

2007

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Ana Maria Garcia
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Evaluation of Scrap Tire-Derived Porous Rubber Tubing as a Green Membrane
for Sustainable Water Filtration (*ECOL-Mem* Process)

by

Ana Maria Garcia

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
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Date of Approval:
July 9, 2007

Keywords: Millennium development goals, sanitation, developing countries,
global water crisis, life cycle analysis

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DEDICATION

To my parents, Ricardo Garcia and Jenny Sanchez, for supporting me every step of the way and for being exactly the kind of parents I would choose if given the chance.

ACKNOWLEDGEMENTS

Although this thesis bears a sole name on its title page, it is far from being an individual effort. For that reason I feel urged to thank all of those people and organizations that have helped me throughout my journey.

I would like to thank my advisor, Dr. Daniel Yeh, whom I approached a couple of years ago looking for an opportunity to do research through the Research Experience for Undergraduates Program at USF. It is because of his vote of confidence and continuous support that I am now concluding my Master's and for that I will be forever grateful. At the same time, I was lucky to have worked with all of the members of Dr. Yeh's research group.

Specifically, I would like to thank Ana Lucia Prieto, with whom I built (and tore down) so many things in the lab. I would also like to thank Russell Ferlita for providing me with all the Scanning Electron Microscopy images shown in this work. Finally, I extend my gratitude to Jessica Linville and Mike Ayer for helping me collect numerous samples. To the rest of the research group, I am thankful for the many discussions that helped me along the way.

I would also like to thank my committee members, Dr. Vinay Gupta and Dr. Foday Jaward for taking the time to read over my thesis and make the recommendations that contributed to making this manuscript what it is today. I am also grateful to Dr. Delcie Durham for her valuable input and for her interest in my work.

Finally, I wish to thank all the sources of funding I received throughout my career at USF. I am a proud recipient of scholarships provided by the URS Corporation, Dr. Wayne and Iris Echelberger, and Margaret Davis. In addition, it would have been impossible for me to complete my degree without the help of the Patel Center for Global Solutions, which funded my education during 2 years, and the Lee Project for Global Freshwater, which funded much of the equipment I used.

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EVALUATION OF SCRAP TIRE-DERIVED POROUS RUBBER TUBING AS A
GREEN MEMBRANE FOR SUSTAINABLE WATER FILTRATION
(*ECOL-MEM* PROCESS)

Ana Maria Garcia

ABSTRACT

Increasing population and extensive urbanization have strained resources around the world, promoting water scarcity and solid waste accumulation. Addressing the issues of access to safe drinking water and basic sanitation in developing countries is challenging due to limited technological and financial resources. Therefore, it is imperative that durable, low-cost, and sustainable technologies are developed to help alleviate these problems. At the same time, the production of solid waste has increased and includes waste tires, which pose a health and environmental hazard. Although efforts have been made to develop new markets for recycled scrap tires, a vast majority are still being stockpiled or landfilled. This study aims to evaluate a water treatment system that addresses the problem of access to safe drinking water and sanitation, while providing a new market for recycled scrap tires.

The system, termed *ECOL-Mem*, utilizes commercially available porous rubber tubing (PRT), which is marketed for drip irrigation purposes. To our knowledge, this is the first time this product has been used in a water treatment system. The PRT is manufactured through a hot extrusion process and contains 65% recycled crumb rubber and a binder (e.g. polyethylene). The proposed configuration simulates a hollow fiber membrane filtration system driven by a vacuum that operates inside-out. The system was first tested using clean water to obtain intrinsic characteristics. It was then tested using bentonite and sludge solutions that simulated impaired source water. For the case of a bentonite solution containing 700 mg/L, 20L of permeate could be obtained in one hour while the total solids removal remained around 20%. In order to improve the water quality, a flocculation-enhanced filtration phase was explored. The flocculant is chitin, a biopolymer that can be derived from waste shellfish. Upon addition of the chitin, between 60% and 70% of total solids removal could be obtained for different feed waters.

