**2013 Project Abstract**
For the Period Ending June 30, 2016

**PROJECT TITLE:** Membranes for Wastewater-Generated Hydrogen and Clean Water
**PROJECT MANAGER:** Paige Novak
**AFFILIATION:** University of Minnesota
**MAILING ADDRESS:** 122 Civil Engineering Building, 500 Pillsbury Drive SE
**CITY/STATE/ZIP:** Minneapolis, MN 55455
**PHONE:** (612) 626-9846
**E-MAIL:** novak010@umn.edu
**WEBSITE:** N/A
**FUNDING SOURCE:** Environment and Natural Resources Trust Fund
**LEGAL CITATION:** M.L. 2013, Chp. 52, Sec. 2, Subd. 05g

**APPROPRIATION AMOUNT: $ 246,000**

**Overall Project Outcome and Results**
In this project we developed a technology that could extract energy from wastewater: a polymer film containing bacteria that generate hydrogen (a clean energy source) while cleaning the wastewater. The system also contained a mesh of small, permeable tubes ("fibers") for efficient hydrogen collection. A finding of this study was that the wastewater treated needed to be high strength to generate adequate quantities of hydrogen. This type of high strength wastewater is produced by food and sugar beet processing facilities, and dairies, among other industries, and is plentiful throughout Minnesota. This technology efficiently produced and collected hydrogen in the laboratory with synthetic wastewater and wastewater from a dairy and a sugar beet processor. When used with vacuum gas collection, the exit gas was approximately 51% hydrogen, which is suitable for use in a fuel cell or for direct combustion. The system was also deployed at a pilot-scale at a brewery and was able to produce and collect hydrogen from the brewery wastewater. After further optimization for ease of scale-up and manufacture, the composite membrane system could allow the extraction of high-quality energy from wastewater while also saving industries on their treatment fees and reducing the need for expensive centralized treatment. In fact, based on our (un-optimized) results, the hydrogen generated in the Metro area would yield approximately $82,000/yr through electricity generation. This same assumption yields over $312,000/yr from the sugar beet industry in the state through electricity generation. This does not include the cost savings associated with reduced treatment fees, which for two Metro area processors alone exceeds $1,000,000/year/company. A patent application was submitted on this technology and has been approved; the University of Minnesota is exploring commercialization and licensing options. A peer-reviewed manuscript was published from this work and has been submitted to the LCCMR.

**Project Results Use and Dissemination**
Information from this project has been shared with several large water technology companies in Minnesota who may have the interest and capability to assist in optimizing and eventually deploying this technology for large-scale energy production from wastewater. Information from this project has also been shared with personnel from the Metropolitan Council Environmental Services, who treat the high strength wastewater of many large food- and beverage-processing plants, the sugar beet industry, and the brewery at which the pilot study was performed. As stated above, a peer-reviewed manuscript was published from this work and has been

submitted to the LCCMR. Multiple presentations about the research have been given at both regional and national/international conferences. Additional funding has been obtained from the Minnesota Department of Commerce to study and improve the scalability and manufacturability of the technology and optimize it for deployment.

# Environment and Natural Resources Trust Fund (ENRTF) M.L. 2013 Work Plan Final Report

**Date of Status Update Report:** August 15, 2016

**Final Report**

**Date of Work Plan Approval:** June 11, 2013

**Project Completion Date:** June 30, 2016

**PROJECT TITLE:** Membranes for Wastewater-Generated Hydrogen and Clean Water

**Project Manager:** Paige Novak

**Affiliation:** University of Minnesota

**Mailing Address:** 122 Civil Engineering Building, 500 Pillsbury Drive SE

**City/State/Zip Code:** Minneapolis, MN 55455

**Telephone Number:** (612) 626-9846

**Email Address:** novak010@umn.edu

**Web Address:** N/A

**Location:** Minneapolis, Minnesota 55455; Pilot studies will likely take place at the Metropolitan Wastewater Treatment Plant, Saint Paul, Minnesota, in the last year of the project.

