
TF	trickling filter
TIN	total inorganic nitrogen
TKN	total kjeldahl nitrogen
TMDLs	total maximum daily loads
TS	total solids
TSS	total suspended solids
VOC	volatile organic compound
VS	volatile solids
VSS	volatile suspended solids

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse research topics including

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to indirect potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluation and methods for managing salinity and desalination
- Economics and marketing of water reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, Foundation subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and other funding relationships.

This research report presents 9 months of results from the operation of two parallel membrane biofilm reactor (MBfR) pilot plants. The pilot plants were used to evaluate the MBfR's ability to successfully denitrify a secondary effluent. This MBfR pilot study represents the first commercial application of this promising treatment process in an advanced wastewater treatment train.

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Executive Summary

Project Background and Objectives

This research report presents 9 months of results from the operation of two parallel membrane biofilm reactor (MBfR) pilot plants. The pilot plants were used to evaluate the MBfR's ability to successfully denitrify a secondary effluent. This MBfR pilot study represents the first commercial application of this promising treatment process in an advanced wastewater treatment train.

An MBfR uses a membrane, not for filtration of water or mixed liquor, but to deliver H_2 gas as an electron donor to an autotrophic biofilm growing on the membrane surface that reduces contaminant oxyanions (e.g., nitrate, nitrite, perchlorate, selenate) (Lee and Rittmann, 2000; Nerenberg and Rittmann, 2004; Chung et al., 2006a). The H_2 gas diffuses, rather than bubbles, through the microporous membranes. This prevents excess H_2 gas from entering the bulk water and more of the hydrogen gas is consumed in biological redox reactions at the membrane surface. The water to be treated is passed through a vessel containing this H_2 -fed biofilm, and the oxyanion contaminants are reduced as they pass through the reactor. Because the microorganisms for the H_2 -fed MBfR are slow growing autotrophs, less biomass is produced and fewer solids require treatment and disposal.

Although many short-term bench-scale studies have been done to assess the effect of individual parameters on MBfR performance in the drinking water and ground water settings (Adham et al., 2004; Lee and Rittmann, 2000; Nerenberg and Rittmann, 2004; Chung et al., 2006a), little work has been performed at the pilot scale. In addition, there are questions about potential impacts of treating the higher suspended solids and organic content typically present in wastewater with this membrane process. As a result, the specific objectives of this study were

- To evaluate the MBfR process for meeting strict nutrient requirements in advanced wastewater treatment for water reuse or reclamation;
- To study the effect of individual operating parameters such as recycle rate (or superficial velocity and mixing), membrane area-based loading rate (flux), H₂ pressure, and the type and frequency of cleaning required (reverse flow, air scouring, and chemical cleaning);
- To study the effect of emergency shutdowns or mechanical failures on operational performance; and
- To compare MBfR construction and operations and maintenance costs to an existing methanol-fed denitrifying reactor (including foot print requirement, sludge disposal, etc.).

Results Summary

In general, the MBfR process successfully denitrified wastewater to very low nitrate levels and often achieved undetectable concentrations, depending on operating conditions. In contrast to groundwater applications, the high microbial concentrations and wide diversity of microbes in the feed water resulted in an established biofilm process in a relatively short period of time (typically 10 to 14 days). This ability to establish an effective biofilm so quickly also means that following a shutdown or process interruption (i.e., lack of H₂), the process is capable of resuming effective nitrate removal within a few days. If an extended shutdown is encountered, the process will re-establish effective nitrate removal in the same time frame as a start-up (10 to 14 days). This study demonstrated the following significant conclusions:

- Peak nitrate flux rates of 2725 mg N/m²·d were demonstrated to be achievable at the pilot scale.
- Hydrogen pressure plays a critical role in MBfR process performance. Doubling the hydrogen pressure from 15 to 30 psi more than doubled the peak nitrate flux from 1050 to 2725 mg N/m²·d.
- Directing the recycle flow to an atmospheric tank reduced the required recirculation pressure by approximately 50% at the conditions tested. The required recycle rates and pressures are significant factors in MBfR operation and maintenance costs and need further optimization.
- Recycle rate played a significant role in the process optimization and enough recycle flow was needed to ensure adequate mass transfer (superficial velocity) and mixing. In general, the higher the recycle rate, the more effective the treatment was for a given condition. However, it was demonstrated that there is an optimal recycle rate beyond which there was no improvement for higher recycle rates.
- The MBfR process was capable of >95% nitrate removal with hydraulic retention times (HRT) as short as 20 minutes. It is important to note that the MBfR performance was not dependent on the HRT at HRTs greater than 20 minutes. The HRT can be further optimized through module and process design.
- Two different types of membrane modules were provided by the MBfR manufacturer. The first membrane (42 m² area) exhibited a wider pore size distribution that resulted in more hydrogen loss than the second module (12 m² area). It is critical that investments be made to ensure membranes considered for full-scale MBfR applications exhibit a pore size distribution that allows the module to be pressurized without bubbling hydrogen gas into the module.
- The MBfR modules require an effective washing system to prevent biosolids from accumulating in the module. Accumulated biosolids contribute additional head loss and possibly increase the effluent ammonia concentration. This is an important consideration in the module designs and continues to be improved by the MBfR manufacturer. This wastewater application was particularly sensitive to biomass accumulation, as the MBfR modules behaved as an effective filtration process.
- The MBfR process is in the early years of commercialization, and the MBfR process, as tested, was not more cost effective than the conventional denitrifying filter to which it was compared. Cost estimates were also prepared for an alternative submerged MBfR configuration, currently under development by the MBfR manufacturer for full-scale application but not tested, which should have lower energy requirements than the MBfR module tested. This submerged configuration seemed competitive, from a cost point of view, with the conventional denitrifying filter.

In summary, the MBfR process design continues to evolve and developments will further reduce treatment costs. It is important to note that the hydrogen market and future hydrogen costs will play a significant role in the overall cost effectiveness of this process.

Chapter 1 Introduction

1.1 Background

In an effort to satisfy growing water demand in the face of dwindling water resources, many communities throughout the United States and the world are turning to water reclamation and reuse (Recycled Water Task Force, 2003; US EPA, 2004). Reclaimed water is a renewable and droughtproof resource that is directly proportional to potable water use. Reclaimed water supplements conventional water supplies by capturing and treating wastewater that would otherwise be disposed into the environment. In addition, reclaimed water is increasingly the most cost-effective means of diversifying a municipality's water portfolio.

The secondary effluent typically generated by wastewater treatment plants contains relatively low chemical oxygen demand (COD) and low total suspended solids (TSS) concentrations. However, this treated water may still contain excessive nutrient concentrations for discharge to sensitive water bodies or groundwater aquifers. As a result, there is a need to treat secondary effluents for nutrients in addition to the typical filtration and disinfection processes required to produce a disinfected tertiary effluent. With this kind of tertiary treatment, reclaimed water applications can be used in places where nutrient-sensitive water bodies, reservoirs, or underground aquifers may be impacted (Asano et al., 1992).

1.2 Tertiary Treatment

The primary objective of tertiary treatment is to ensure that reclaimed water would be of sufficient quality for a specific application. Nutrients, total dissolved solids (TDS), disinfection byproducts (DBPs), and other emerging constituents of concern are frequently addressed in a component of the tertiary treatment at water reclamation plants. Strictly speaking, tertiary treatment implies a treatment process in addition to primary (sedimentation) and secondary (biological) treatment. However, the need for nutrient reduction is often, at least partially, performed in the biological process. Although the secondary process often provides some nutrient removal, the term "tertiary treatment" is still commonly used when treatment goals extend beyond COD and TSS removal. Generally, tertiary treatment is performed in water reclamation applications to ensure adequate disinfection and to minimize suspended solids. However, nutrient removal is now almost always required in some form by industrial users or regional water quality control boards. Frequently, modern water reclamation facilities implement advanced wastewater treatment processes, such as membrane filtration, reverse osmosis, and advanced oxidation.

1.3 Need for Advanced Nutrient Removal

To protect underlying aquifers or influenced water bodies from the adverse impacts attributed to water reuse, nutrient removal processes are frequently implemented in the water reclamation treatment train. In addition, industrial users might require reduced nutrient levels in the reclaimed water depending on the application. In projects where reclaimed water is percolated to recharge a groundwater table, the treated water quality is frequently regulated

for a total inorganic nitrogen (nitrate+nitrite)¹ concentration of ≤ 10 mg/L-N. However, regulations are generally becoming increasingly stringent regarding nutrient loads. The Environmental Protection Agency (EPA) and many states are studying proposals to develop new total maximum daily loads (TMDLs) to reduce nutrient pollution of surface and subsurface water bodies. This means that many wastewater treatment facilities will have to meet "advanced" nutrient removal standards for nitrogen (N) and phosphorus (P). These new standards are not yet defined. However, various locales in California have started regulating total nitrogen concentration to ≤ 6 mg/L-N, and some regional water quality control boards are enforcing an effluent total nitrogen concentration of ≤ 1 mg/L-N.

Existing wastewater treatment processes are typically capable of taking effluent total inorganic nitrogen (TIN) down to 10 mg/L-N without providing supplemental carbon or enlarging the anoxic tank. If effluent TIN goals are ≤ 6 mg/L-N, a supplemental organic carbon addition or a modified nitrification/denitrification (NDN) process, such as Bardenpho, is required to produce the desired effluent quality. Both these conventional options for achieving the desired water quality goals dramatically increase the operational and capital costs of the process. Facilities that do not have a single sludge process (i.e., a single unit process that performs organic oxidation, nitrification, and denitrification) typically implement an additional biological process to denitrify the treated wastewater using large amounts of supplemental carbon (such as methanol) to serve as the required electron donor for denitrification and carbon source for biomass synthesis. The addition of organic chemical feed to support a heterotrophic denitrification process is extremely inefficient compared to the innovative MBfR process pilot tested in this research.

1.4 Autotrophic Versus Heterotrophic Reduction of Contaminants

The terms autotrophy and heterotrophy describe differences in how two classes of microorganisms synthesize new biomass while reducing oxidized contaminants. An autotrophic organism uses an inorganic carbon source for synthesizing new biomass, most commonly HCO₃, whereas a heterotrophic organism requires an organic carbon source (such as methanol or acetate). In a heterotrophic biological process, the same organic donor also serves as the electron donor for biological reactions. Methanol is a popular organic electron donor because of its relatively low cost. However, methanol is regulated as a hazardous air pollutant and is also toxic to humans. In addition, methanol requires a healthy methanotroph population to denitrify properly and careful handling and process dosing procedures. Even with elaborate dosing procedures, methanol addition may not be adequately controlled and can result in organic overdosing that increases effluent biochemical oxygen demand (BOD) and wastes money.

The principal advantage of an autotrophic process is that the electron donor does not serve as a carbon source and the electron donor is used exclusively for the biological oxidation or reduction reaction. This means that although some of the electron donors (e.g., methanol) are converted to unwanted and excess biomass in a heterotrophic process, essentially all of the electron donors (e.g., H₂) react with the oxidized contaminants in an autotrophic process (some donated electrons are used in biomass synthesis). In other words, less biomass is produced and fewer solids require treatment and disposal. (For clarity, autotrophic in this report refers to "H₂-oxidizing bacteria," which may include mixotrophs in addition to autotrophs.) Hydrogen gas is an ideal electron donor to fuel the autotrophic biological

¹ This study is not interested in ammonia.

processes. Despite its inherent advantages, autotrophic denitrification has not been very popular in the past because there was no efficient and safe method available for delivering hydrogen gas to the bacteria. The low solubility of hydrogen gas (1.2 mg/L in equilibrium with 1 atmosphere), combined with its flammability, effectively prevented the use of hydrogen gas in the wastewater industry. This project investigated a new treatment process, an MBfR, that overcame the limitations of H_2 delivery. This process promises to transform denitrification in water treatment, water reclamation, and wastewater treatment.

1.5 Membrane Biofilm Reactor (MBfR)

1.5.1 Principal of Operation

Hollow fibers deliver hydrogen directly into the biofilm: An MBfR uses a hollow-fiber membrane, not for filtration of water or mixed liquor, but to deliver H_2 gas as an electron donor to autotrophic bacteria naturally growing on the membrane surface to reduce oxidized contaminants (e.g., nitrate, nitrite, perchlorate, selenate, etc.). When using microporous membranes, the hydrophobic nature of the hollow-fiber membrane material, combined with small discontinuous pore sizes, ensures delivery of hydrogen gas directly into the biofilm without the risk of bubbling. As shown in Figure 1.1, these "bubbleless" fibers are open at one end through which hydrogen gas is supplied and they are sealed at the other end, so 100% of the hydrogen supplied to the MBfR passes into the biofilm. This means that virtually all of the hydrogen gas that is supplied to the membrane will be utilized for reducing the oxidized contaminants. This combined with counter current transport of hydrogen and oxidized contaminants in the biofilm (see Figure 1.1) greatly reduces the hydrogen wastage and reduces the risk of hydrogen off-gassing that otherwise could create an explosion hazard.



Figure 1.1. Schematic cross section of one hollow-fiber membrane delivering hydrogen into the biofilm that grows naturally at the surface of the fiber. Adapted from Rittmann, B. E. *Membrane Technology* 2002, 6–10.

Biofilm on the membrane outer wall plays a central role: Because the hydrogen (electron donor) meets the oxidized contaminants as soon as it diffuses out from the hollow fibers, a biofilm of bacteria that oxidizes hydrogen naturally grows on the membrane's outer wall (Rittmann, 2002). A bacterially catalyzed reaction at the membrane surface drives the diffusion of the hydrogen gas across the membrane wall. If the load of oxidized contaminants

increases, the diffusive flux of hydrogen increases in response to increased hydrogen gradient and demand. This means that the MBfR system is self-regulating to deliver hydrogen gas to the biofilm on an "on-demand basis," making electron donor overdosing and underdosing issues irrelevant. Therefore, unlike conventional biological denitrification, the MBfR process does not require an elaborate dosing system to ensure adequate denitrification rates are maintained while preventing excess organics (e.g., BOD) from carrying over to the effluent.

Hollow fibers provide a large surface area for slow growing autotrophs: One disadvantage of autotrophic processes is that autotrophs have a slow growth rate. This is not a problem for the MBfR where biomass grows in a fixed film on hollow fibers, providing the long, solid residence times needed for an autotrophic population to become established.