Although optimization is needed, the PRT system has shown promising results, while providing a technology that targets the needs of developing countries in the areas of safe drinking water, basic sanitation, and solid waste recycling.

CHAPTER 1

INTRODUCTION

Even in the 21st century, the problem of access to safe drinking water and sanitation has not been solved globally despite efforts by different organizations and governments. It is a fact that underdeveloped regions of the world are at a disadvantage due to their lack of financial resources and trained personnel that can help address the issues. The problem worsens in rural areas, where centralized water and wastewater treatment is not an option.

In an effort to solve the problem, the United Nations established the Millennium Development Goals (MDG) in 2000 during the Millennium Summit in New York City (United Nations, 2002). These goals address the needs of people around the globe in terms of education, poverty, hunger, disease, and discrimination; all of which can be related in some way to the lack of access to safe drinking water and sanitation. In this specific area, the goal is to halve the population suffering from the burden of lack of access to safe drinking water and sanitation by 2015 (United Nations, 2005a). With the targets established, it is now necessary to develop the appropriate technologies. In many areas of the world, the efforts are lagging and it is estimated that the goals will not be met by 2015 (United Nations Children's Fund, 2006).

Membrane filtration is a promising and reliable technology in the area of water and wastewater treatment because it can provide a semi-permeable barrier that can reject contaminants and pathogens while allowing clean water to flow through. However, there is still much work to be done in order to improve the characteristics of a technology and allow its application in

developing regions of the world. An attempt to use the technology as-is would not yield long-term solutions even if the initial capital investment could somehow be covered. Other problems, such as costs related to replacement and maintenance, cleaning procedures, trained personnel, and required pretreatment would be encountered. Therefore, in order to apply membrane filtration in developing regions on a sustainable basis, significant modifications and adaptations must be made.

Another problem faced in many regions of the world is that related to the disposal of scrap tires. These pose an environmental threat due to their high calorific value and void volume which make them an excellent breeding ground for mosquitoes and rodents and a common cause for fires (USDOE, 2000). In the United States alone, the problem is significant since scrap tires constitute 12% of all solid waste and most of them are stockpiled or disposed of illegally (Conesa *et al.*, 2004). Such statistics are not available for most developing countries, so the severity of the problem may be underestimated.

Attempts have been made to address this problem in industrialized nations by encouraging recycling and alternative tire-derived products. However, these unconventional markets are not enough to transform the entire supply of scrap tires into useful goods. Furthermore, these types of uses for waste tires have not been developed in many regions of the world.

In an attempt to simultaneously address the problem of access to safe drinking water and sanitation as well as the problem of scrap tires, an alternative approach was developed. It is based on the principles of membrane filtration while being low-cost, durable, and sustainable. This process has been termed *ECOL-Mem*. In its name, each of the letters in the abbreviation ECOL stand for a characteristic that is important for the application of this type of technology in an underdeveloped environment. In this manner, E stands for "environmentally friendly", C stands for "capacity-building", O stands for "obtainable", and L stands for "low-cost". The candidate that was evaluated during the study is a porous rubber tubing

made from 65% recycled tire rubber that is commonly used for irrigation purposes.

The filtration characteristics and ability of the porous rubber tubing material to simulate a membrane were then investigated in order to better understand its behavior when used to this type of application. The study was divided into three phases to provide insight into the intrinsic and filtration characteristics of the material and its ability to serve as a sustainable technology to satisfy the needs for safe drinking water and sanitation in developing countries.

CHAPTER 2

BACKGROUND

2.1 The Water and Sanitation Problem in Developing Countries

Water scarcity has affected many regions around the world, including developed and underdeveloped areas. However, poor water resource management and lack of infrastructure, which is common in developing countries, contributes greatly to the deficient access to safe drinking water and sanitation.