| **Total ENRTF Project Budget:** | | |
|---|---|---|
| | **ENRTF Appropriation:** | **$246,000** |
| | **Amount Spent:** | **$245,352** |
| | **Balance:** | **$ 648** |

**Legal Citation:** M.L. 2013, Chp. 52, Sec. 2, Subd. 05g

**Appropriation Language:**
$246,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to develop, optimize, and test membranes made of thin film polymers embedded with selected bacteria to generate clean water and energy in the form of hydrogen from wastewater. This appropriation is available until June 30, 2016, by which time the project must be completed and final products delivered.

**I. PROJECT TITLE:**
Membranes for wastewater-generated hydrogen and clean water

**II. PROJECT STATEMENT:**
In our current energy climate, we can no longer afford to think of anything as merely a waste stream. As a result, researchers have been working to develop technologies to extract energy in usable forms from wastewater, including microbial fuel cells and algal-based biofuel production. We propose to develop another technology that can be used to extract energy from wastewater: a polymer membrane (a plastic film typically used for gas or liquid separations) containing bacteria that generate hydrogen while cleaning the wastewater. By putting the bacteria in the membrane, we can make sure that they are present in the numbers necessary to generate hydrogen, they are protected, and their growth is encouraged. The system will also contain a mesh of small, permeable tubes ("fibers") for efficient hydrogen collection. This should lead to sustained maximal hydrogen production from wastewater for use on site (e.g., in a fuel cell). After the hydrogen production step, it will also be possible to add a methane production step, providing a second source of high energy per mass fuel from the waste stream. The modular design envisioned for such a system—composite membrane racks fitted with gas collection manifolds—should enable use of the system at any scale and for any liquid waste stream containing biodegradable substrates (primarily for municipal sanitary waste, but also agricultural and industrial wastes). This project adapts proven technologies for a new application, and we therefore feel it is positioned to succeed. The goals of the project are to:

- Test the proposed system at the laboratory scale (about 1 liter),
- Optimize the design of the bacteria-embedded membranes, and
- Build and test a pilot-scale module at a municipal wastewater treatment plant.

The envisioned system will operate for long time periods and provide improved wastewater treatment coupled with fuel generation. Patent protection is being sought by the University of Minnesota for the technology, which could lead to potential income for the state.

Please note that, as part of the patent protection process, an Intellectual Property Disclosure has been filed with the Office of Technology Commercialization at the University of Minnesota on the technology proposed to be developed through this project. As a result, some information pertaining to this project is confidential at this time. This work plan omits confidential information and provides lesser detail than it otherwise might.

**III. PROJECT STATUS UPDATES:**

**Project Status as of January 31, 2014**:
A provisional patent was filed approximately a year ago. Patent protection is being sought by the University of Minnesota for the membrane modules developed in this work and the patent will be filed in the spring of 2014.

Membrane modules were constructed with two different chemistries of polymers cast on top of the hollow gas collection fibers. Bacteria could be encapsulated in these polymers and remained viable and able to produce hydrogen. The hydrogen could be captured and measured. Pure and mixed cultures of hydrogen-producing bacteria were tested with a glucose solution and synthetic wastewater. Efforts will focus on optimizing the operational parameters of the reactor/module prior to additional optimization of the polymer chemistry.

**Project Status as of July 31, 2014:**
A patent was filed by the University of Minnesota in March, 2014.

Experiments were performed in a flow-through reactor with synthetic and real wastewater. Membrane modules constructed with polyvinylalcohol-encapsulated bacteria on hollow fibers of polyethylene were able to generate hydrogen from synthetic wastewater at room temperature. The hydrogen (approximately 45-50 mL/g hexose) was successfully captured by the fibers. Faster gas flow rates through the fibers appeared to improve gas capture. Increasing the feed pH improved gas production and capture. After approximately 700 hours of operation the system experienced problems and hydrogen production declined. Experiments with similar modules and real wastewater were not successful, although the wastewater did produce hydrogen in batch reactors, suggesting that the system should be capable of hydrogen production.