1.5.2 Process Evolution

Hollow-fiber membranes were originally developed for applications in gas separation including gas-to-gas separations (e.g., He/N₂ separation for He recovery) and gas-to-liquid separations (e.g., NH₃ recovery) (Qi and Cussler 1985a; 1985b). The concept of cell immobilization on membrane fibers in combination with gas transfer across hollow fibers (e.g., the first MBfR) transformed the biotechnology industry in the 1980s (Rittmann and McCarty, 1980; Vickroy, 1986). Advances in material science in the late 1980s and early 1990s led to the development of bubbleless hollow-fiber membranes that were capable of achieving high gas transfer efficiency (Ahmed and Semmens, 1992; Cote et al., 1988, 1989). Because of their unique characteristics, hollow-fiber membranes found their application in wastewater treatment applications where oxygen requirements were too high for conventional aeration methods and attempts to meet these intensive oxygen demands would induce foaming and stripping of volatile organic compounds (VOCs) (Cote et al., 1988, 1989). Traditionally, the wastewater community has investigated the MBfR process as a possible substitute for the activated sludge process to oxidize COD and NH3 (Ahmed and Semmens, 1992; Cote et al., 1988,1989; Pankhania et al., 1994). However, in the last decade or so, MBfR applications have extended from nitrification and substrate oxidation to reduction of an assortment of oxidized contaminants (e.g., nitrate, perchlorate, arsenate, chromate, and selenite) (Adham et al., 2003, 2004; Celmer et al., 2006; Chung et al., 2008; Chung and Rittmann, 2006, 2007; Chung et al., 2006a, 2006b, 2006c; Chung et al., 2007a, 2007b; Cowman et al., 2005; Ergas and Reuss, 2001; Lee and Rittmann, 2000, 2002, 2003; Nerenberg and Rittmann, 2004; Rittmann et al., 2004; Shin et al., 2008). At the heart of these advancements lies the MBfR's ability to support biofilm growth and supply bubbleless H_2 gas to biodegrade the oxidized contaminants.

1.5.3 Current State-of-the-Art

Since the inception of the H₂-fueled MBfR concept by Professor Rittmann in 2000, extensive work has been done with this technology for treating drinking water or groundwater contaminated with nitrate, perchlorate, chromate, arsenate, selenate, and many other oxyanions and oxidized contaminants (Adham et al., 2003, 2004; Celmer et al., 2006; Chung et al., 2008; Chung and Rittmann, 2006, 2007; Chung et al., 2006a, 2006b, 2006c; Chung et al., 2007a, 2007b; Cowman et al., 2005; Ergas and Reuss, 2001; Nerenberg and Rittmann, 2004; Rittmann et al., 2004; Shin et al., 2008). Table 1.1 summarizes the literature and presents the operating conditions used in these studies.

		-	На	Oxya Concen	anion tration*		Membrane Surface	Fiber Packing	Oxvanion	Recycle	-
Reference	Treatment Process	Oxyanion	Pressure (ATM)	Influent (mg/L)	Effluent (mg/L)	HRT (hours)	Area (cm ²)	Density (%)	Loading Rate (mg/m ² •d**)	Rate (gpm)	Comments
Lee and	Drinking	NO ₃ ⁻	0 21 0 42	10, 12.5	2.44, 0.95	0.70	750	27	2540, 2596	0.46	Composite fiber (non-porous
2000	Water	NO ₂	0.31-0.42	0	0.9, 0.7	0.70	750	2.1	0	0.40	two porous layers)
Ergas and	Drinking	NO ₃ -	0.28	60-200	0-30	5 0 30 0	3700	2.5	130 2600	ND	Homogenous membrane
2001 ^{#,^}	Water	NO ₂	0.28	0	0	5.0-50.0	3700	2.3	130-2600	INK	with 0.05 mm pore size
Lee and Rittmann	Drinking	NO ₃ -	0.20-0.56	5.0-15.0	0.4-9.0	0.70-2.1	750	2.7	109-1702	0.46	Composite fiber (non-porous
2002 Wa	Water	NO ₂	0.20-0.50	0	<1				0	0.40	two porous layers)
Nerenberg	Drinking Water	ClO ₄	0.10-0.37	0-25	0-22.5	0.73	624	2.5	0-5770	0.46	Optimal pH: 8.0 and depitrifying culture:
et al., 2002 [#]		NO ₃ ⁻		0-15	0-0.3				0-3394	0.10	Ralstonia Eutropha
Lee and Rittmann	Drinking	NO ₃	0.42	12.5	0.14-0.25	0.70	750	27	2426.4	0.46	Nitrite accumulation at pH 9.5
2003 Water	Water	NO ₂ ⁻	0.12	0	0.12-0.36	0.70	750	0 2.7	0	0.10	Minine accumulation at pri 9.5
		NO ₃		5	< 0.05				835.0		
Nerenberg		ClO ₄ -		1	0.64			2.0	168.6		These were short-term experiments and lasted ~ 3 h for each contaminant.
and Rittmann 2004	Drinking Water	ClO ₃	NR	1	0.71	0.40	73		168.6	0.04	
		ClO ₂ -		1	0.33				168.6		
		BrO ₃ ⁻		1	< 0.05				168.6		

Table 1.1. Summary of the Literature on MBfR Operating Conditions and Oxyanions Treated

	Treatment	-	H ₂ Pressure	Oxys Concen	anion tration* Effluent	HRT	Membrane Surface	Fiber Packing Density	Oxyanion Loading Rate	Recycle	-
Reference	Process	Oxyanion	(ATM)	(mg/L)	(mg/L)	(hours)	(cm ²)	(%)	(mg/m ² •d**)	(gpm)	Comments
Nerenberg	Drinking	CrO ₄ ²⁻		1	< 0.25				168.6		These were short-term
Rittmann, 2004	Water	SeO ₄ ²⁻	NR	1	0.26	0.40	73	2.0	168.6	0.04	experiments and lasted \sim 3 h for each contaminant.
		H ₂ AsO ₄		1	<0.5				168.6		
		ClO ₄ -	0.20-0.40	0.006, 0.05, 0.1	0-0.004	0.73	624	2.5	1.38-23.1		Reactor responded well
Adham et	Drinking	NO ₃	2	2.6-3.0	0.01-0.03				600-700	0.46,	when influent perchlorate concentration was suddenly increased from 6 mg/L to
al., 2004 [#]	Water	ClO ₄		0.04-0.07	0.002-0.04		146000- 480000	3.0-27.0	0.05-5.0	1.8 - 15	100 mg/L.
		NO ₃ -	0.20	4.3-6.9	0.02-2.0	0.25-1			200-900		Groundwater pilot study at La Puente, CA.
Cowman et al., 2005	Wastewater	NO ₃ -	0.14-0.17	0-1.1	<0.67	3.0	71	~2	0-25	0.013, 0.04	Feed water is nitrified effluent.
Shin et al.,	Westowator	NO ₃ -	ND	150-200	0-7	20.40	1200	21	21 000 1250	ND	Feed water is nitrified
2005	wastewater	NO ₂ ⁻	INK	0	0-2	2.0-4.0	1500	~31	900-1350	INK	effluent.
Chung et al., 2006c		SeO ₄ ²⁻		0.1-1	0-0.1		73	2.0	2.6-24		
	Drinking Water	HSeO ₃ -	0.17-0.27	0	0, 0, 0.05, 0.2	0.40			0	0.04	Denitrifying bacteria was
	water	NO ₃ -		5	0.25				0-7226		pH was 7.5.

			H_2	Oxya Concen	anion tration*		Membrane Surface	Fiber Packing	Oxyanion	Recycle	-
Reference	Treatment Process	Oxyanion	Pressure (ATM)	Influent (mg/L)	Effluent (mg/L)	HRT (hours)	Area (cm ²)	Density (%)	Loading Rate (mg/m ² •d**)	Rate (gpm)	Comments
		CrO ₄ ²⁻		0.1-1	0.1-0.6				2.4-65		
Chung et	Drinking	Cr(III)	0 17 0 27	0	0.2-0.6	0.40	71	~2	0	0.04	Denitrifying bacteria was
al., 2006b	Water	NO ₃ -	0.17-0.27	2.5-10	0-2.0	0.40			0-8370		used as inoculum. Optimum pH was 7.0.
		NO ₂		0	0				0		
Chung et	Drinking Water	H ₂ AsO ₄ ⁻	0.17-0.37	0.3	0.04-0.19	0.40	73	2.0	0.45-24.5	0.04	Inoculum came from the pilot-scale MBfR used for perchlorate and nitrate reduction at La Puente, CA (Adham et al., 2004).
		H ₂ AsO ₃ ⁻		0	0.08-0.23				0		
al., 2006a		NO ₃ ⁻		5.0-15.0	0-5.625				0-16400		
		NO ₂ ⁻		0	0-0.92				0		
Downing and	Drinking Water	NO ₃ -	0.34	0-5	> 99% removal	0.83	30.5	NA	0-1180	0.04	Denitrifying bacteria was
2006	water	BrO ₃ ⁻		0.1-7	0.01-6.9				140-5530		used as moculum.
Shin et al., 2008	Synthetic wastewater	NO ₃ -	0.3-0.7	51-54	92-96	6-10	31	0.8	960-2000	NR	Bench scale testing, inoculated with activated sludge.

Notes. NR = Not Reported, * nitrate and nitrite concentration as mg N/L, ** nitrate and nitrite loading rate as mg N/m²d, [#]Feed water is groundwater spiked with oxyanion of interest, $^{\circ}$ carbon source is CO₂.

Synthetic water was used as a feed water for all studies, except for those marked as "#". Carbon source is NaHCO₃ for all studies except for Ergas and Reuss, 2001.

The parameters of interest in these studies included influent concentration, hydraulic retention time (HRT), loading rate, membrane area, H₂ pressure, type of bacterial community, and process performance. It should be noted that of the 13 research articles in Table 1.1, only one study looked at long-term pilot-scale performance treating nitrate-contaminated groundwater. Most MBfR literature presents short-term bench-scale studies treating a synthetic water source. It is evident from the literature that operation and maintenance issues associated with full-scale MBfR installations are not clearly understood.

Nevertheless, these bench-scale studies did demonstrate that the MBfR process could produce a low effluent nitrate concentration (removal > 90%) for a wide range of loading conditions $(0.1-16.5 \text{ g N/m}^2 \text{ d})$ within relatively short HRTs (0.4–2 hrs in most cases) and at low H₂ pressures (0.1–0.6 atm). In all cases, under optimal pH operation (6.5–8), little nitrogen dioxide (NO₂) accumulation was reported (<1 mg N/L). These studies revealed that both composite (nonporous sandwiched between two porous layers) as well as homogenous membranes could be employed to deliver H₂ gas. The results from a long-term pilot study (Adham et al., 2004) indicated module geometry and membrane packing density played a crucial role in the overall performance of the MBfR process. The success of these studies is continuing to fuel the development of the MBfR process for the drinking water community.

However, little to no information is available for nitrate removal by the MBfR in the wastewater setting. Moreover, design criteria for wastewater MBfR could not be extrapolated directly from experience in potable water systems. Drinking water MBfRs are generally operated at constant nitrate and hydraulic loading rates under relatively low suspended solids loadings. Unless equalization is provided, a wastewater plant must handle a varying rate of flow with peak hydraulic, nitrogen, and solids loadings occurring simultaneously.

The research performed in this project attempted to systematically evaluate the MBfR process for denitrification in a wastewater setting as an alternative to conventional treatment processes for meeting strict nutrient requirements in advanced wastewater treatment applications.

1.6 Project Objectives

Although many short-term bench-scale studies have been done to assess the effect of individual parameters on MBfR performance in the drinking water and groundwater setting, little work has been performed on nitrogen removal in the wastewater setting. In addition, little pilot MBfR work has been performed, and as a result, the process design is not yet optimized. Also, the application of MBfR to water reclamation is innovative, and design lessons will be learned at the pilot scale. Thus, the specific objectives of this research were

- To evaluate the membrane biofilm reactor (MBfR) process for meeting strict nutrient requirements in advanced wastewater treatment for water reuse or reclamation;
- To study the effect of operating parameters such as superficial velocity (recycle rate), HRT, H₂ pressure, and membrane area on reactor performance;
- To study the effect of emergency shutdowns or mechanical failures on operational performance;
- To develop design criteria and investigate operational and maintenance issues associated with full-scale MBfR; and

• To compare MBfR costs to an existing methanol-fed denitrifying reactor (including footprint requirement, sludge disposal, etc.).

For this purpose, two custom-built pilot-scale MBfRs were employed to treat secondary effluent from nitrifying trickling filters at the Grass Valley Wastewater Treatment Plant (GVWWTP). This project comprehensively investigated the nitrate removal rate as a function of loading rate, HRT, substrate (or H₂) utilization rate, and membrane area for both long-term and short-term use. Employing pilot-scale MBfRs to treat secondary effluent was instrumental in establishing the actual design criteria for full-scale facilities and closely captured the operation and maintenance issues associated with full-scale implementation. Another important aspect of our project included a direct comparison between results obtained from an H₂-fueled reactor and a conventional denitrifying biological filter that was currently being fed methanol to support denitrification at the GVWWTP. This comparison determined the process benefits and economics of operation using autotrophic denitrification (our approach) and heterotrophic denitrification (traditional approach).

2.1 Background

This chapter provides a detailed description of the pilot site location, feed water composition, MBfR pilot design, the two MBfR module designs that were evaluated, and the analytical methods that were used to assess the water quality. A detailed experimental protocol outlined the procedures and materials used during the 9 months of pilot testing the MBfR process on nitrified secondary effluent.

2.2 Pilot Site and Feed Water

All pilot testing was conducted at the Grass Valley Wastewater Treatment Plant (GVWWTP), located in Lake Arrowhead, CA. This is a 2.3 million gallons per day (MGD) tertiary treatment facility that employs two 24-feet deep trickling filters designed to nitrify in cold weather conditions. The solids from the trickling filters are settled out in the secondary clarifiers prior to flowing to a methanol-fed deep-bed biological filter for denitrification (see Figure 2.1). The clarified water from the secondary settling tank was used to feed the MBfR pilot plants after passing through a fine mesh (~500 micron) screen. Two pumps in series, a submersible pump, and a centrifugal booster pump were used to provide the necessary flow and pressure to the pilot units.

To evaluate the effects of seasonal variation on the feed water quality, temperature, turbidity, and nitrate data were collected from the full-scale plant over the 9-month pilot testing period (from March through December 2007) and are shown in Figure 2.2. There were seasonal fluctuations in feed water temperature. During the spring season, average temperature fluctuated between 40 and 65 °F, whereas in the summer season it fluctuated between 70 and 85 °F. (Note: The one temperature measurement above 100°F on Day 216 was due to equipment failure and not representative of seasonal temperature fluctuations.) However, no such trend was observed for turbidity or nitrate concentration.

Table 2.1 summarizes additional feed water quality parameters with median, maximum, and minimum values. The secondary effluent (e.g., MBfR feed water) had relatively low alkalinity, low hardness, high turbidity (and high suspended solids), low TDS, and high DOC. Like many other wastewater treatment facilities, the secondary effluent had a low BOD/N ratio that necessitated addition of an external carbon source for heterotrophic denitrification. Because of the potential of comparing results from the GVWWTP conventional methanol-fed biological filters to the pilot H₂-fed MBfR reactors, this pilot site provided a unique opportunity to study the techno-economic feasibility of autotrophic reactors.

It should be noted that the suspended solids concentration in the clarified effluent was higher than all previous MBfR studies conducted on drinking water sources (Adham et al., 2004; Ergas and Reuss, 2001). The high concentration of suspended solids in the feed water posed membrane fouling and other operational challenges for successfully operating the MBfR.

Therefore, modifications in the physical configuration of the traditional MBfR design were necessary to accommodate influent solids without fouling the MBfR.