2.1.1 The Current Problem

According to the World Health Organization (WHO), inadequate water and sanitation are the primary causes of diseases like malaria, cholera, and diarrhea. These diseases are associated with 3.4 million deaths each year. Of that total, approximately 1.5 million deaths are from children under the age of 5 and are caused by diarrhea (UNICEF, 2006). Most of these deaths take place in developing countries in Asia, Africa, and Latin America; where at any given moment, almost half of the population is sick from untreated water (WSSCC, 2003). The problem becomes even more substantial considering the increase in population growth that is seen around the world. Even industrialized countries are beginning to feel strained by the increasing demand for freshwater. This has created an urgent need for alternative technologies that could help solve the problems that communities face. Global projections estimate that the worldwide population of over 6 billion in 2000 will increase about 20% to over 7 billion by 2015, making water supply problem even more critical (WHO and UNICEF, 2000).

Agricultural activities have also worsened the water crisis as there has been a move towards more water-intensive crops. For example, fruits are being preferred over cereals. Furthermore, lake eutrophication which is stimulated by fertilizer run off, suspended solids from increased erosion after deforestation and stream flow modification to allow irrigation, have also impacted water supply (UNEP, 2006a).

According to a report prepared by the World Health Organization, the United Nations Children’s Fund, and the Water Supply and Sanitation Collaborative Council, only 47% of the rural population in Africa and 62% of the rural population in Latin America have access to safe drinking water. However, the biggest proportion of people without access to improved water supply is in Asia (See Figure 1), bringing the global total to over 1 billion people (WHO and UNICEF, 2000).

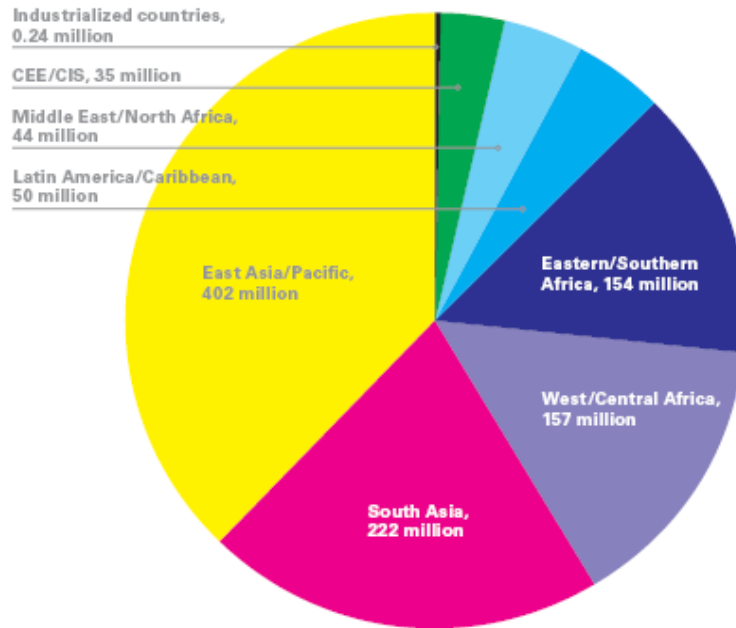


Figure 1. Regional Breakdown for Population Lacking Access to Safe Drinking Water (UNICEF, 2006)

The problem is even more critical in the area of sanitation since over 2.6 billion people lack access. Of this total, 2 billion are living in rural areas

(UNICEF, 2006). Once again, the highest proportion of people without access to basic sanitation is in Asia (see Figure 2).