Additional membrane modules constructed with electrospun bacteria on hollow fibers were also able to generate hydrogen from synthetic wastewater at room temperature. The hydrogen (approximately 25 mL/g hexose) was again successfully captured by the fibers. This experiment has been running for approximately 800 hours with no problems. Experiments with real wastewater will begin shortly with this second membrane module.

**Amendment Request (08/15/2014):**
The addendum is to formally request a re-budgeting of funds for this project.

As part of the project, we would like to establish two additional personnel categories: postdoctoral researcher and undergraduate researcher. The undergraduate will assist the postdoctoral researcher with routine activities (running reactors) to enable the postdoctoral researcher to spend more time on higher-level functions such as data analysis and membrane module creation. The graduate research assistant that was working on the project will graduate in early September with his Masters of Science degree. Rather than taking time to train a new Masters of Science student, who will also be taking courses and may be new to research, we would like to hire a postdoctoral researcher who can immediately begin contributing to the project in a meaningful way, spending full time on research. All of the required rebudgeting will remain within the "**Personnel**" category and will simply move from sub-category to sub-category.

The movement of money between sub-categories will not affect project objectives or timelines.

**Amendment Approved: <u>08/21/2014</u>**

**Project Status as of January 31, 2015:**
The electrospun module was transitioned from synthetic to real wastewater. Under flow through conditions, hydrogen was neither produced/captured in the module nor in the liquid matrix. Additional efforts to improve hydrogen capture efficiency involved coating the module with a polymeric film (i.e., silica gel coating). The coating functions as a seal, protecting the encapsulated bacteria from contamination and avoiding leakage of cells to the liquid matrix. While using synthetic wastewater, the silica-coated modules were able to produce/capture about 28 mL $H_2$/hexose and the hydrogen capture efficiency increased to 73%. Once transitioned to real wastewater, the hydrogen production declined. Operational parameters such as the hydraulic retention time (HRT) will be standardized to improve the system's resilience to environmental shocks (e.g., variable wastewaters). Further experiments will be focused on improving the chemical surface characteristic of the different layers in the module (i.e., protective coat, polymeric layer with bacteria, and hollow fibers) such that the bacteria can be maintained closer to the hollow fibers. Experiments are also starting to focus on industrial wastewaters that might serve as viable feedstocks for hydrogen generation. A collaboration with Applied Membrane Technologies has begun, which will enable use of chemically modified hollow fibers in experiments.

**Project Status as of July 31, 2015:**
Since the last reporting period, research efforts have focused on optimizing the membrane modules for maximum $H_2$ production/capture and further deployment. The silica-coated electrospun module was modified by increasing the cell density and acclimating the bacteria to the target waste prior to encapsulation. This modification showed positive results in terms of $H_2$ yield (mL $H_2$/g hexose) and $H_2$ capture efficiency (Figure 1). This module (called M3b) was tested with actual dairy production wastewater and showed a $H_2$ yield of 14.7 mL $H_2$/g hexose at an increased captured efficiency of 76% (Figure 1). These results confirm the applicability of this

technology to real wastewater. Further improvements were made to the physical and chemical characteristic of the membrane modules by: (i) immobilizing the bacterial cells directly onto the membrane surface (module called M4a), (ii) increasing the cell density (module called M4b), and (iii) improving the module's mechanical properties with the addition of a flexible outer layer of PVA (module called M5) (Figure 1). With a $H_2$ yield of 48.4 mL $H_2$/g hexose and a capture efficiency of 71%, M5 is a promising option for future pilot studies.