Figure 2.1. Schematic of the tertiary treatment process at the GVWWTP.



Figure 2.2. Turbidity, temperature, and nitrate concentration profiles for the secondary nitrified effluent (monitoring period: 03/07–12/07).

Parameter	Units	Median	Minimum	Maximum
pН	-	7.4	7.3	7.6
TDS	mg/L	372	336	420
Temperature	°F	66	24	104
TSS*	mg/L	17.8	7.7	34.7
VSS*	mg/L	14.4	7.0	28.3
Turbidity	NTU	11.3	4.2	35.1
NO ₃ -N ⁻	mg/L	13.5	5.8	27.3
BOD	mg/L	16.9	10.5	28.9
DOC	mg/L	20.3	14.2	23.5
Alkalinity	mg/L as CaCO ₃	68.6	25.0	29.4
Hardness	mg/L as CaCO ₃	101	94.1	109
Calcium	mg/L	26.8	25.0	29.4
Magnesium	mg/L	7.3	6.5	8.10
Sulfate	mg/L	39.2	35.0	47.5

Table 2.1. Secondary Effluent Water Quality at GVWWTP

* Total suspended solids (TSS) and volatile suspended solids (VSS) prior to 500 micron screen.

2.3 MBfR Module Design

Unlike previous designs, the MBfR modules in this study were composed of a central perforated vertical tube through which feed water entered the reactor under pressure and was distributed radially toward hollow fibers (see Figure 2.3). The perforations in the vertical tube consisted of approximately 300 3/8-inch holes around the diameter of the tube, and the rows of holes were spaced approximately 1 inch apart. This unique feature ensured uniform distribution of feed flow, in addition to even contact between feed water and hollow fibers. Both ends of the fibers were potted and sealed in epoxy headers. The top end of the fiber was open and flush with the epoxy header; the bottom end of each fiber was sealed to maximize the hydrogen use.



Figure 2.3. Schematic of the flow distribution in the MBfR module.

The hollow fiber membranes served as a support medium for biofilm growth and these hollow fibers were housed in transparent vessels. Pilot-scale MBfR modules, measuring 6 in. by 48 in. (diameter x height) and designed to operate with variable HRT and recycle rates, were provided by APT (Pleasant Hill, CA). Overall, two types of full-scale membrane bundles were tested in this pilot study. The first type had 42 m² surface area, whereas the second type had a significantly reduced surface area of 12 m².

Unlike previous hollow-fiber designs that were made with thin-film composite material (Adham et al., 2004; Lee and Rittmann, 2002), both fiber bundles in this research were

homogenous in nature and were made with cellulose triacetate (or CTA). Based on information provided by the pilot unit supplier, the fibers were cast and cured under different conditions. As a result, their hydrogen permeability, as well as hydrogen bubble-point pressure (pressure at which hydrogen will start bubbling in the bulk liquid), were different. One of the serious limitations of the 42 m^2 membrane area modules was that they had a low bubble-point pressure. This meant that the lumen-side hydrogen pressure could not be adjusted independently of the shell-side pressure without bubbling hydrogen gas into the reactor. Thus, to ensure efficient use of hydrogen gas for all the experiments with 42 m^2 membrane area modules, the hydrogen pressure was maintained between the water feed pressure and effluent pressure. On the other hand, the 12 m^2 membrane area modules were less permeable to hydrogen and could hold higher hydrogen pressure without the risk of bubbling hydrogen into the bulk liquid, which allowed the project team to adjust the hydrogen pressure independently.

Figure 2.4 compares the physical arrangements of the hollow fibers potted in the 12 m² and 42 m² membrane area modules. As illustrated, the 12 m² membrane area module had a significantly reduced number of fibers (12,000 compared to 42,000 for the 42 m² membrane). The significant difference in the number of hollow fibers resulted in a much thinner bundle, 0.5 in. for the 12 m² module compared to 1.25 in. for the 42 m² membrane area module were separated by diamond-shaped mesh spacers, which are denoted as red circles in Figure 2.4c. The spacer was expected to generate localized turbulence and reduce the boundary layer on the biofilm, in addition to avoiding clogging and clumping of the fibers. The empty volume of the vessel housing the fiber bundle (including the recycle line and water in the pipes, tubing, and connections) was 11 gallons. The effective volume of 42 m² and 12 m² membrane area modules were 10.5 gallons (void ratio = 95.5%) and 10.75 gallons (void ratio = 97.7%), respectively, when the hollow fibers were free of biofilm. The other physical characteristics of these fibers are provided in Table 2.2.



Figure 2.4a. 42 m^2 area module with 1.25 in. thick fiber bundle.



Figure 2.4b. Visual of 42 m² membrane area module (diameter of the module is ~4.5 in.).



Figure 2.4c. 12 m² area module with 0.5 in. thick fiber bundle.



Figure 2.4d. Visual of 12 m² membrane area module (diameter of the module is ~3.0 in.).

Figure 2.4. A side-by-side illustration of 42 m² and 12 m² membrane area modules.

Parameter	Units	42 m ² membrane area module	12 m ² membrane area module
Vessel inside diameter	cm	15.2	15.2
Vessel length	cm	122	122
Fiber outside diameter	m	330	330
Fiber inside diameter	m	200	200
Active length of fibers	cm	96.5	96.5
Number of fibers		42,000	12,000
Surface area of fibers	m^2	42	12
Specific surface area	m^{-1}	1060	302
Void ratio	%	95.5	97.7

Table 2.2. Characteristics of the Hollow-Fiber Modules Tested in this Study

2.4 MBfR Pilot Plant

A simplified process schematic of the MBfR pilot unit is shown in Figure 2.5. Two pilot units were tested side-by-side and each pilot unit can be described by Figure 2.5 (details of the testing protocol are discussed in the next section). The feed water was fed upwards into the perforated core tube through a Magmeter (model # 2551, Georg Fisher Signet, El Monte, CA) that was used to automatically control the flow. The Magmeter provided a digital display of the instantaneous and cumulative flows. The digital display on the Magmeter was verified weekly using manual volumetric measurements. The water passing through each reactor was recirculated to

- maintain adequate mixing in the bulk solution,
- ensure even distribution of the feed flow on the membrane fibers, and
- reduce boundary layer effects on the biofilm.



Figure 2.5. A simplified process schematic of the MBfR pilot units.

To avoid heating the reactors with the heat generated from the centrifugal pump, the recycle line was equipped with a copper heat exchanger that flowed treated wastewater effluent from the GVWWTP through the cooling loop. In addition, a temperature sensor was provided to automatically shut down the system if the reactor temperature exceeded 95 °F.

Because of the low feed water alkalinity, CO_2 gas was continuously sparged into the recycle line to compensate for the rise in pH that was due to base production from the denitrification process. A pH controller regulated the CO_2 flow based on the instantaneous pH conditions in the reactor. Hydrogen (H₂) was fed to the top of the module, into the hollow fibers, through a compressed hydrogen cylinder using a high precision needle valve for flow control. To promote safe working conditions, both pilot units were equipped with H₂-gas alarm systems (Scott Sentinel II LEL sensor) to detect any increase in H₂ levels, caused by an unlikely event such as a leak in a hydrogen line. A separator was provided so that gas could be separated from the effluent water and vented to the atmosphere. Both reactors were supported by a steel frame structure constructed with slotted mild steel angles. Figure 2.6 shows a picture of the pilot plant.


Figure 2.6. The MBfR pilots showing the open tent shelter.

2.5 Experimental Protocol

By carefully studying the available literature, the key parameters affecting MBfR performance were identified to be the following:

- membrane area based loading rate (flux),
- recycle rate (or superficial liquid velocity and mixing),
- hydrogen pressure, and
- type and frequency of cleaning (reverse flow, air scouring, and chemical cleaning).

The loading rate depended on the nitrate concentration, total membrane area, flow rate, and HRT. The effects of these parameters on MBfR performance were investigated with short-term and long-term experiments as described in the following subsections.

There were two phases of this research. Phase 1 employed 42 m² membrane area modules; phase 2 employed 12 m² membrane area modules. These two module types were tested in long-term and short-term experiments during each phase. For clarification throughout this report, reactors that were tested in the long-term experiments were designated as R1 (42 m² membrane area module) and R3 (12 m² membrane area module), whereas the reactors that were tested in the short-term experiments were designated as R2 (42 m² membrane area module) and R4 (12 m² membrane area module). A summary of these designations, module type, phase, and experiment type is presented in Table 2.3. In general, it was the goal of the short-term experiments to identify the loading limits and specify design parameters for an MBfR system, whereas the long-term experiments were designed to identify process stability and operations and maintenance (O&M) issues associated with extended operation.

Phase	Designation	Experiment Type	Module Type
1	R1	Long-term	42 m^2
1	R2	Short-term	42 m ²
2	R3	Long-term	12 m^2
-	R4	Short-term	12 m^2

 Table 2.3. Summary of Experiments Performed and Reactor

 Designation

2.5.1 Long-Term Experiments

The long-term experiments were performed for extended periods of time (minimum of 600 h) to observe changes in MBfR performance. As shown in Table 2.4, these long-term experiments with reactors R1 and R3 were performed in a wide range of loading conditions (300 to 1200 mg N/m²·d), recycle rates (1 to 20 gpm), and recycle ratios (5 to 133). During these extended periods of operation, periodic N₂ sparging and flow reversal were employed to (1) control the overall biomass content, (2) maintain an acceptable head loss, and (3) ensure adequate system mixing (for details refer to Section 2.7, Reactor Maintenance and Cleaning). In addition, all tubing and connections were cleaned once a week to avoid growth of bacteria on the inner walls of the tubes and connections.

R1 (42 m ² membrane area module)			R3 (12 m ² membrane area module)				
HRT, min	Recycle rate, gpm	Recycle ratio	Loading*, mg N/m ² ·d	HRT, min	Recycle rate, gpm	Recycle ratio	Loading*, mg N/m ² ·d
70	20	133	300	50	10	50	1200
70	10	67	300	30	10	30	1200
20	20	36	1200	50	1	5	1200
20	10	18	1200	30	1	5	1200

Table 2.4. Long-Term Experiments:Effects of Module Configuration, HRT,Recycle Rate, and Recycle Ratio

*Calculated based on 13.5 mg N/L median influent concentration.

2.5.2 Short-Term Experiments

Short-term experiments were conducted on each module type to systematically investigate how the nitrate loading, recycle rate, HRT, and sudden increase in loadings influence MBfR pseudo-steady state performance. Each of these pseudo-steady state experiments, with reactors R2 and R4, lasted 2 to 3 days, a period long enough to achieve steady effluent concentration and yet short enough to avoid any appreciable change in the biomass concentration.

Effect of Step-Increase in Loading and Recycle Flow Rate: In the first set of short-term experiments, individual and combined effects of HRT and recycle rate on the reactor performance were studied. The R2 module was initially operated at 70 min HRT. Following completion of the 70 min HRT condition, the feed flow rate was increased stepwise to assess the maximum reactor loading capacity and reactor performance under these different loading conditions (see Table 2.5).

Because the recycle rate influenced local mass transfer and flow distribution in the module, the effects of recycle rates at various HRTs were also studied with reactor R2. Moreover, because a high recycle ratio translated into higher energy costs, optimization of the recycle rate for a given HRT was an important issue in evaluating the overall feasibility of the MBfR technology. It was anticipated that higher recycle rates might be required at elevated nitrate loadings compared to lower nitrate loadings. To investigate this, three recycle rates (5, 10, and 20 gpm) were employed at each HRT condition, which resulted in a set of 21 experiments (see Table 2.5). The resultant nitrate loading rates tested ranged from approximately 240 to 2000 mg N/m²·d.

-	HRT [*] (flow rate)						
-	70 min (0.15 gpm)	40 min (0.25 gpm)	30 min (0.35 gpm)	25 min (0.45 gpm)	20 min (0.55 gpm)	15 min (0.7 gpm)	10 min (1 gpm)
Recycle rate			R	ecycle ratio			
20 gpm	133	80	57	44	36	29	20
10 gpm	67	40	29	22	18	14	10
5 gpm	33	20	14	11	9	7	5

 Table 2.5. Short-Term Experiments with R2: Effect of HRT and Recycle Rate/Ratio

*Based on 10.5 gal reactor volume.

*Effect of H*₂ *Pressure:* The fundamental driving force for H₂ mass transfer to the biomass was the H₂ pressure maintained inside the membrane lumen. To explore the benefits of increased H₂ availability to the biomass, a series of short-term experiments, with reactor R4, were conducted at 15 and 30 psi hydrogen pressure. The experimental conditions for these pseudo-steady state experiments are provided in Table 2.6.

 Table 2.6. Short-Term Experiments with R4: Effect of Hydrogen Pressure and HRT

15 psi Hydrogen Pressure			30 psi Hydrogen Pressure				re			
HRT, min	70	50	40	30	15	70	50	40	30	15
Recycle ratio	67	50	40	33	16	67	50	40	33	16

Note: All experiments were conducted at constant recycle rate, 10 gpm.

Effect of System Shutdown: Several unintended process interruptions occurred during the 9month pilot operation. These process interruptions were both short-term (24 to 96 hours) and long-term in nature (more than 10 days). Short-term interruptions were due to interruptions in H₂ supply, feed and recycle pump failures, leak in the influent line and MBfR vessel, clogging of feed water in-line prescreen, and interruptions in the power supply. The longterm shutdown was experienced once during the pilot testing of R3 and R4. The reason for this shutdown was a major fire incident in the San Bernardino National Forest that nearly included the GVWWTP. The project team studied the effect of each shutdown on MBfR process performance.

2.6 Data Collection and Analytical Methods

All the reactor operational data (effluent flow rate, recycle flow rate, influent, effluent, and hydrogen pressure) were recorded twice per day, 7 days a week. The MBfR performance monitoring schedule, along with a summary of analytical procedures for various water quality parameters, are shown in Table 2.7. All water quality analyses were performed by GVWWTP laboratory, a Regional Water Quality Board certified laboratory. The laboratory followed a stringent QA/QC protocol for compliance monitoring samples from the GVWWTP plant. The same QA/QC protocol was extended for the analysis of influent and effluent samples from the MBfR pilot plant. Briefly, all water quality analyses were performed as described by Standard Methods for the Examination of Water and Wastewater (APHA et al., 1998). Upon sample collection in 2 L polycarbonate plastic bottles, samples were labeled appropriately and documented in a logbook. In addition, samples were refrigerated at 4 °C and were analyzed within 2 days of sampling. The method detection limits for nitrate and nitrite was 0.05 mg N/L. For nitrate and nitrite analysis, a fresh calibration curve was made monthly. For each group of samples, a midrange calibration check with standards was performed. Within each group of samples, a sample was run in duplicate and spiked with a known addition (matrix spike) to validate the accuracy and precision of the analytical methods employed.

In addition to these QA/QC procedures for water quality analyses, several measures were taken to ensure the integrity of the operational data, such as

- the digital flow display on Magmeter was verified weekly using manual volumetric measurements;
- daily desktop pH measurements were taken to double check the accuracy of the online pH probes; and
- the pressure gauge for hydrogen was tested using two verification gauges, once at the start of the pilot testing and once at the completion of all testing.