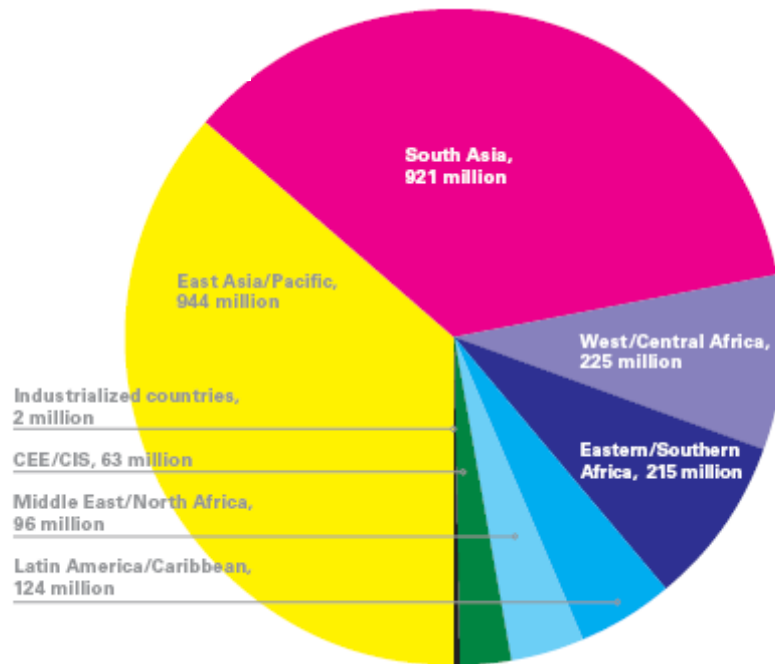


Figure 2. Regional Breakdown for Population Lacking Access to Basic Sanitation (UNICEF, 2006)

2.1.2 Future Predictions

Population projections estimate that the global population will stabilize around 2050 with the number totaling between 8 and 9.5 billion people. It is also estimated that most of this growth will take place in the developing world. Currently, developing countries account for over 81% of the total world population. This is an alarming situation when considering the trends that have been observed within the past century, which show that population has tripled while water usage has increased six-fold. It is also expected that water resources will be strained in localized areas as the population continues to migrate towards urban settings. By 2030, it is estimated that over 60% of the population will reside in cities (UNPD, 2004). Growing population and unplanned urbanization will lead to water shortages worldwide that will be concentrated mostly in Africa and Central America (See Figure 3).