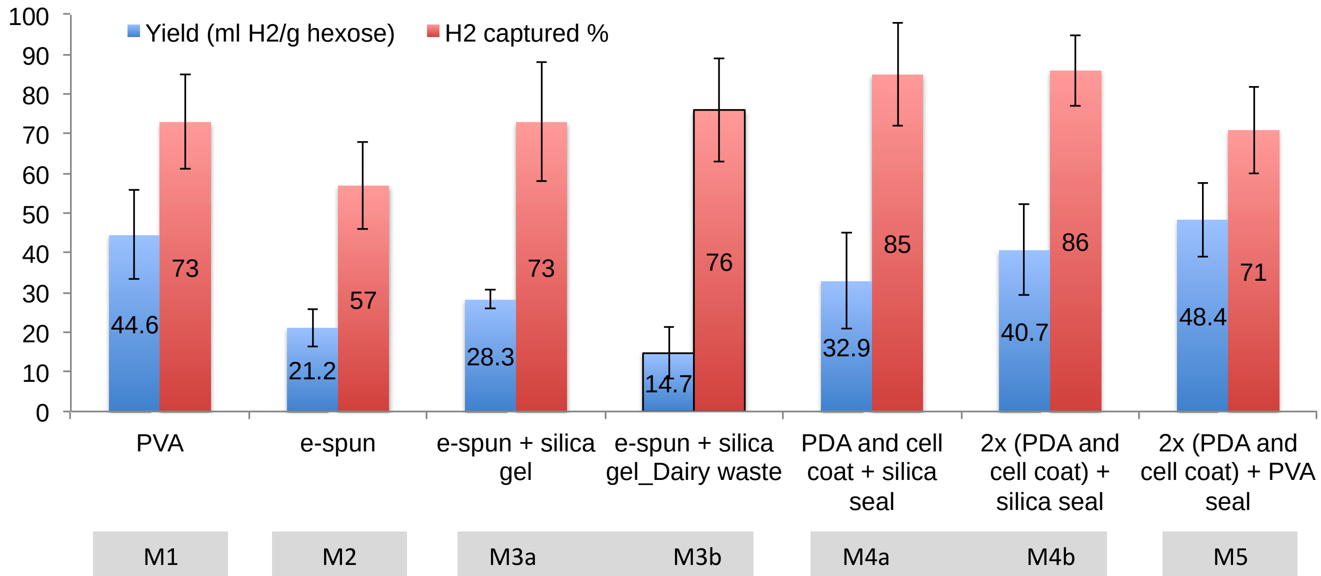



**Figure 1.** Summary of $H_2$ yield and $H_2$ capture efficiencies of the different membrane modules tested in this study.

Our team is currently in conversations with our industry partner Kemp's Inc. (Farmington, MN), to set up a pilot scale system at their facility. Additional implementation sites are under consideration and these include the Surly Brewery (Minneapolis, MN) and the Empire WWTP (Empire, MN).

**Project Status as of January 31, 2016:**

Our team continued to optimize the membrane (called M5, see previous project status update) and completed the construction of a pilot scale system. Figure 2 below summarizes the optimization efforts during this period. The resulting membrane module consists on a dense layer of $H_2$ producing bacteria, immobilized onto bare hollow fibers, and covered by a flexible polymeric material (i.e., PVA) for membrane strength and flexibility. Important membrane construction parameters and reactor operational parameters were defined during this period as well. Cell density was increased (10 times greater than previous modules), but did not significantly increase $H_2$ production. Also, the hydraulic retention time of the reactor was set at 2 days, which also increased the degradation of incoming waste with concomitant increases in $H_2$ production. The $H_2$ content of the produced gas was improved by applying vacuum to M5's off-gas line as opposed to using a sweep gas stream. In addition to synthetic wastewater, the module was further tested with different waste streams (dairy production and sugar beet wastewaters). M5 successfully produced and captured $H_2$ from the two feedstocks, proving the applicability and versatility of the technology. M5 is ready for pilot tests.