Analysis	Sampling Location			Method Number
	Influent	Effluent- Pilot Unit-1	Effluent- Pilot Unit-2	
pH	Daily	Daily	Daily	SM4500 B
Temperature	Daily	Daily	Daily	
Turbidity	3 per week	3 per week	3 per week	SM2130B
Nitrate	3/week	3/week	3/week	SM4500-NO ₃ E
Nitrite	Daily	Daily	Daily	SM4500-NO ₂ B
Ammonia [*]	2 per week	2 per week	2 per week	
Dissolved oxygen	1 per week	1 per week	1 per week	SM4500 G
TSS	1 per week	1 per week	1 per week	SM2540 B
VSS	1 per week	1 per week	1 per week	SM2540 E
Backwash TSS	1 per week	1 per week	1 per week	SM2540 B
Backwash VSS	1 per week	1 per week	1 per week	SM2540 E
Hardness	1 per week	1 per week	1 per week	SM2340C
Alkalinity	1 per week	1 per week	1 per week	SM2320B
Calcium	2 per month	2 per month	2 per month	SM3111B
Sulfate	2 per month	2 per month	2 per month	SM4500 E
Magnesium	2 per month	2 per month	2 per month	SM3111B
DOC	1 per week	1 per week	1 per week	SM5310B
TDS	1 per week	1 per week	1 per week	SM2540 C
BOD ₅	2 per month	2 per month	2 per month	SM5210B

 Table 2.7. MBfR Performance Monitoring Schedule and a Summary of

 Analytical Procedures Employed During 9-Month Pilot Testing

*Ammonia analysis was done using Hach handheld colorimeter.

2.7 Reactor Maintenance and Regular Cleaning

In order to control the biomass around the membrane fibers, the pilot system went through a regular backwash cycle consisting of an N_2 scour for an initial period followed by a combination of N_2 scour-reverse flow direction. Nitrogen is used for scouring rather than air because increases in dissolved oxygen can suppress denitrification. First, by bubbling an N_2 gas stream (for 5 to 10 seconds) in the vertical perforated feed tube, loose biomass on the feed tube and membrane bundles was dislodged. Next, the feed flow was reversed, and N_2 was pulsed in the casing to remove solids from the surface of fibers. Finally, the backwash water was drained from the reactor through a drain valve. The entire backwash duration lasted 1 minute before the reactor was put back into service. This backwash procedure was performed twice per day, 7 days a week.

3.1 Background

As detailed in Chapter 2, the experimental tasks were divided into two phases. Phase 1 employed 42 m² membrane area modules and Phase 2 employed 12 m² membrane area modules. During each phase, one pilot unit was tested with long-term experiments and the other pilot unit was tested with short-term experiments. Reactors that were tested in long-term experiments were designated as R1 (42 m² membrane area module) and R3 (12 m² area membrane module), whereas the reactors that were tested in short-term experiments were designated as R2 (42 m² membrane area module) and R4 (12 m² membrane area module; see Table 2.3 for summary).

In general, the goals of the short-term experiments are to identify loading limits and specify design parameters for the MBfR system, whereas the long-term experiments are designed to identify process stability and O&M issues associated with extended operation. This chapter presents the compilation of performance data from all the experiments. The observed performance of the different module designs under different operating conditions is discussed with respect to reactor start-up, nitrate and nitrogen removals, nitrate flux into the biofilm, recycle ratios and the associated flows, pressure drop across the fiber bundle, solids removal, and hydrogen consumption. Further, O&M issues associated with long-term operation of the MBfR modules are identified. Finally, results of the unintended shutdowns on MBfR performance and start-up are discussed.

3.2 Phase 1: Testing 42 m² Membrane Area Modules

3.2.1 Reactor Start-Up and Biofilm Development

The goal of the start-up was to establish a denitrifying biofilm on the membrane fibers. Because secondary effluent from a nitrifying trickling filter (TF) was populated with an assortment of indigenous autotrophs along with the micronutrients necessary to establish a healthy population of autotrophic denitrifiers, no external inoculums or micronutrients were added to the MBfR modules during the start-up. Both pilot units, R1 and R2, were operated side-by side in a continuous low-flow mode with 0.15 gpm of feed water (empty bed HRT of 70 min) and a 20 gpm recycle rate (recycle ratio of 300). A low feed-flow rate was used to avoid washout and promote biomass attachment to the membrane fibers, whereas a high recycle rate (and ratio) was used to facilitate completely mixed conditions inside the reactor and growth of a dense biofilm.

During this period, lumen-side H_2 pressure was maintained at 15 to 17 psi. The influent to the MBfR had nitrate concentrations ranging from 8 to 14 mg N/L. A non-uniform biofilm, pale brown in color, was very noticeable on membrane fibers after 4 days of operation. The biofilm continued to grow, and after 10 days of operation, a dark brown uniform biofilm completely covered the membrane fibers. Figure 3.1 provides visual evidence of the biofilm

development for R2, contrasting the clean fibers at start-up to the biofilm-covered fibers after 11 days of operation. Identical results were obtained for R1.



(a) No biofilm at start-up



(b) Biofilm after 11 days of operation

Figure 3.1. Visual evidence for biomass growth in R2.

During the start-up period, nitrate concentrations in the influent and effluent were monitored for both reactors, and results for reactor R2 are shown in Figure 3.2. The influent nitrate concentration was reduced by 50% after only 7 days of operation, and close to complete removal ($NO_2^- + NO_3^- < 1 \text{ mg N/L}$) was observed after 11 days. Nitrite concentrations of up to 2.5 mg N/L were observed during the first couple of weeks of the start-up period but decreased to below the detection limit of 0.05 mg N/L after the denitrification rate stabilized on Day 11. Similar results were obtained for reactor R1.



Figure 3.2. Nitrogen profiles during the start-up period.

Following this start-up period, the project team began investigating the effects of various parameters on the MBfR process with short-term and long-term experiments as described in Chapter 2, Experimental Protocol. For this Phase 1 work, reactor R1 was dedicated to long-term experiments and reactor R2 was used to perform short-term testing.

3.2.2 Short-Term Experiments

3.2.2.1 Effect of Step-Increase in Loading at 20 GPM Recycle Rate

After completing start-up and establishing stable denitrification, the nitrate loading rate in reactor R2 was increased by decreasing the HRT from 70 min to 40 min, 30 min, 20 min, 15 min, and 10 min. The empty-bed reactor volume was used to calculate HRT. Note that these experiments were conducted in random order to avoid any systematic effects. The flow rate and water-quality parameters (including nitrate, nitrite, pH, and turbidity) were measured at least 48 h after changing conditions. The decrease in HRT from 70 min to 10 min resulted in a 7-to-8-fold increase in nitrate loading rate (mass rate of nitrate entering normalized to membrane area) from ~240 to 2000 mg N/m² d. Figure 3.3 summarizes the dependence of effluent nitrate and nitrite concentrations (Figure 3.3a) and nitrogen removal efficiency (Figure 3.3b) on the nitrate loading rate for these short-term experiments. Several observations can be made from Figure 3.3: (1) the effluent nitrate concentration increased from 0.03 to 12.2 mg N/L. (2) the effluent nitrite concentration increased from 0.03 to 2.0 mg N/L, (3) the nitrate removal efficiency dropped from >99% to 12%, and (4) the TIN (defined as summation of nitrate and nitrite concentration) removal efficiency dropped from >99% to 3%, all with an increase in loading from 240 to 2000 mg N/m^2 d. These results suggest that the hydrogen-fed biofilm reactor reached its maximum capacity for nitrogen removal when the loading rate approached 2000 mg N/m²·d.



Figure 3.3a. Dependence of nitrate and nitrite effluent concentrations on loading rate.



Figure 3.3b. Dependence of percentage of nitrogen removal on loading rate.

Next, an estimate of nitrate flux into the biofilm (J) was made by normalizing the mass of nitrate removed in the system with the membrane surface area (A_m) , using the following equation:

$$J = \frac{Q(C_{in} - C_{out})}{A_m}$$
(3.1)

where Q was the feed water flow rate (L/d), and C_{in} and C_{out} were influent and effluent nitrate concentration, respectively. Figure 3.4 shows the dependence of nitrate flux into the biofilm on nitrate loading rate. As observed, nitrate flux increased with the nitrate loading rate, but reached a maximum of ~ 1030 mg N/m²·d. This maximum flux corresponded to a 25 min HRT at which ~80% nitrate removal efficiency was observed. At this peak flux condition, the nitrate utilization rate was 1090 g N/m³·d based on reactor volume (corresponding to a 25 min HRT).



Figure 3.4. Effect of membrane area-based loading rate on nitrate flux into the biofilm.

The sudden drop in nitrate flux for loading >1200 mg N/ m²·d could be attributed to the presence of oxygen in the nitrified feed water, which ranged from 5.5 to 7.5 mg /L. As the feed flow rate was increased, both nitrate and oxygen mass loadings to the biofilm increased, which exerted hydrogen demand as indicated in equations 3.2 and 3.3. (Note: The hydrogen used in biomass syntheses is not included here, as the predominant competing reactions for hydrogen are between oxygen and nitrate reduction. If biomass synthesis was included, the ratio of "mass of H₂/mass of nitrogen" would increase from 0.357 to 0.403.)

$$O_2 + 2H_2 \rightarrow 2H_2O$$
 (mass of H₂/mass of oxygen = 0.125) (3.2)

$$2NO_3^- + 2H^+ + 5H_2 \rightarrow N_2 + 6H_2O$$
 (mass of H₂/mass of nitrogen = 0.357) (3.3)

Thermodynamically, oxygen was a preferred electron acceptor, and oxygen provided significant competition to nitrate for hydrogen based on the stoichiometry presented in equations 3.2 and 3.3. In addition to this competition for hydrogen, there might also have been some inhibition of the biofilm's ability to reduce nitrogen when large quantities of oxygen were being consumed in the biofilm. This inhibition effect provided a plausible explanation for the dramatic deterioration in nitrate flux beyond a certain loading (Figure 3.4).

To estimate the reaction order and characterize the biofilm response to changes in the bulk concentration, log(nitrate flux, J) versus log(effluent concentration, N) was plotted in Figure 3.5. The slope was 0.31, which was close to the well-known half order kinetics for deep biofilms (Rittmann and McCarty, 2001). A reaction order smaller than 1 implied that flux into the biofilm did not increase proportionally with N, which caused nitrate removal efficiency to decline at higher loadings; this further explained the trends observed in Figure 3.4. These results indicate that the denitrification rate was possibly limited by the conditions

under which these tests were performed; specifically, biomass was not given adequate time to completely adapt to new nitrate loading flux, or the biofilm was hydrogen-limited.



Figure 3.5. Dependence of nitrate flux on effluent nitrate concentration (in log scale).

3.2.2.2 Effect of Recycle Rate

For the MBfR modules investigated in this study, a portion of the treated effluent was recycled primarily to decouple the hydraulic and nitrate loading rates. Without this recycle stream, an increase in hydraulic loadings would be necessary to keep the fibers wetted and would result in a concurrent increase in nitrate loadings. In addition to the decoupling of the hydraulic and nitrate loadings, the recycle stream improved the overall reactor mixing, which was necessary to avoid short-circuiting and channeling. Moreover, the recycle flow increased the turbulence at the biofilm interface that decreased the external resistance to mass transport. A significant disadvantage of this recycle stream was that the recycle flow diluted the influent stream, which reduced the nitrate concentration throughout the reactor, thereby retarding both the rates of mass transport and nitrate removal. More important, the recycle stream represented a significant increase to the overall operational costs. Therefore, an optimized recycle rate was an important parameter to ensure the MBfR's commercial viability.

To map the effect of the recycle rate over a wide range of HRTs, seven HRT conditions, spanning 70 to 10 min, were employed. At each HRT, three recycle rates—20 gpm, 10 gpm, and 5 gpm—were employed to produce a total of 21 experiments (refer back to Table 2.5).

Figure 3.6a illustrates the impact of recycle rates on the nitrate removal efficiency for the range of HRTs tested. As observed, nitrate removal (1) decreased with reduced HRT regardless of the recycle rate employed, (2) was relatively less sensitive to a recycle rate decrease from 20 gpm to 10 gpm, and (3) decreased significantly at a recycle rate of 5 gpm.

Figure 3.6b depicts the effect of recycle rate on the nitrate flux for the range of nitrate loadings tested. Nitrate flux increased with nitrate loading, but reached a maximum flux of $\sim 1030 \text{ mg N/m}^2 \cdot d$ for the 20 and 10 gpm recycle rates. For the 5 gpm recycle rate, the nitrate

flux also increased with nitrate loading, but reached a maximum flux at only 520 mg N/m²·d, about one-half the flux obtained for the higher recycle rates tested. As explained in the previous section, the sudden drop in nitrate flux for all three recycle rates, once a certain nitrate loading had been exceeded, was assumed to be caused by oxygen in the nitrified feed water, which ranged from 5.5 to 7.5 mg /L. Regardless of the nitrate loading, the 5 gpm recycle rate resulted in lower nitrate fluxes compared to the 10 and 20 gpm recycle rates for all conditions tested in this study.

These results demonstrate that the reactor performance improved when the recycle rate was increased from 5 to 10 gpm, but the benefits of an increased recycle rate diminished when the recycle rate was further increased from 10 to 20 gpm. These results show that the effects of decreased external mass transfer resistance were most important between the transition from 5 to 10 gpm. Beyond 10 gpm, the improvements to the external mass transfer resistance provided little additional benefit. This finding is significant for full-scale application of this process, as an increased recycle rate for no improvement in nitrate removal would be a large and unnecessary expense.



Figure 3.6a. Influence of recycle rate on nitrate removal efficiency.



Figure 3.6b. Influence of recycle rate on nitrate flux.

Figure 3.7 shows the combined effect of recycle ratio and loading rate on nitrate removal. A wide range of recycle ratios, from 9 to 140, was employed in this study. As shown, nitrate removal increased with recycle ratio and decreased with loading. It is important to note that even though the percentage of nitrate removal decreased with increased loading, this does not mean the total mass of nitrate removed was reduced. Regardless of the nitrate loading rate, the nitrate removal increased with the recycle ratio. However, nitrate removal was only weakly dependent on the recycle ratio at lower nitrate loading conditions. For example, nitrate removal efficiency dropped to 94% from 99% when the recycle ratio was reduced from 143 to 33 at nitrate loading rates of ~250 mg N/m²·d. Similar trends were observed for loadings up to 500 mg N/m²·d. Conversely, the recycle ratio had a significant influence on nitrate removal at higher loading rates. For example, nitrate removal efficiency dropped from 92% to 65% when the recycle ratio was decreased from 44 to 11 at a nitrate loading rate of ~ 1000 mg N/m²·d. These results underscore the fact that mixing and even distribution of feed flow were important for successfully operating the MBfR, especially at higher loadings.



Figure 3.7. Combined effects of recycle ratio and nitrate loading on nitrate removal.