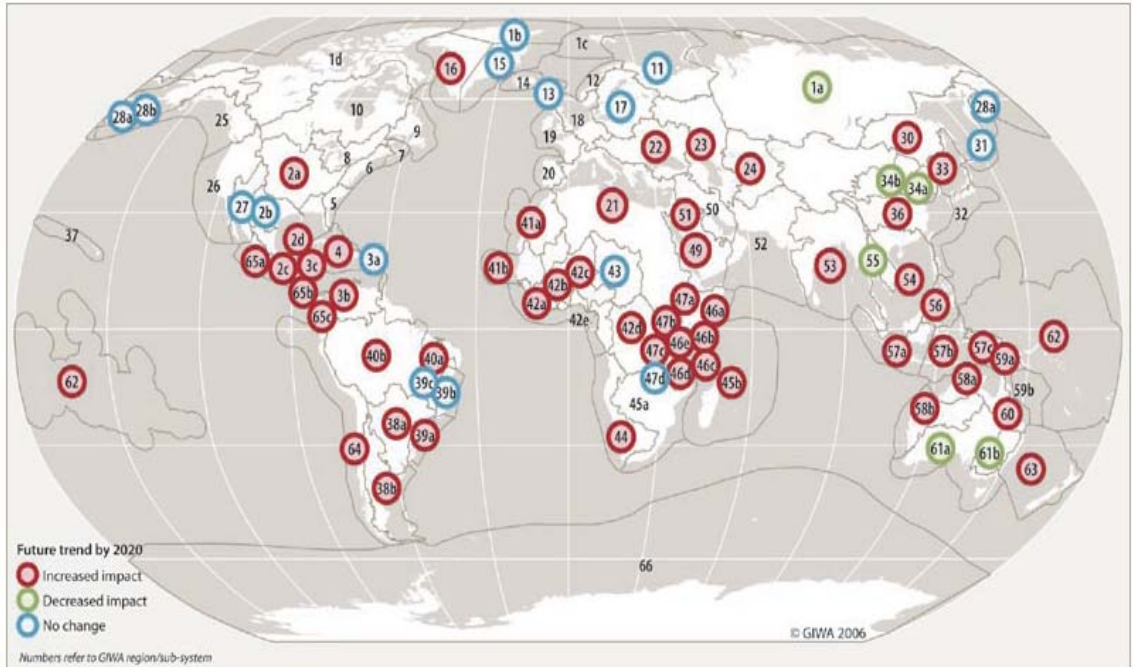


Figure 3. Future Environmental Trends of Freshwater Shortage (UNEP, 2006a)

2.1.3 The United Nation's Millennium Development Goals (MDGs)

The 2000 United Nations Millennium Summit, the largest gathering of heads of state or government to that date, addressed the challenges to be faced with the upcoming of a new century. In 2000, there were 1 billion people living in extreme poverty and lacking safe drinking water and proper nutrition (United Nations, 2005). As a result, the MDGs were established as a way to target specific areas that hinder the advancement of developing regions of the world.

The seventh goal in the series of eight is to ensure environmental sustainability. Under this MDG, there are three specific targets that are to be met by 2015 (United Nations, 2002). One of the targets is related to the reduction in the amount of slum dwellers and the improvement of their quality of life. The other two are related to sustainability and access to safe drinking water and basic sanitation. The MDGs specifically call for halving the population without access to safe drinking water and sanitation by 2015 (United Nations, 2005a).

However, access to safe drinking water and sanitation is directly related to each of the first seven goals adopted by the United Nations. As presented during the Japan Water Forum, the total contribution of water is significant for every goal. This total contribution includes improvement of water supply, improvement of sanitary facilities, diffusion of sanitary education, and measures to water disasters. Table 1 summarizes the estimates.

Table 1. Summary of Contribution of Water to MDGs

Goal	Total Contribution of Water
1. Eradicate extreme poverty and hunger	30%
2. Achieve universal primary education	30%
3. Promote gender equality and empower women	20%
4. Reduce child mortality	30%
5. Improve maternal health	45%
6. Combat HIV/AIDS, malaria, and other diseases	25%
7. Ensure environmental sustainability	100%

Despite the efforts to establish set objectives and deadlines, half of the developing countries' population were still lacking access to basic sanitation according to a report released by the United Nations in 2006. The actual number of people lacking sanitation is estimated to be 2.4 billion people due to population growth (UNICEF, 2006). It is estimated that the target is unlikely to be met by 2015. As far as access to safe drinking water, the target is likely to be met (See Figure 4). However, in both areas, there is great disparity between rural and urban settings. For example, in sub-Saharan Africa, people living in urban areas are twice as likely to have access to potable water than their rural counterparts (United Nations, 2006).