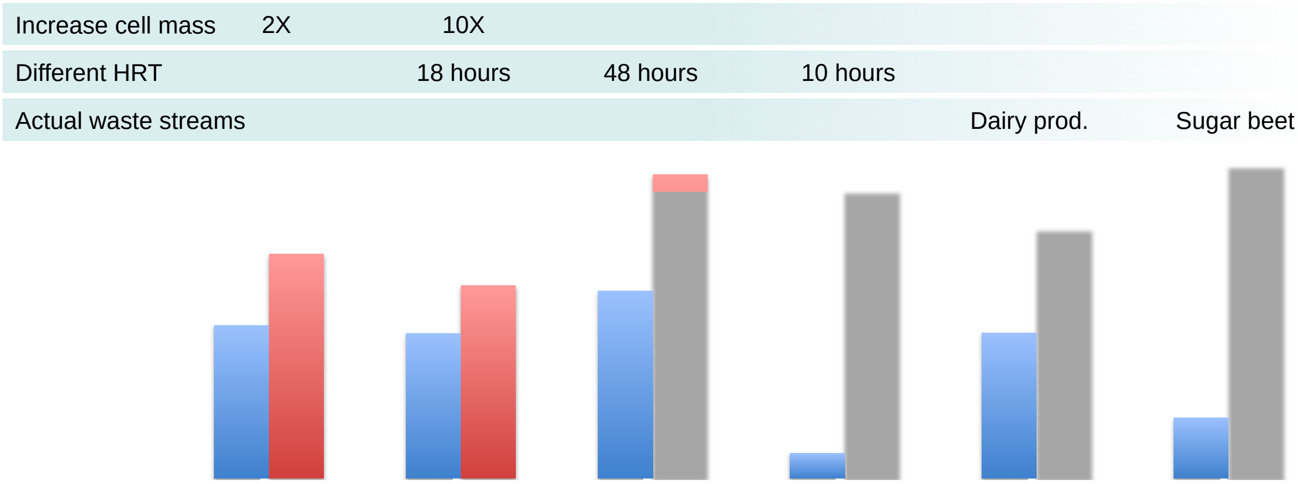



**Figure 2.** Summary of $H_2$ yield and $H_2$ capture efficiencies under different experimental conditions tested for the optimization of M5. Conditions for each test are described on the top of the figure.

**Overall Project Outcomes and Results**

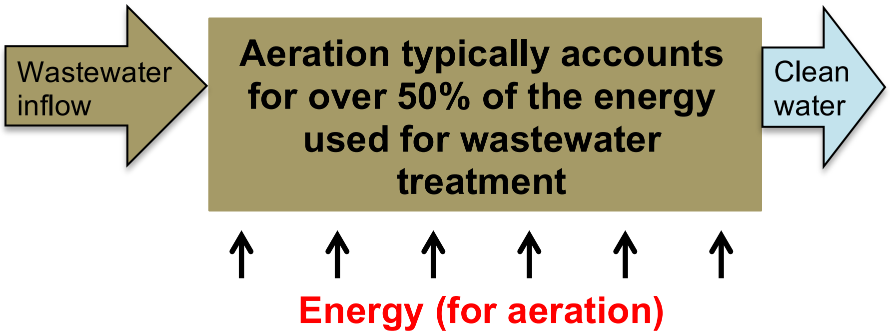
In this project we developed a technology that could extract energy from wastewater: a polymer film containing bacteria that generate hydrogen (a clean energy source) while cleaning the wastewater. The system also contained a mesh of small, permeable tubes ("fibers") for efficient hydrogen collection. A finding of this study was that the wastewater treated needed to be high strength to generate adequate quantities of hydrogen. This type of high strength wastewater is produced by food and sugar beet processing facilities, and dairies, among other industries, and is plentiful throughout Minnesota. This technology efficiently produced and collected hydrogen in the laboratory with synthetic wastewater and wastewater from a dairy and a sugar beet processor. When used with vacuum gas collection, the exit gas was approximately 51% hydrogen, which is suitable for use in a fuel cell or for direct combustion. The system was also deployed at a pilot-scale at a brewery and was able to produce and collect hydrogen from the brewery wastewater. After further optimization for ease of scale-up and manufacture, the composite membrane system could allow the extraction of high-quality energy from wastewater while also saving industries on their treatment fees and reducing the need for expensive centralized treatment. In fact, based on our (un-optimized) results, the hydrogen generated in the Metro area would yield approximately $82,000/yr through electricity generation. This same assumption yields over $312,000/yr from the sugar beet industry in the state through electricity generation. This does not include the cost savings associated with reduced treatment fees, which for two Metro area processors alone exceeds $1,000,000/year/company. A patent application was submitted on this technology and has been approved; the University of Minnesota is exploring commercialization and licensing options. A peer-reviewed manuscript was published from this work and has been submitted to the LCCMR.