3.2.3 Long-Term Experiments

Long-term experiments were performed with R1 for extended periods of time (minimum of 600 h) to observe long-term O&M issues and changes in reactor performance. Overall, four experiments were conducted with R1 to determine the long-term effects of recycle rate and nitrate loading on reactor performance (see Table 3.1). Experiments I and II were conducted to assess long-term reactor performance under low loading conditions, whereas experiments III and IV were conducted to evaluate long-term reactor performance at the nitrate loading condition (~ 1200 mg N/m²·d) that corresponded to the peak nitrate flux observed in the short-term experiments. During these long-term experiments, R1 was backwashed twice per day to remove loose solids and debris just as in the other experimental runs.

Loading Condition	20 gpm Recycle Rate	10 gpm Recycle Rate
70 min HRT	Experiment I	Experiment II
20 min HRT	Experiment IV	Experiment III

 Table 3.1. Experimental Matrix for Long-Term Experiments

3.2.3.1 Nitrogen Removal

Figures 3.8 and 3.9 present the nitrogen removal observed during these long-term experiments with R1. Figure 3.8 shows the temporal influent nitrate, effluent nitrate, and effluent nitrite concentrations during these long-term experiments. The percentage of TIN presented in Figure 3.9 was based on the amount of nitrate and nitrite leaving the reactor and the amount of nitrate in the influent. Figure 3.9 also shows the variations in percentage of nitrate removal and feed water temperature during the long-term experiments.

Experiment I (70 min HRT, 20 gpm recycle rate, and 133 recycle ratio) was conducted for 42 days. The first 11 days were a start-up phase, where nitrate was partially converted to nitrite. Following this start-up phase, R1 completely denitrified for the next 5 days. Between Days 17 through 32, a severe snowstorm resulted in multiple power outages, and the feed water temperature reached close to freezing for a couple of nights. At the same time, when the power came back on-line, there were problems with the hydrogen solenoid valve. A combined effect of all these events was multiple system shutdowns that caused incomplete or no nitrate removal for a little more than 10 days (these events are shaded over on Figures 3.8 and 3.9). However, once steady operation resumed, the biofilm quickly became active again and significant nitrate removal (>90%) was achieved. This high nitrate removal continued for the next 10 days, and during that time both effluent nitrate and nitrite concentrations were below method detection limits of 0.05 mg N/L.

On Day 42, Experiment II began and the recycle rate was decreased to 10 gpm (recycle ratio was dropped to 68 from 133) while the HRT was kept constant at 70 min. The R1 MBfR was operated for approximately 40 days at these conditions. Again, high nitrate removal efficiency (>90%) was achieved, and reducing the recycle rate from 20 to 10 gpm did not deteriorate reactor performance even after operating for more than 40 days. It is important to note that during these low nitrate loading experiments, the feed water nitrate concentration varied from 9 to 19 mg N/L. This translated to a variation in nitrate loading rate between 120 to 443 mg N/m²·d. Finally, R1 experienced significant seasonal variations in feed water temperatures that ranged from 38 to 80 °F. As shown in Figures 3.8 and 3.9, the MBfR performance was virtually unaffected by these variations in the feed water quality.

On Day 91, Experiment III began and the HRT was reduced to 20 min while the recycle rate was held constant at 10 gpm (recycle ratio of 18). The R1 MBfR was operated for approximately 21 days at these conditions. Consistent with the data obtained from the short-term experiments, the nitrate flux into the biofilm increased and nitrate removal efficiency decreased with the increased nitrate loading rate. However, unlike Experiments I and II, the performance of MBfR at the increased nitrate loading rate deteriorated with time. The first week of operation at the higher loading rate (~950 mg N/m²·d) was characterized by a high

nitrate removal efficiency (~95%) with a high effluent nitrite concentration (up to 5 mg N/L). Following the first week, the nitrate flux and removal efficiency dropped to ~500 mg N/L and 45%, and nitrite effluent concentration stabilized at ~ 2 mg N/L. As a result, the percentage of TIN removal values during Experiment III varied between 80 and 30%.

This deterioration in MBfR performance with time could be attributed to (1) poor distribution of the feed flow on to the fibers, (2) poor mixing of the bulk liquid, (3) inadequate utilization of all the fibers (e.g., water in the fibers²), and (4) inefficient hydrogen transfer. Because the 42 m² membrane area module employed in R1 was densely packed with 42,000 fibers, two backwashes per day were insufficient to remove excess biomass at these high loading rates. As a result, the pressure drop across the fiber bundle increased to more than 25 psi in Experiment III (a detailed discussion is provided in the next section), and the feed pressure approached ~ 40 psi. This increased feed pressure drove water into the lumen side, and a portion of the fiber bundle was not feeding hydrogen into the biofilm. Moreover, excess biofilm growth and additional secondary effluent solids also resulted in fiber clogging and clumping, which resulted in poor mixing and short-circuiting of the feed water.



Figure 3.8. Effect of long-term operation on nitrogen mass removal rates.

Experiment IV was performed to investigate the benefits of an increased recycle rate on overall mixing and mass transfer resistance (between the biofilm and bulk liquid) at this higher loading rate. On Day 111, the recycle rate was increased to 20 gpm from 10 gpm, while the HRT was kept constant at 20 minutes. Following this change, the nitrate removal

²Detected using a drain valve located directly below the cartridge header.

efficiency generally increased from 45 to 85% and the nitrate flux increased from 500 to 795 mg $N/m^2 \cdot d$. Overall, the percentage of TIN removal also increased from 30 to 55%; all of these improvements came with time. These results clearly demonstrate the importance of adequate mixing and flow distribution on to the fibers for sustainable long-term performance, especially at elevated nitrate loading conditions.



Figure 3.9. Effect of long-term operation on nitrate and total inorganic nitrogen percentage removal.

3.2.3.2 Pressure Drop Across the Fiber Bundle

Figure 3.10 shows the evolution of the pressure drop across the R1 membrane fiber bundle for the entire 142 days of operation. It was observed that the pressure drop across the membrane fiber bundle differed from one operating condition to another. For Experiment I, the pressure drop across the fiber increased with time at a rate of 0.22 psi/day, reaching 20 psi after 40 days of operation. Reducing the recycle rate to 10 gpm from 20 gpm (Experiment II), stabilized the pressure drop at 20 psi, and it did not increase with time for the following 12 days. However, with 20 psi of head loss, the feed pressure required to maintain the 10 gpm feed flow was significant at 35 psi. This made pilot operations and routine backwashes difficult. Moreover, this high feed pressure caused water to enter the lumen side, reducing the effective membrane area available for denitrification. Backwashing with the nitrogen gas scour alone was insufficient to remove the excess solids from the reactor. To solve these operational issues, it was decided to physically clean the reactor on Day 53. Following the physical cleaning, the pressure drop was reduced to 12 psi from 20 psi. Continued operation at 70 min HRT and 10 gpm recycle rate resulted in only a marginal increase in pressure drop, 0.05 psi/day, and the pressure drop only rose to 15 psi from 12 psi after 40 days of operation.

On Day 91, after another physical cleaning was performed, Experiment III began and the HRT was decreased to 20 min from 70 min while the recycle rate was kept constant at 10 gpm. Even after the physical cleaning, the pressure drop across the fiber bundle was close to 17 psi. This was due to the fact that the majority of the biomass was still trapped between the fibers after the physical cleaning process. Regardless, the pressure drop across the fiber bundle increased gradually with time in Experiment III at a rate of 0.07 psi/day, which was a rate ~ 3 times smaller than that observed during Experiment I. The authors believe that this was due to the lower recycle rate of 10 gpm. This was an encouraging result because at higher nitrate loadings both biomass production within the MBfR and solids loading from the influent steam were increased and could be difficult to manage. It appeared that backwashing twice per day was sufficient for controlling the excess biomass at the conditions tested in Experiment III.

After physically cleaning the module, Experiment IV was started on Day 111, and the recycle rate was increased to 20 gpm from 10 gpm while the HRT was kept constant at 20 min. As in Experiment III, the physical cleaning of the R1 MBfR module did not reduce the pressure drop. The pressure drop at the start of this experiment was 23 psi and rose at a rate of 0.2 psi/day, reaching close to 31 psi after 30 days of operation.

In summary, higher recycle rates resulted in a greater pressure drop, even for the same loading conditions. Because water flow was more turbulent at higher recycle rates, energy dissipated faster than it would have at lower recycle rates. So, the high recycle rate not only increased the energy cost that was due to pumping, but also it could cause several operational problems, which must be taken into consideration when designing an MBfR for a full-scale application.



Figure 3.10. Evolution of pressure drop across the R1 fiber bundle during long-term experiments.

3.2.3.3 Suspended Solids Concentration

During long-term operation of R1, weekly volatile suspended solids (VSS) and TSS measurements were made in the influent, effluent, and backwash streams. In addition, daily turbidity measurements of the streams entering and leaving the reactor were also made. These results are all summarized in Figure 3.11. Initially, the R1 MBfR partially served as a filtration device, reducing the influent turbidity and TSS and VSS concentrations by more than 50%. However, as R1 treated more water, the influent and effluent turbidity and TSS and VSS concentrations eventually became very similar. These results suggest that the 42 m^2 membrane area module behaved like a filter that removed influent solids until the filter reached breakthrough. Filter breakthrough occurred when a filter had exceeded its solids holding capacity. It was this accumulation of solids in the reactor that resulted in the increased pressure drop across the fiber bundle, which could not be restored by twice daily backwashes or even by manual cleaning toward the end of R1 experiments. This was a significant issue that needed to be addressed to ensure smooth long-term operational performance of the MBfR in wastewater applications. Occasional spikes of effluent TSS, VSS, and turbidity were also seen which could be due to the periodic sloughing of excess biomass, a typical characteristic of an attached growth process.

As mentioned, a backwash (by sparging nitrogen gas and reversing the flow) was performed twice per day in an attempt to remove excess solids from the reactor. Figure 3.11d compares the backwash TSS concentration with the effluent TSS concentration (in log-scale). As expected, an order of magnitude higher TSS concentration was observed in the backwash samples. Similar trends were also observed when backwash VSS values were compared

against influent VSS concentration (figure not shown). This demonstrated that the backwash did remove some of the excess solids in the reactor even though it was not completely effective in the long term. Figure 3.11e summarizes the ratio of VSS to TSS for the influent, effluent, and backwash streams, showing that all three streams had similar ratios. The median value of the VSS to TSS ratio varied between 0.82 and 0.85, which suggests that almost all of the total solids entering and leaving the system were derived from volatile components.



Figure 3.11. Solids profiles in the influent, effluent, and backwash streams.

3.2.3.4 Solids Control and Physical Scouring of the Reactor

As described, the build-up of solids during the long-term experiments with R1 led to increased head loss across the fiber bundles, especially at higher recycle ratios (see Figure 3.10). To compensate for this additional head loss, the feed pressure was increased and on occasion reached 45 to 50 psi. This not only caused difficulty in sustaining the pilot operation, but also caused water to enter the lumen side, displacing the hydrogen gas and reducing the effective surface area available for denitrification.

Ideally, with twice daily routine backwashing, the MBfR should have dislodged the excess biomass. However, with the 42 m² membrane area module design, manual physical scouring was performed to sustain the long-term operation. To accomplish this, the membrane module was removed from the reactor vessel and the water jet from a $\frac{1}{2}$ -in. hose was used to remove the excess biomass (see Figures 3.12a and 3.12b). The washed out solids were collected in a 100-L tank and analyzed for VSS and TSS to assess the effectiveness of physical scouring.

In total, three physical cleanings of R1 were performed to ensure its uninterrupted operation. The mass of total solids (TS) and volatile solids (VS) collected during these physical cleanings are reported in Table 3.3. Again, because of the dense fiber packing, the project team could not completely clean the fibers with this technique. Based on the poor pressure drop recovery shown in Figure 3.10 on the second and third cleanings, the physical scouring appears to provide only a superficial cleaning, and a significant amount of biomass remained inside the fiber bundle. It is important to note that, despite the system interruption that was due to these manual physical cleanings, the pilot units recovered quickly and returned to normal operation within 48 hours.



Figure 3.12a. The MBfR cartridge removed from the module casing with biomass covering the membrane fibers.



Figure 3.12b. Biomass washed from the module.

Day	Total solids (g)	Volatile Solids (g)	VSS/TSS
55	74.5	59.7	0.80
90	78.9	66.1	0.84
111	70.9	59.5	0.84
142*	387	236	0.60

Table 3.2. Solids Recovered During Physical Scouring and Module Autopsy

*Module autopsy performed at the conclusion of Experiment IV with R1 on Day 142.

At the conclusion of the long-term experiments (Day 142), an autopsy of the R1 module was performed (see Figure 3.13) and the biomass accumulated within the fiber bundle was measured and is reported in Table 3.3. Note that the mass of TS and VS collected during the module autopsy was about 5 to 6 times greater than the biomass recovered during the three physical cleanings. This clearly demonstrates that a majority of the biomass remained inside the fiber bundle, and physical scouring only provided superficial cleanings. This could also explain the poor pressure drop recovery following physical cleanings two and three in Figure 3.10. In addition, the lower VSS/TSS ratio measured for the autopsy sample (0.60 versus ~0.84) may be due to the presence of a larger fraction of digested material, with lower VSS, deep inside the membrane bundle.



Figure 3.13. Module Autopsy: Majority of the biomass was inside the tightly packed fiber bundle.

3.2.3.5 Hydrogen Consumption

An inventory of the mass of hydrogen consumed during this project was kept so that a comparison between actual hydrogen consumption and theoretical consumption could be made. Based on the mass loadings of nitrate and oxygen and their percentage removals, a theoretical hydrogen demand could be calculated using equations 3.1 and 3.2. This theoretical hydrogen demand was compared with the actual consumption of hydrogen during the long-term experiments with R1. It was found that only approximately 50% of the hydrogen used in biomass synthesis was not included in this calculation of theoretical hydrogen consumption. With biomass synthesis included, however, the percent hydrogen utilization [theoretical consumption] would be approximately 5% higher.) This was one of the most significant limitations of the 42 m² membrane area module. The poor hydrogen consumption was primarily due to the pore size distribution of the CTA fibers bubbling

hydrogen into the liquid. This not only limited the ability to increase the hydrogen pressure to drive the denitrification process, but also allowed water to enter into the hollow fibers on several occasions. A new module design with a "tight" membrane material was necessary to improve the hydrogen consumption. A new module with a tighter membrane material was implemented in Phase 2 of this work and is discussed in Section 3.3, Phase II: Experiments with 12 m² Membrane Area Modules.