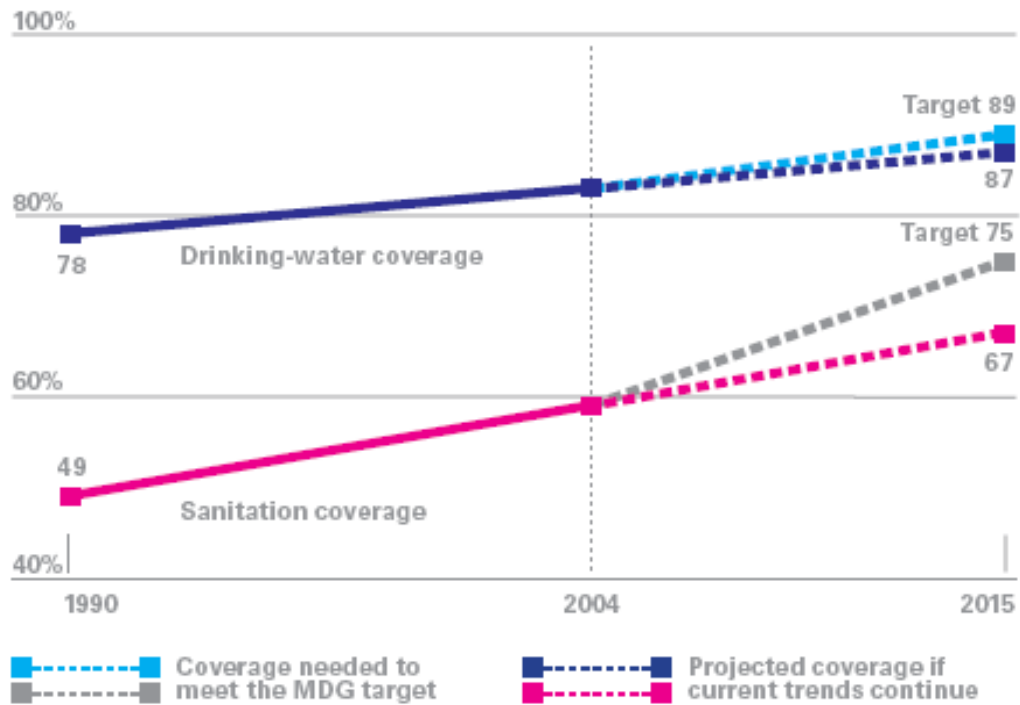


Figure 4. Global Trends Towards the MDG's Water and Sanitation Targets (UNICEF, 2006)

Since estimates indicate that the MDGs will not be met by 2015 if progress continues at the rate that was seen during the first five years, the United Nations has called 2005-2015 its Decade for Action. The Millennium Project, established in 2002 to provide guidelines for the fulfillment of the Millennium Development Goals, has made ten specific recommendations that aim to help meet the goals. Among these recommendations are minimizing pollution levels in surface waters and groundwater sources, investing in cost-effective and environmentally sustainable energy, and mobilizing science on a national scale to improve the use of scientific and indigenous knowledge (United Nations, 2005b).

Furthermore, the environmental sustainability task force implemented by the Millennium Project has gone on to state that many of the other MDGs are related to access to safe drinking water and sanitation. As an example, lack of access to potable water inhibits education since it is often children who are in charge of traveling to rivers or lakes to collect water for the daily

house chores. This is a time that could have been used for schooling if there was an on-site system that could satisfy the needs of the household.

2.2 Point-of-Use Treatment Systems as a Solution

On-site water treatment systems are those that are intended for use directly by the consumer and that do not require a centralized plant or a distribution system. These systems have been traditionally used by people in small rural communities but growing concerns with regards to the safety of drinking water have pushed for their use even in urban settings. However, point-of use technologies vary greatly in terms of the types of contaminants or pathogens they target. It is safe to say, however, that all on-site systems attempt to mimic one or more steps that are carried out in a centralized water treatment facility. The two steps that are most commonly used are coagulation and disinfection.

Although most systems share one or both of these major treatment steps, they differ significantly in the way they achieve their goal. The way a system works can be influenced by the social, geographic, and economic condition of their consumers. Therefore, industrialized and developing nations vary greatly in the types of on-site treatment alternatives they use.

2.1.1 Filters

Filters make use of different materials, including clay and sand, which act as a physical barrier for pathogens and contaminants in raw water. Often, the filter pore size will determine the type of particulates that can be removed, although it is possible for microorganisms like viruses to be rejected when agglomerating with large particles. Filtration is often coupled with disinfection in order to provide a residual protection against pathogens and subsequent recontamination.

Filtration with various materials has shown to be a promising technology. However, it is still necessary to understand that each community

has different needs that will influence whether or not a filter will be the optimum choice for water treatment.