**<u>Retroactive Amendment Request (08/15/2016):</u>**

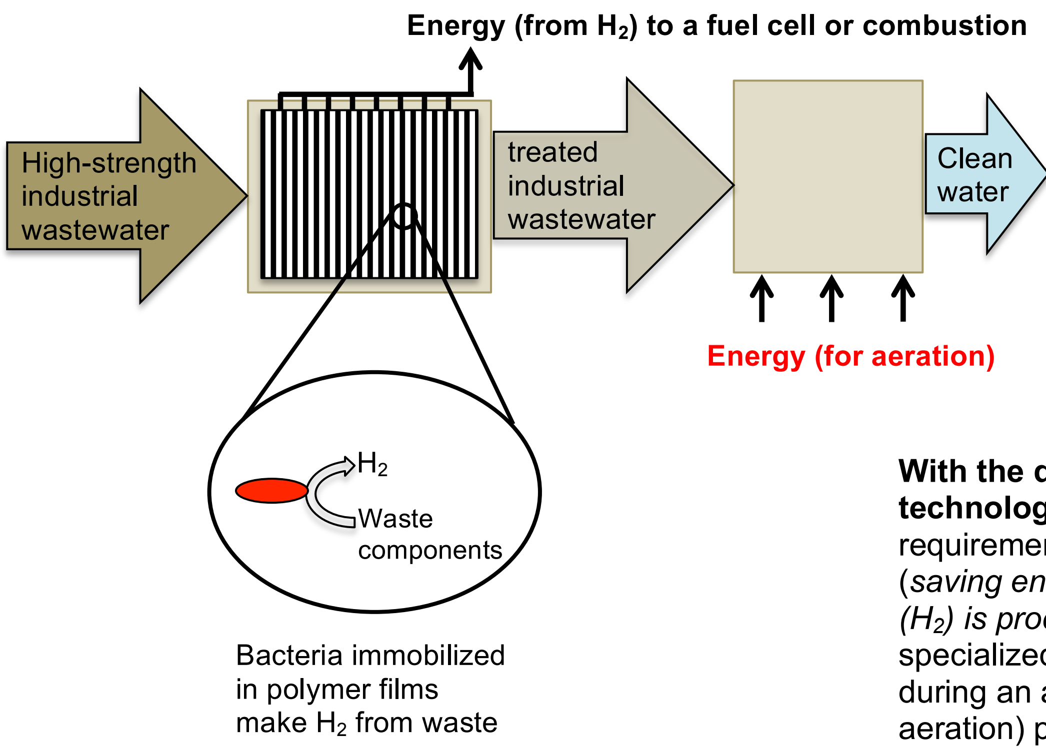
The addendum is to formally request a re-budgeting of funds for this project.