3.2.4 Limitations of the 42 m² Membrane Area Module

Although the long-term and short-term experiments with the 42 m² membrane area modules resulted in reasonably high nitrate removals and nitrate fluxes, the project team identified several shortcomings with this design, listed in order of importance:

- 1. Inability to control hydrogen pressure independent of shell side water pressure. This limitation was due to the larger membrane pore size of the CTA fibers. To prevent excessive hydrogen loss and to prevent water from filling the lumen of the membrane fibers, hydrogen pressure was kept below the inlet water (or feed) pressure and above the module outlet (or recycle stream) pressure, which prevented the project team from investigating the effect of hydrogen pressure on nitrate removal with this module.
- 2. Inefficient hydrogen transfer. Because of the larger membrane pore size, 50% of the hydrogen was bubbled into the bulk liquid and did not contribute to the denitrification process.
- 3. Excessive head loss and inability to control solids accumulation. The pressure drop across the fiber bundle increased with time and on a few occasions reached 35 to 45 psi. The high pressure drop (1) increased the feed pressure to 50 psi, (2) made backwashing difficult, and (3) caused water to enter the lumen side of the membrane, reducing the membrane area available for denitrification. Even with twice-per-day backwashing and periodic physical washing, the true amount of solids trapped in the densely packed fiber bundle could not be measured until the module was autopsied. When the module was autopsied, 5 to 6 times the amount of solids attained from a physical washing were collected.
- 4. High recycle rate. As the 42 m² membrane area modules were densely packed with 42,000 fibers, high recycle flow was required to ensure uniform distribution of feed flow and mixing in the bulk liquid.

These shortcomings needed to be addressed to improve the overall process economics and reliability. Two possible modifications of the original design were considered. The first modification used the same 42 m² membrane area module, but the system hydraulics were altered to reduce the head loss across the fibers, which improved the ease of operation and the hydrogen consumption. The second modification included a redesigned MBfR module with "tight" membrane material and reduced membrane area, 12 m² (or 12,000 hollow fibers) compared to the original 42 m² membrane area design (42,000 hollow fibers).

3.2.5 42 m² Membrane Area Module with Improved Hydraulics

To address some of the limitations with the 42 m^2 membrane area module design, the original MBfR pilot configuration for R2 was modified by including an 18 gal external tank in the

recycle line. For discussion purposes, R2 with this revised flow configuration was referred to as R2-m. The external tank was exposed to atmospheric pressure, and this simple modification reduced the outlet fiber bundle pressure, without changing the module design (see Figure 3.14). The other benefits realized by the addition of an external tank in the recycle line were

- a reduced inlet feed pressure;
- less water inside the membrane lumens, as a direct result of the reduced feed pressure, ensuring that only hydrogen gas filled the membrane fibers; and
- dramatically improved ease of pilot operation.



Figure 3.14. By providing an external tank (the 100 L white tank) in the recycle line, pressure outside the fiber bundle in reactor R2 was decreased to atmospheric pressure.

Similar to experiments with the original design reported in Section 3.2.2, Short-Term Experiments, several short-term experiments with this revised configuration were conducted to evaluate the effects of nitrate loading on reactor performance. By varying the system HRT from 70 min to 10 min, nitrate loading on the MBfR module was increased from 150 to 1650 mg N/m²·d. Note that because the 18-gal external tank did not contribute to denitrification, HRT was calculated based on the effective volume of the R2 MBfR module, 10.5 gal. All these experiments were conducted at a fixed recycle rate of 10 gpm.

Figure 3.15 summarizes the dependence of nitrate removal and TIN (nitrate and nitrite) removal (Figure 3.15a) along with nitrate flux (Figure 3.15b) as a function of the nitrate loading rate for these short-term experiments. Close to 100% nitrate and TIN removal was observed for loadings between 150 and 750 mg N/m²·d. With a further increase in loading from 750 to 1650 mg N/m²·d, both nitrate and TIN removals dropped. However, the drop in TIN removal was always greater than the drop in nitrate removal efficiency because of nitrite accumulation at the higher loadings rates.

Figure 3.15b compares the nitrate flux as a function of nitrate loading rate for R2 (the original design without the external tank) and R2-m (the modified design with the external tank).

Note that the membrane area was unchanged at 42 m² for both configurations. Whereas hollow circles represent data from the original configuration (no external tank), the filled symbols represent results from the reactor with the 18-gal external tank. The solid line denotes 100% removal of nitrate at any given loading. As seen, nitrate flux increased linearly with the nitrate loading rate and overlapped for both reactors in the loading range 150 to 1000 mg N/m²·d. This suggests that all of the denitrification was mediated by the biofilm on the 42 m² membrane area, and additional tankage in the recycle line only provided operational ease and a reduced inlet feed pressure.



Figure 3.15. Results for short-term experiments with the 42 m^2 area module: (a) Effect of nitrate loading on percentage of nitrate and TIN removals and (b) effect of nitrate loading on nitrate flux for reactors R2 and R2-m.

With a further increase in loading (>1000 mg N/m²·d), the nitrate flux quickly dropped for R2 (no external tank); however, it remained more stable for R2-m (with external tank) in the nitrate loading range from 1000 to 1350 mg N/m².d. The stable performance of R2-m in this nitrate loading range could be attributed to the hydrogen availability in the hollow fibers. Because the tank addition to the recycle line reduced the module inlet and outlet pressures, leakage of water from the shell side into the fiber lumen was eliminated, and more membrane area was available to deliver hydrogen to the biofilm (e.g., less water on the lumen side, more hydrogen gas).

Consistent with these observations for R2, nitrate flux dropped to 600 from 1050 mg N/m²·d for the reactor R2-m when nitrate loading exceeded 1350 mg N/m²·d. This sudden drop in nitrate flux could be attributed to the presence of oxygen in the nitrified feed water. As explained earlier in Section 3.2.2.1 (*Effect of Step-Increase in Loading at 20 GPM Recycle Rate*), oxygen not only competed for hydrogen (that reduces its availability for denitrification) but it might also cause inhibition of the denitrifying microbial population within the biofilm. These two combined effects provide a plausible explanation for the dramatic deterioration in nitrate flux beyond a certain loading (Figure 3.15b).

Although, the required feed pressure dropped from 40 to 50 psi to 25 to 35 psi with the addition of an 18 gal external tank, this also increased the overall footprint requirement, which was a design disadvantage. This disadvantage could easily be overcome by using a much smaller size tank (at atmospheric pressure) because the open tank in the recycle line only served to reduce the pressure on the outlet of the fiber bundle to atmospheric pressure, and it did not provide additional reaction time for denitrification. A more serious limitation of the R2-m design is related to the porous nature of the CTA fibers, which required that hydrogen pressure be maintained below the module inlet feed pressure and above the module outlet pressure to prevent water leakage into the lumen. A fundamental change in the module design was still necessary to allow the hydrogen pressure to be controlled independently of the reactor hydraulics.

3.3 Phase 2: Testing 12 m² Membrane Area Modules

Some of the limitations of the 42 m² area modules were addressed using a new module design where (1) membrane area was reduced to 12 m² (0.5-in. thick fiber bundle) and (2) "tight" CTA fibers improved hydrogen delivery into the biofilm. The details of the module design were provided in Chapter 2, Section 2.3, MBfR Module Design. Similar to experiments with the 42 m² membrane area module, two modules with 12 m² membrane area, designated as R3 and R4, were tested in long-term as well as short-term, respectively.

3.3.1 Reactor Start-Up and Biofilm Development

Based on our start-up experience with the 42 m^2 area module, no external inoculum was added to reactors R3 and R4 for the start-up phase. Both units were operated in a continuous mode with 0.21 gpm of feed water flow and a 10 gpm recycle rate (recycle ratio of 48). During this period, the lumen-side hydrogen pressure was maintained at 17 to 20 psi. The influent nitrate concentrations ranged from 8 to 16 mg N/L and a non-uniform biofilm, pale brown in color, was very noticeable on the membrane fibers after a week of operation. The biofilm continued to grow and again, after 2 weeks of operation, a dark brown uniform biofilm completely covered the membrane fibers. Figure 3.16a provides visual evidence of the biofilm development. During the start-up period, influent and effluent nitrate concentrations were monitored for both reactors, and the results for R3 are shown in Figure 3.16b. The influent nitrate concentration was reduced by more than 60% after 6 days of operation and more than 90% after 2 weeks of operation. Similar results were also observed for reactor R4.

The 10- to 14-day start-up time for the 12 m^2 membrane area modules was similar to that observed for the 42 m² membrane area modules. Compared to an MBfR pilot study on a groundwater application where the start-up time was 6 to 8 weeks (Adham et al., 2004), results from this study suggested that the start-up time for the MBfR in the wastewater setting required 1/3 the time. This result was expected because wastewater is inherently rich in micronutrients and indigenous autotrophs needed to quickly establish a healthy population of autotrophic denitrifies in the MBfR.



Figure 3.16a. Visual evidence of biofilm development (after 2 weeks of operation).



Figure 3.16b. Nitrogen profiles during the start-up period.

3.3.2 Short-Term Experiments

3.3.2.1 Effect of Loading and Hydrogen Pressure

Following the start-up, short-term experiments were conducted to explore the benefits of increased hydrogen availability to the biomass with R4. The nitrate loading was changed from 750 to 4000 mg N/m²·d, in random order, by varying the HRT from 70 to 10 min. The reactor performance was assessed at 15 and 30 psi hydrogen pressure with a fixed recycle rate of 10 gpm for each loading condition.

Figure 3.17 summarizes the influence of the nitrate loading rate with 15 psi of hydrogen pressure on effluent nitrate and nitrite concentrations (Figure 3.17a) and TIN removal efficiency (Figure 3.17b). As the nitrate loading increased from 800 to 1050 mg N/m².d, as shown in Figure 3.17, the following observations could be made: (1) the effluent nitrate concentration increased only slightly from 0.1 to 0.3 mg N/L, (2) the effluent nitrite concentration increased from 1.0 to 2.3 mg N/L, (3) the nitrate removal efficiency remained unchanged at ~98.5%, and (4) the TIN removal efficiency dropped from 83% to 70%. When the nitrate loading was further increased from 1050 to 1500 mg N/m²·d, R4 performance deteriorated significantly. The effluent nitrate concentration rapidly increased to 12.2 mg

 N/m^2 d, and the removal efficiencies dropped to ~21%. These results suggest that the 12 m² membrane area module reached its capacity for nitrate removal at 1050 mg N/m² d loading rate with a hydrogen pressure of 15 psi.



Figure 3.17a. Dependence of nitrate and nitrite effluent concentrations on loading rate.



Figure 3.17b. Dependence of percentage of nitrogen removal on loading rate.

Figure 3.18 compares the performance of R4 as a function of nitrate loading at 15 and 30 psi hydrogen pressure. As shown in Figure 3.18a, the effluent nitrate concentration increased with loading for both hydrogen pressures tested, but at 30 psi, the sudden rise in effluent nitrate concentration occurred at a much higher loading rate than it did with only 15 psi of hydrogen pressure. At 15 psi, the effluent nitrate concentration increased dramatically from

0.3 to 12.2 mg N/L when the loading was increased from 1050 to 1500 mg N/m²·d. In contrast, the effluent nitrate concentrations remained below 0.2 mg N/L as the nitrate loading approached 1800 mg N/m²·d when the hydrogen pressure was increased to 30 psi. As loading was further increased to 2800 mg N/m²·d, the effluent nitrate concentration increased to ~1.5 mg N/L, but as the loading approached 4000 mg N/m²·d, there was a rapid increase in the effluent nitrate concentration from 1.4 to 6.4 mg N/L. It is important to note that even at a loading rate of 4000 mg N/m²·d, R4 continued to denitrify and did not reach its maximum capacity with a hydrogen pressure of 30 psi.

Figure 3.18b shows the nitrite concentration as a function of nitrate loading rate at 15 and 30 psi hydrogen pressure. For loading conditions between 850 and 1050 mg N/m²·d, the effluent nitrite concentration ranged from 1.0 to 2.3 mg N/L, and 0.17 to 0.3 mg N/L for the 15 and 30 psi hydrogen pressure, respectively. Further, nitrite accumulation (~ 2mg N/L) for 30 psi hydrogen pressure was observed at loadings >1800 mg N/m2·d, which suggests that hydrogen was limiting the rate of nitrite reduction.

Figures 3.18c and 3.18d show that nitrate and TIN percentage removal was greatly influenced by an increase in hydrogen pressure. The nitrate and TIN removal efficiencies increased significantly when the applied hydrogen pressure was increased, especially when the nitrate loading was high. For example, the nitrate removal dropped only marginally from 99% to 90% when the loading was increased from 850 to 2800 mg N/m² d at 30 psi hydrogen pressure. Likewise, the TIN removal dropped from 99 to 70% as the loading was increased from 850 to 2700 mg N/m² d, whereas both nitrate and TIN removal dropped significantly (e.g., 99% to 10%) when a similar increase in the range of nitrate loading occurred with 15 psi hydrogen pressure.



Figure 3.18. Influence of nitrate loading on R4 performance at 15 and 30 psi hydrogen pressure.

Figure 3.19 presents the nitrate flux as a function of loading rate at 15 and 30 psi hydrogen pressure. Consistent with the R2 results in Figure 3.6b, the nitrate flux increased with an increase in nitrate loading, but arrived at a maximum. This maximum flux was ~1050 mg N/m²'d with a hydrogen pressure of 15 psi, but when the hydrogen pressure was increased to 30 psi, the nitrate flux approached 2725 mg N/m²·d. Thus, the maximum nitrate flux was shown to be directly related to the availability of an electron donor (e.g., hydrogen). By increasing the hydrogen pressure, the diffusive flux of hydrogen into the biofilm increased, which compensated for the increased hydrogen demand posed by nitrate and oxygen (presented in the nitrified trickling filter effluent) at elevated mass loadings. The maximum nitrate flux of 2725 mg N/m²·d corresponded to a 25 min HRT at which ~96% nitrate removal efficiency was observed. At this flux, the calculated nitrate utilization rate was 780 g N/m³·d (corresponding to a 25 min HRT), which was ~ 30% less than that obtained with the 42 m² membrane area module. This was largely due to unnecessary void spaces in the R4 module design.



Figure 3.19. Effect of hydrogen pressure on nitrate flux.

3.3.3 Long-Term Experiments

Longer experiments were performed with R3 (minimum of 600 h) to observe long-term O&M issues and changes in reactor performance. Two long-term experiments were performed to determine the impact of the recycle rate and ratio on reactor performance (see Table 3.3). Experiment I was conducted at 50 min HRT (0.20 gpm feed flow rate, which corresponded to ~ 1100 mg N/m² · d loading) with a 10 gpm recycle rate that resulted in a recycle ratio of 50. Because this recycle ratio made the operational costs of this process prohibitive unless it was optimized, the project team conducted a second experiment (Experiment II) at a recycle ratio of 5 with the same nitrate loading ~1100 mg N/m² · d (corresponding to a 0.2 gpm feed water flow rate and a 1 gpm recycle flow rate). During both experiments, the hydrogen pressure was maintained at 30 psi, and R3 was backwashed twice per day to remove loose solids and debris.

	Experiment I	Experiment II
HRT, min	50	50
Recycle rate, gpm	10	1
Recycle ratio	50	5

Table 3.3. Long-Term R3 Performance at 30 psi Hydrogen Pressure and ~1100 mg N/m²⁻d Loading

3.3.3.1 Nitrogen Removal

Figures 3.20 and 3.21 present the nitrogen removal observed during the long-term experiments with R3. Figure 3.20 presents the temporal influent nitrate concentration and effluent nitrate and nitrite concentrations. Figure 3.21 shows the temporal variations in

percentage of nitrate and TIN removal along with the feed water temperature for the long-term experiments.

Experiment I (50 min HRT, 10 gpm recycle rate, and 50 recycle ratio) was conducted for approximately 2 months. The first 15 days represented pilot start-up, where the effluent nitrate concentration continually improved with time and partial denitrification resulted in effluent nitrite. Following this start-up phase, R3 continued to completely denitrify for the next 7 days. On Day 23, a problem with the Magmeter was identified (highlighted on Figures 3.20 and 3.21), and it was determined that R3 was not able to regulate the flow to the required setting of 0.2 gpm and was fluctuating between 0.4 and 0.8 gpm. Figures 3.20 and 3.21 show that even with a 2- to 4-fold increase in nitrate loading, the reactor's capacity was not exceeded and R3 was able to reduce $\sim 50\%$ of the influent nitrate. Following repair of the Magmeter on Day 30, the long-term experiments were continued at the target 0.2 gpm feed flow with 30 psi of hydrogen pressure. During the next 30 days, the feed water nitrate concentration, nitrate loading rate, and temperature varied from 12.7 to 15.8 mg N/L, 1130 to 1600 mg N/m²·d, and 40 to 77 °F, respectively. As shown in Figures 3.21, high removals of nitrate (>90%) and TIN (>97%) were observed throughout the long-term experiment at a 50 min HRT and 10 gpm recycle rate, regardless of daily variations in the feed water quality, loading conditions, and temperature.

Experiment II was initiated on Day 61 in an effort to optimize MBfR operational costs. During this experiment, the recycle rate was reduced from 10 to 1 gpm, whereas the HRT remained at 50 min. The MBfR operated for approximately 50 days for Experiment II, but during the first week of operation, a major fire broke out in Lake Arrowhead that resulted in a 12-day shutdown.

Following this extended shutdown, R3 was restarted on Day 77, and the nitrate and TIN removals were approximately ~70% after 48 hours of uninterrupted operation. These high nitrogen removal rates were not sustained, however, and by Day 81 the nitrate and TIN removal rates dropped to 41% and 31%, respectively. The high nitrogen removals observed immediately after the extended shutdown were believed to be attributed to a combination of heterotrophic and autotrophic denitrifiers. This was because anaerobic conditions arose during the extended shutdown, and without a hydrogen supply, it was likely that much of the autotrophic biomass decayed. The decaying biomass provided the necessary carbon source for heterotrophic denitrification as R3 was restarted. It appeared that heterotrophic bacteria significantly contributed to the denitrification for the first 3 days following restart. Once the carbon source was depleted, the nitrogen removal declined significantly, and the reactor performance was unstable as nitrate and total nitrogen removal efficiencies fluctuated between 25 to 88% and 20 to 51%. This period between Days 81 and 95 represented a transition period where the autotrophic population was being reestablished in R3. Once this transition period was completed, more stable reactor performance was observed and the nitrate and TIN removal increased from 75 to 95% and 55 to 80%, respectively.

It is important to note that Experiment II represented a 10-fold decrease in the recycle ratio from Experiment I, but the effluent nitrate and nitrite concentration increased by only 20 to 30%. These long-term results suggest that the 12 m² membrane area module could be operated at a recirculation ratio of 5—even at loadings as high as 1100 mg N/m²·d—without significant deterioration in the MBfR effluent water quality. This result was of practical significance because energy cost per 1000 gal of treated water for an MBfR process, when operated at a recirculation ratio of 5, would be comparable to other wastewater processes, such as a membrane bioreactor (MBR).

Compared to the 42 m^2 membrane area modules, the improved performance with the 12 m^2 membrane area modules could be primarily attributed to

- the non-porous fiber material that allowed increased hydrogen pressures to be sustained without bubbling, which enhanced hydrogen transfer into the biofilm and minimized water accumulation in the hollow fibers and
- lower fiber packing density and a more structured spacing arrangement minimized fiber clogging and clumping, which ensured even flow distribution over the fibers.



Figure 3.20. Effect of long-term operation on nitrogen removal.



Figure 3.21. Effect of long-term operation on nitrate and TIN removal.

3.3.3.2 Pressure Drop Across the Fiber Bundle

Figure 3.22 shows the pressure drop evolution across the fiber bundle during the entire 110 days of operation with R3. For Experiment I (10 gpm recycle rate), the pressure drop increased slowly at a rate of 0.05 psi/day and fluctuated between 9 and 12 psi after 60 days of operation. When the recycle rate was reduced to 1 gpm (Experiment II), the pressure drop decreased to 8 psi and remained stable between 6 and 9 psi for the next 50 days of operation.

It is important to note that, unlike the 42 m^2 membrane area modules, no manual cleaning of the 12 m^2 membrane area module was required or performed. A backwash was performed twice per day, 7 days a week, and this appeared to be sufficient cleaning to maintain a stable pressure drop. These promising operational results for R3 (12 m^2 membrane area module) could be primarily attributed to the use of thinner fiber bundles, fiber placement/arrangement, and spacer nettings that reduced the pressure build up across the fibers. Lower pressure drop across the fiber bundle also meant that the required feed pressure was reduced, which is a significant operational advantage when evaluating operating costs.


Figure 3.22. Pressure drop across the fiber bundle during long-term operation of R3.

3.3.3.3 Suspended Solids Concentration

Weekly VSS, TSS, and turbidity measurements were made of the influent, effluent, and backwash streams during the long-term operation of R3. The turbidity of the influent and effluent streams was also made on a daily basis and all these results are summarized in Figure 3.23. Typically, the effluent TSS, VSS, and turbidity values were observed to be less than their influent concentrations (see Figures 3.23a, b, and c), indicating the R3 design, similar to the R1 design, behaved like a filtration device. Figure 3.23d presents a probability plot of TSS removal, with an observed TSS removal at 50 percentile greater than 50%, supporting the observation that the redesigned R3 membrane fiber bundle still behaved like a filter.

Backwashing twice per day with a nitrogen sparge was employed to remove excess reactor solids. Figure 3.23e compares the backwash TSS concentration with the effluent TSS concentration (in log-scale). An order of magnitude higher of TSS concentration was observed in the backwash samples, suggesting some removal of trapped solids during the reactor backwash. It is important to note that similar results were obtained with R1 (42 m² membrane area module), so it was not clear that this backwash was effective with this module design. Figure 3.23f summarizes the ratio of VSS to TSS for influent, effluent, and backwash streams. Similar to observations with R1, the median ratio of VSS to TSS ranged between 0.83 and 0.9, and the majority of the solids entering and leaving the system were derived from volatile components.



Figure 3.23a. Variations in influent and effluent TSS concentration.



Figure 3.23c. Variations in influent and effluent turbidity.



Figure 3.23e. Comparison of TSS in backwash and influent streams.



Figure 3.23b. Variations in influent and effluent VSS concentration.



Figure 3.23d. Probability plot of TSS removal.



Figure 3.23f. Comparison of VSS/TSS ratios in influent, effluent, and backwash streams.



3.3.3.4 Hydrogen Consumption

Because fibers in the 12 m² membrane area module were less porous than the fibers in the 42 m² membrane area module, an improvement in hydrogen consumption was expected. It was found that with these 12 m² membrane area modules, actual hydrogen consumption accounted for 75% of the theoretical demand (based on Equations 3.2 and 3.3), and only 25% was lost because of bubbling in the reactor. Considering that the 12 m² membrane area modules were tested at a higher pressure, 30 psi compared to 15 to 20 psi, this was a significant improvement over the previous design, where 50% of hydrogen was lost at the lower hydrogen pressure.

3.4 Effect of System Shutdown

Several unintended process interruptions occurred during the 9 months of pilot operation. These process interruptions were both short-term (24-96 hours) and long-term (more than 10 days) in nature. Short-term interruptions were due mainly to mechanical failures and interruptions in hydrogen supply. Various process failures that caused short-term interruptions during this study were the following:

- Recycle pump failure
- Feed pump failure
- Leak in the MBfR vessel
- Leak in the influent line
- Clogging of the in-line filter in the feed line
- Hydrogen solenoid valve malfunctioning
- Interruptions in power supply

Following each of these short-term interruptions, the MBfR process began denitrifying within 24 hours of resumed operation, and the reactor performance remained stable over time. These results suggest that the autotrophic population in the MBfR biofilm was fairly robust and was not greatly impacted by short shutdown periods.

A long-term shutdown was experienced only once during pilot testing (while R3 was in operation) and was caused by a major fire incident in Lake Arrowhead. This unfortunate incident affected the team's ability to operate the pilot plant for 12 days. Following the restart, high removals of nitrate and total nitrogen were observed (> 70%) within 24 hours, but the nitrate removal efficiency gradually deteriorated with time, and after 96 hours of operation the nitrate and TIN removal had dropped to 20 to 30% (see Figures 3.20 and 3.21). The high nitrogen removals immediately following this extended shutdown period could not be attributed entirely to autotrophic denitrification. As explained earlier, it was possible that during the extended shutdown most of the autotrophic biomass in the reactor decayed, which provided the necessary carbon source for heterotrophic bacteria to denitrify once the reactor was put back on-line. Once the carbon was depleted, the MBfR performance continued to deteriorate over the next 96 hours, and the MBfR performance remained unstable with low nitrogen removals. This period could be imagined as a transition phase where the autotrophic denitrifiers were re-populating the reactor, and denitrification remained unstable until approximately 2 weeks later, similar to when the MBfR pilot units were first started up. In summary, the extended shutdown (12 days) had a significant impact on the autotrophic

denitrifier population in the MBfR process and required a minimum of a 2-week start-up period before the denitrifying capacity of the MBfR was completely restored.

3.5 MBfR Effluent Water Quality Results

Table 3.4 summarizes results from the weekly analyses of influent and effluent samples (for both R1 and R3) for BOD₅, DOC, TDS, hardness, alkalinity, calcium, magnesium, and sulfate. Because of the hydroxide ion generated during the denitrification process, an increase in alkalinity occurs, which can lead to calcium and magnesium scale formation on the MBfR membranes. However, scale formation was not an issue for Lake Arrowhead water; the nitrified feed water for this pilot study was soft, the pH was controlled with carbon dioxide (CO₂) addition, and Table 3.4 shows there was no removal of calcium through either MBfR R1 or R3. Thus, calcium carbonate ($CaCO_3$) precipitation on the fiber bundle was not an issue. Similarly, the magnesium concentration did not change through either reactor, so magnesium scale also was not an issue. The sulfate concentration entering and leaving both reactors did not change (see Table 3.4), indicating that hydrogen sulfide was not being formed in the reactor. Compared to other studies on drinking water and groundwater sources (Adham et al., 2004; Ergas and Reuss, 2001), the background DOC in the nitrified water from GVWWTP was high. These groundwater and drinking water studies also reported generation of organic carbon (effluent DOC higher than influent concentration) that was due to release of soluble microbial products (SMP) from the biofilm reactor. In this study, the median influent and effluent DOC values were very similar. The DOC in the effluent could be a result of SMP produced during denitrification or organic carbon carryover from the feed, but was likely some combination of both.

Parameter	Phase I: Reactor R1 (42 m ² membrane area module)		Phase II: Reac membrane a	Phase II: Reactor R3 (12 m ² membrane area module)	
	Influent	Effluent	Influent	Effluent	
BOD ₅ (mg/L)	16.9±4.5	14.6±6.9	13.2±3.95	17.8±3.5	
DOC (mg/L)	20.30±3.0	22.2±4.7	20.6±5.1	19.7±5.4	
Hardness (mg/L as CaCO ₃)	109±4.2	98±5.7	107±4.3	105±6.1	
TDS, mg/L	372±20.7	341±18.4	421±28.0	390±24.5	
Alkalinity (mg/L as CaCO ₃)	68.6±12.5	102±31	69.4±8.9	124±14.3	
Calcium (mg/L)	26.8±1.2	26.6±1.3	30.8±2.1	30.6±1.8	
Magnesium (mg/L)	7.3±0.40	7.3±0.4	$8.2{\pm}0.70$	7.9±0.59	
Sulfate (mg/L)	39.6±3.9	39.7±4.1	44.1±3.2	44.8±1.8	

 Table 3.4. Summary of Weekly Water Quality Results (median±standard deviation values are reported)

Chapter 4

MBfR Process Economics and Comparison with Conventional Denitrifying Biological Filter

4.1 Background

After 9 months of pilot testing the MBfR process on secondary nitrified effluent, this project has demonstrated that a hydrogen-fed MBfR can be used to meet strict nutrient requirements in advanced wastewater treatment for water reuse or reclamation. The objectives of this chapter are to (1) discuss the economic feasibility of a full-scale MBfR application based on the current state of MBfR process technology and (2) compare the MBfR costs to an existing methanol-fed denitrifying reactor.

Using the results obtained from this MBfR piloting study at the GVWWTP, a representative comparison could be made of the hydrogen-fed MBfR system to the full-scale methanol-fed denitrifying biological filter operating at the GVWWTP. Conceptual design and operating costs for an MBfR system were developed, which incorporated the module design tested in this pilot study. These costs allowed a conceptual level estimate of construction cost, operation and maintenance costs, and present worth costs. These conceptual costs for the MBfR system were compared to adjusted actual costs for the conventional denitrifying filter at the GVWWTP. To perform this comparison, additional data and information were collected on the GVWWTP's operations of the denitrifying biological filters. In addition, conceptual costs were developed for a new generation MBfR system that was not tested in this study but is currently being developed by the equipment manufacturer. The lack of an established hydrogen market makes the comparison of electron donor costs difficult to accurately quantify, and it should be recognized that the true costs for hydrogen are even more site- and application-specific than methanol.

The reader should be aware that the MBfR system cost estimates provided in this report are conceptual-level estimates only and should not be used for estimation of actual construction costs.

4.2 GVWWTP Denitrifying Biological Filter

The GVWWTP is a 2.3 MGD tertiary treatment facility that employs pretreatment, primary clarification, deep-bed nitrification trickling filters, secondary clarification, deep-bed denitrification filters, and disinfection. The plant has a total effluent nitrogen limit of 8 mg N/L based on a 30-day mean and 10 mg N/L limit based on a daily maximum.

The current facility has 3 denitrifying downflow granular media deep-bed biological filters, each 10 ft by 30 ft with a total surface area of 300 sq ft. The filters contain 6 ft of sand and rely on heterotrophic microorganisms that grow on this media. The design hydraulic loading for each of these filters is 1.4 gpm/sq.ft, so each denitrifying filter is capable of treating 0.6 MGD, and together the 3 filters can treat 1.8 MGD. Operation of the biological filters is similar to operation of any water treatment filter, except for necessary nitrogen release cycles (referred to as "bumps"). This nitrogen release cycle results from the nitrogen gas that

accumulates in the denitrification filter, which can cause "air binding" and increased filter head loss. At the GVWWTP, nitrogen gas trapped in the filters is typically released 14 to 16 times per day using backwash water only (rather than water-plus-air scour).