We would like to move funds ($3,274 total) from the personnel category (from both Activity 1 and Activity 2) to the laboratory supplies category to cover an over-expenditure of $3,274 total. Funds will also be moved from the laboratory supplies category in Activity 1 to cover the laboratory supplies over-expenditure in Activity 2. The cost of retrofitting the pilot-scale system was greater than anticipated and resulted in overruns in the laboratory supplies category associated with Activity 2. It is difficult to estimate in advance (at the proposal stage) exactly

# Wastewater and energy use/potential production




**In traditional wastewater treatment,** energy is *used* to aerate (and therefore treat) mixed industrial and municipal wastewater.




**With the developed technology,** aeration requirements are reduced (*saving energy*) and *energy ($H_2$) is produced* within specialized polymer films during an anaerobic (no aeration) phase of pre-treatment for high-strength industrial (*i.e.*, food processing) wastewater.

**Final Attachment A: Budget Detail for M.L. 2013 Environment and Natural Resources Trust Fund Projects**

**Project Title:** *Membranes for wastewater-generated hydrogen and clean water*
**Legal Citation:** M.L. 2013, Chp. 52, Sec. 2, Subd. 05g
**Project Manager:** *Paige Novak*
**M.L. 2013 ENRTF Appropriation: $** *246,000*
**Project Length and Completion Date:** *6/30/2016*

| **ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET** | **Activity 1 Budget** | **Revised Activity 1 Budget (8/15/16)** | **Amount Spent** | **Balance** | **Activity 2 Budget** | **Revised Activity 2 Budget (8/18/16)** | **Amount Spent** | **Balance** | **TOTAL BUDGET** | **TOTAL BALANCE** |
|---|---|---|---|---|---|---|---|---|---|---|
| **BUDGET ITEM** | ***Protoype development, laboratory testing, and design optimization*** | | | | ***Pilot-scale testing*** | | | | | |
| **Personnel Overall (Wages and Benefits)** | ~~141,500~~ | 140,057 | | 0 | ~~69,500~~ | 67,669 | | 41 | 207,726 | 41 |
| Paige Novak (PI, 6% time per year for three years, salary 73.5% of cost, fringe benefits 26.5% of cost) | | | 11,939 | | | | 17,259 | | | |
| William Arnold (co-PI, 6% time per year for three years, salary 73.5% of cost, fringe benefits 26.5% of cost) | | | 21,984 | | | | 19,660 | | | |
| Graduate Research Assistant (50% time per year for one year, 56% salary, 33% tuition, 11% fringe benefits) | | | 42,934 | | | | 0 | | | |
| Undergraduate Research Assistant (approximately 500 hours) | | | 4,803 | | | | 0 | | | |
| Postdoctoral Researcher (full time for 1.5 years, 82% salary, 18% fringe benefits) | | | 58,397 | | | | 30,709 | | | |
| **Equipment/Tools/Supplies** (Laboratory supplies include, but not limited to: chemicals for membrane construction, bacterial cultures, gas tanks for the membrane flow, hollow fibers, analysis needs such as standards, gas tanks, needles, and septa, supplies for bacterial enumeration and identification, and consumables such as gloves and solvents (~~$7,300/yr,~~ for a total of ~~$21,900~~ $25,174). Additional funds are budgeted for equipment repair and maintenance ($6,000) and the automated data acquisition system (Qubit hydrogen analyzer, computer, flow meters) and software for data acquisition ($6,100).) | ~~20,500~~ | 19,452 | 19,452 | 0 | ~~13,500~~ | 17,822 | 17,822 | 0 | 37,274 | 0 |
| **Travel expenses in Minnesota.)** **(**Mileage charges to Metropolitan Council wastewater facilities and outstate wastewater treatment plants for sample collection and monitoring of Phase II pilot system. Mileage will be reimbursed $0.55 per mile or current U of M compensation plan. | 0 | 0 | 0 | 0 | 1,000 | 1,000 | 393 | 607 | 1,000 | 607 |
| **COLUMN TOTAL** | **~~$162,000~~** | **$159,509** | **$159,509** | **$0** | **~~$84,000~~** | **$86,491** | **$85,843** | **$648** | **$246,000** | **$648** |