During normal operation, the solids removed from the secondary effluent accumulate on the 72 in. of filter media, plus additional solids from biological growth build up on the media. This accumulation of solids increases filter head loss. Backwash cycles (with air scouring and air-water) are initiated on the basis of head loss through the filter. On average, the backwashing frequency is twice per day, and the entire backwash cycle takes about 30 minutes. This generates a waste stream with a high TSS concentration (~850 mg/L, see Figure 4.1e) that totals approximately 2 to 3% of the treated water volume.

Figure 4.1 summarizes the operational performance of the denitrifying filters for the period of March 2007 through November 2007 (this period coincided with MBfR pilot testing). Typically, 10 to 17 mg N/L of nitrate entered the denitrification filters, and the effluent stream left with 2 to 5 mg N/L of nitrate (Figure 4.1a). Figure 4.1b shows that the plant exceeded the daily maximum limit for total nitrogen once in the month of August. This was due to a malfunction of the methanol feed-pump that resulted in a short episode of methanol underdosing. (This failure illustrates that neither type denitrification system is immune to mechanical failure, and effective operation depends on the duration of the failure and how quickly the microbes recover.) During this outage, the effluent BOD was always less than the daily maximum limit of 30 mg/L (Figure 5c), which suggests that problems with methanol overdosing were not observed at this facility. Influent TSS concentrations (secondary effluent) ranged from 9 to 27 mg/L, and at the filter effluent they ranged from 2 to 5 mg/L (Figure 4.1d). During backwash, 800 to 1000 mg/L of total solids were wasted from each filter (Figure 4.1e). Figure 4.1f shows that methanol consumption ranged from 1.9:1 to 5:1 kg of methanol per kg of nitrogen removed, with a median value of 2.7:1. The price of methanol delivered to Lake Arrowhead fluctuated between \$3.00 and \$3.50/gal between March 2007 and December 2007. Approximately 2.6 kg of CO₂ was produced for each kg of nitrogen that was removed (this is a theoretical estimate based on stoichiometry). Carbon dioxide is a product of the heterotrophic denitrifying filter, not of the hydrogen-fed MBfR process. Rather, CO₂ was fed into the pilot MBfR system to regulate the pH of the low alkalinity water.



Figure 4.1a. Influent and effluent nitrate concentration.



Figure 4.1b. Effluent total nitrogen concentration.



Figure 4.1c. Effluent BOD profile.



Figure 4.1d. Influent and effluent total suspended solids concentration.



Figure 4.1e. Waste biomass during backwash cycles.



Figure 4.1f. Probability plot for kg methanol consumed per kg nitrogen removed.

Figure 4.1. Summary of conventional biological denitrifying filter performance.

4.3 Opinion of Probable Cost for Conventional Filter and Full-Scale MBfR Process

The following conceptual-level estimates were developed to compare the costs of a full-scale conventional heterotrophic denitrification filter with a full-scale MBfR process:

- Construction cost
- Operating cost
- Life cycle cost

For the MBfR process, two cost estimates were prepared by Trussell Technologies, Inc. The first cost estimate was for the MBfR system tested and presented in this report (identified as MBfR-As-Tested). The second MBfR estimate was prepared for a future MBfR (identified as MBfR-In-Development) because the MBfR treatment components are currently in the process of being commercialized (permitting costs not included). There has been significant progress in reactor and module design for the MBfR process. With this in mind, and the fact that the manufacturer's price was not fully developed because they have not yet sold equipment for this application, cost estimates for a future MBfR equipment design (MBfR-In-

Development) were developed to incorporate design advances currently being implemented by APT. It is important to recognize that this was the first commercial MBfR pilot project ever performed on wastewater, and this technology will continue to experience rapid development.

The following section summarizes the cost comparison results, whereas the complete breakdown of the construction, operation, and life cycle costs are presented in Appendix A.

4.3.1 Construction Cost Estimate

Table 4.1 presents the construction cost summaries for 1.2 MGD facilities that reduce nitrate from 13.5 mg N/L (median secondary effluent value at GVWWTP over test period) to 3 mg N/L. This ensures, with a significant degree of safety, that the GVWWTP permit limits would never be violated. The effluent nitrate concentration of 3 mg N/L was determined by targeting an effluent total nitrogen concentration 20% lower than the permit limit of 8 mg N/L (design was therefore 6 mg N/L). A careful review of GVWWTP laboratory reports showed that the effluent total kjeldahl nitrogen (TKN) could reach levels as high as 3 mg N/L. In order to meet the total effluent nitrogen concentration of 6 mg/L, only 3 mg N/L could come from nitrate plus nitrite.

The construction cost for the conventional filter was based on a 90% design estimate provided by CH2MHill Estimating Services to the Lake Arrowhead Community Services District as part of the GVWWTP Expansion. These conventional filters were described in detail in the previous section. The 1.2 MGD capacity required that two filters be constructed.

The construction cost for the full-scale MBfR-As-Tested was based on the type of membrane module used in the pilot tests, operation and performance data from pilot testing, a quote from APT, and follow up discussions with APT. The 12 m² membrane module was used for cost estimating, with an H₂ pressure of 30 psi. A nitrate loading rate of 2,700 mg N/m²·d was used for the MBfR-As-Tested design, which resulted in a total required membrane area of about 17,807 m². The design included 10% additional modules to ensure that capacity could be met.

The construction cost for the full-scale MBfR-In-Development was based on a submerged membrane module that is similar in construction to modules constructed by Mitsubishi Corporation (see Figure 4.2). For the MBfR-In-Development configuration, a reduced nitrate loading rate of 1,000 mg N/m²·d was used to account for the decreased mixing efficiency anticipated with this design. Similar to the MBfR-As-Tested design, this design also included 10% extra modules to ensure that capacity could be met for a total of 2,372 membrane modules.



Figure 4.2. Mitsubishi Corporation's hollow-fiber module for submerged applications. (The MBfR-In-Development Module is similar in construction.)

Table 4.1. Construction Cost Estimates

	Conventional Treatment	MBfR-As-Tested	MBfR-In-Development
Capital Cost	\$ 3,700,000	\$ 4,200,000	\$ 2,150,000

4.3.2 Operation and Maintenance Cost Estimate

Table 4.2 lists the operating cost assumptions. For the MBfR-As-Tested costs, the recycle rate was maintained at 10 gpm in each module (just as pilot-tested), which resulted in a recycle ratio of 18. The pressure drop assumed through the MBfR process was 15 psi. This high recycle ratio and significant pressure drop resulted in an energy consumption of approximately 1 million kW-h/year. In stark contrast, the MBfR-In-Development system, which is a submerged configuration (in development at APT), will use a periodic air blast to scour the biofilm and essentially backwash the MBfR modules, so no recycling flow is provided. This system will consume only 850 kW-h/year.

Category	Assumption
Required methanol dose	3.6 g CH ₃ OH/g N
Required H ₂ dose	$0.7 \ g \ H_2/g \ N$
Methanol cost	\$3.5/gal
Hydrogen cost	\$2.7/lb
Electrical cost	\$0.1/kW-h
Membrane replacement frequency	7 years

Table 4.2. Key Operating Cost Assumptions

The hydrogen consumption for the MBfR-As-Tested was based on the actual piloting results attained with this module where 25% excess hydrogen was fed that was wasted. The hydrogen consumption for the MBfR-In-Development assumes no hydrogen loss will occur. However, even a high estimate of hydrogen demand (due to hydrogen loss) makes little difference in cost when hydrogen was used as an electron donor in place of methanol—the chemical costs are quite similar (\$73,072 vs \$73,456/year). It is important to note that the hydrogen market is less developed than the methanol market, and this cost comparison can fluctuate dramatically depending on the prices of hydrocarbons and the specific hydrogen application (i.e., location, consumption rate, and on-site infrastructure). When the required CO_2 addition (for pH adjustment) for the MBfR reactor was included³, saving money on the electron donor was not possible in today's chemical market. The estimated operation and maintenance costs are summarized in Table 4.3.

Table 4.3.	Annual	Operating	Cost
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Cost	Conventional Filter	MBfR-As-Tested	MBfR-In-Development
O&M Cost	\$ 160,000/year	\$ 490,000/year	\$ 230,000/year

4.3.3 Overall Project Life Cycle Costs

An overall project life cost analysis was performed for each alternative considered and the project life-cycle cost assumptions used in the development of these figures are presented in Table 4.4.

³ No chemical addition was made to adjust pH in the full-scale methanol reactor.

Table 4.4. Present Worth Cost Assumptions

Interest Rate:	8.00%
Project Life:	20 years

Table 4.5 presents the total project life-cycle costs for the three alternatives considered. As evident from this table, the MBfR-As-Tested process is prohibitively expensive with a higher present worth that is due to higher capital and O&M costs. In contrast, the MBfR-In-Development process provides the necessary equipment improvements that make this the most cost-effective alternative. This is due largely to the reduced energy costs associated with the submerged configuration and no recycle flow. It is also important that this submerged configuration incorporate membrane modules that are capable of demonstrating no hydrogen loss as we have assumed in this analysis.

	Conventional Filter	MBfR-As-Tested	MBfR-In-Development
Present Worth	\$ 521,691/year	\$ 903,488/year	\$ 445,726/year

4.3.4 Cost Summary

Table 4.6 presents a summary of the capital and O&M costs developed in the previous subsections. The MBfR-As-Tested system had a higher capital cost and a higher O&M cost than the conventional denitrifying filter. However, incorporating the design innovations that are currently in development at APT, the cost of an MBfR system may become competitive with a conventional system. Because the hydrogen and carbon dioxide costs are currently higher than the cost of methanol, the MBfR-In-Development exhibits slightly higher O&M costs. However, on a present-worth basis, the MBfR-In-Development was the most cost-effective alternative considered.

Table 4.6. Cost Summary

	Conventional Filter	MBfR-As-Tested	MBfR-In-Development
Capital Cost	\$ 3,700,000	\$ 4,200,000	\$ 2,150,000
O&M Cost	\$ 160,000/year	\$ 490,000/year	\$ 230,000/year
Present Worth	\$ 521,691/year	\$ 903,488/year	\$ 445,726/year

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Item No.	Description	Construction Cost Estimate (\$)
1	Mobilization & General Conditions	\$200,000
2	Sitework and Yard Piping	\$35,868
3	Concrete Filter Boxes	\$204,250
4	Mechanical:	
	Blowers	\$240,000
	Backwash Pumps	\$30,000
	Methanol Feed and Storage System	\$1,000,000
	Piping	\$142,974
	Installation of Filter internals, valves and instruments	\$154,641
	Package Control System	\$706,942
5	Electrical and Instrumentation Modifications	\$45,491
	Subtotal (\$)	\$2,760,166
	Contingencies (20%)	\$552,033
	Total Construction Cost	\$3,312,199
	Engineering Cost (10%)	\$331,220
	Total Capital Cost	\$3,643,419

A.1. Conventional Filter Cost Estimate for 1.2 MGD

Item No.	Description	O&M Cost Estimate (\$/year)
1	Chemical Supply and Delivery - Methanol	\$73,456
2	Power	\$8,982
3	General Maintenance (1.5% per year of Total Mechanical Cost-Installation)	\$47,363
4	Staffing Cost	\$20,800
	Subtotal (\$/year)	\$150,601
	Contingencies (20%)	
	Total Operating Cost (\$/year)	\$150,601

Description	Summary
Capital Cost (\$)	\$3,643,419
Operating Cost (\$/year)	\$150,601
Interest Rate (%)	8.00%
Life Cycle (year)	20
Capital Recovery Factor	0.1019
Annualized Capital Cost (\$/year)	\$371,090
Net Present Worth (\$/year)	\$521,691

Item No.	Description	Construction Cost Estimate (\$)
1	Mobilization & General Conditions	\$200,000
2	Sitework and Yard Piping	\$35,868
3	Membrane Area (Shade Structure and Slab on Grade)	\$255,000
4	Mechanical:	
	Hydrogen and Carbon Dioxide Feed System	\$50,000
	Membrane Skid (with Pump, Backwash and Controls)	\$1,000,000
	Membrane Modules	\$1,300,000
	Installation	\$235,000
5	Electrical and Instrumentation Modifications	\$47,000
	Subtotal (\$)	\$3,122,868
	Contingencies (20%)	\$624,574
	Total Construction Cost	\$3,747,442
	Engineering Cost (10%)	\$374,744
	Total Capital Cost	\$4,122,186

A.2. MBfR-As-Tested Cost Estimate for 1.2 MGD

Item No.	Description	O&M Cost Estimate (\$/year)
1	Chemical Supply and Delivery - Hydrogen and Carbon	\$103.912
	Dioxide	\$105,912
2	Power	\$107,783
3	General Maintenance (1.5% per year of Total Mechanical-	\$12.225
	Membranes Modules and Installation)	\$12,225
4	Staffing Cost	\$24,000
5	Liquid Gas Storage Rental	\$50,000
6	Membrane Replacement (every 7 years)	\$185,714
	Subtotal (\$/year)	\$483,634
	Contingencies (20%)	
	Total Operating Cost (\$/year)	\$483,634

Description	Summary
Capital Cost (\$)	\$4,122,186
Operating Cost (\$/year)	\$483,634
Interest Rate (%)	0.08
Life Cycle (year)	20
Capital Recovery Factor	0.1019
Annualized Capital Cost (\$/year)	\$419,854
Net Present Worth (\$/year)	\$903,488

Item No.	Description	Construction Cost Estimate (\$)
1	Mobilization & General Conditions	\$200,000
2	Sitework and Yard Piping	\$35,868
3	Membrane Area (Shade Structure and Slab on Grade)	\$255,000
4	Mechanical:	
	Hydrogen and Carbon Dioxide Feed System	\$50,000
	Membrane Skid (with Tank, Pump, Backwash and Controls)	\$500,000
	Membrane Modules	\$465,342
	Installation	\$101,534
5	Electrical and Instrumentation Modifications	\$20,307
	Subtotal (\$)	\$1,628,051
	Contingencies (20%)	\$325,610
	Total Construction Cost	\$1,953,661
	Engineering Cost (10%)	\$195,366
	Total Capital Cost	\$2,149,027

A.3. MBfR-In-Development Cost Estimate for 1.2 MGD

Item No.	Description	O&M Cost Estimate (\$/year)
1	Chemical Supply and Delivery - Hydrogen and Carbon Dioxide	\$79,554
2	Power	\$85
3	General Maintenance (1.5% per year of Total Mechanical- Membranes Modules and Installation)	\$6,727
4	Staffing cost	\$24,000
5	Liquid Gas Storage Rental	\$50,000
6	Membrane Replacement (every 7 years)	\$66,477
	Subtotal (\$/year)	\$226,843
	Contingencies (20%)	
	Total Operating Cost (\$/year)	\$226,843

Description	Summary
Capital Cost (\$)	\$2,149,027
Operating Cost (\$/year)	\$226,843
Interest Rate (%)	0.08
Life Cycle (year)	20
Capital Recovery Factor	0.1019
Annualized Capital Cost (\$/year)	\$218,883
Net Present Worth (\$/year)	\$445,726

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