Slow Sand Filters

These types of filters have been used since the 1800s to treat water. They operate by passing the water through 100 cm of fine sand at a rate that is slow enough for a layer of biofilm, termed *schmutzdecke*, to grow on the surface. The purpose of the biofilm is to remove pathogens and has been reported to be up to 99% effective. The main advantage of this type of system is that it requires little training and a low capital and maintenance cost. However, since the biofilm needs to be removed periodically, there needs to be a period during which the microorganisms are allowed to repopulate the surface of the sand. During this time, the filter does not provide adequate treatment. Furthermore, when the turbidity in the raw water exceeds 20 NTU, a pretreatment step must precede the slow sand filter (Burch and Thomas, 1997).

Sediment Filters with Iron Oxide

Sediment filters have been used for centuries for the treatment of drinking water since they mimic the way in which water is purified as it flows through different types of sediments. The filters are comprised of several layers, which include rocks and sand, and are arranged in decreasing order of void space. In recent times, it has been discovered that the addition of iron nails to the filters produces a more oxidized form, which can bind heavy metals like arsenic. However, evenly distributing the iron across the filter's layers has proven to be a challenge while implementing the technology as a point-of-use alternative has been difficult due to the low degree of control that can be established (McAllister, 2004).

Activated Carbon Filters

Activated carbon is made by passing water vapor, air, or gases containing carbon dioxide through a carbon substance at temperatures between 700-900°C. Through this process, the carbon atoms are separated forming a high surface area porous matrix that attracts both organic and inorganic compounds. Although many possible contaminants can be removed with activated carbon filters, these are not effective in removing bacteria and should not be used as a primary water treatment step (McAllister, 2004).

Ceramic Filters

Ceramic filters have been used in studies since the high porosity of the materials allows for an acceptable flux while providing a barrier for contaminants and particulates. Unlike point-of-use systems based on chlorine or solar disinfection, these filters can perform even if the source water has moderate turbidity and regardless of temperature or pH. However, they do not provide residual disinfection and the treated water is susceptible to further recontamination if not stored in containers that reduce contact with impure surfaces. In addition, there are doubts about their ability to remove viruses since these are too small to be removed by microfiltration. However, it is believed that these microorganisms can bind to bacteria and other larger particles and be removed at a higher rate than expected based on their size (Clasen *et al.*, 2004).

In order to enhance the performance of ceramic filters, the surfaces have been impregnated with a thin layer of colloidal silver. The colloidal silver is obtained when an electric charge is passed through solids silver suspended in water. The compound inactivates microorganisms by binding to the cell membrane and promoting cell lysis and death (McAllister, 2004). Although the release of the colloidal silver can be a health concern, samples collected after filtration have shown concentrations much lower than the World Health Organization's guideline of 0.1 mg/L (WHO, 1997).

Ceramic filters impregnated with colloidal silver have been manufactured in Nicaragua by a non-governmental organization called Potters for Peace (See Figures 5 and 6). The initial mix used consists of 60% pulverized clay and 40% screened sawdust which is mixed and then press-molded. The filters are then fired at 887°C, cooled, and tested to ensure a permeate flowrate between 1-2 liters/hour. Those filters that pass the initial screening are then coated with a mixture of 3.2% strength Microdyn colloidal silver and filtered water. After this process, the filters are ready for use (Lantagne, 2001).

Among the disadvantages of such filters is its inability to sufficiently remove viruses, chemicals, or hard metals. Furthermore, the production of the pots requires a kiln that can potentially compromise the air quality of the surrounding area while requiring excessive amounts of fuel (McAllister, 2004). The community also needs to be educated as to how to clean the filter so that decreased permeate flow rate does not become a reason to discard the filters (Lantagne, 2001).

This specific type of filter increased the dissolved oxygen concentration by 1.3 mg/L as a result of the dripping of the water after passing through. Turbidity was reduced by an average 83% while the pH increased as compared to the raw water due to the alkalinity dissolved from the ceramic. There was no reduction in conductivity, which suggests that the filter cannot reduce the concentration of total dissolved solids (Lantagne, 2001).

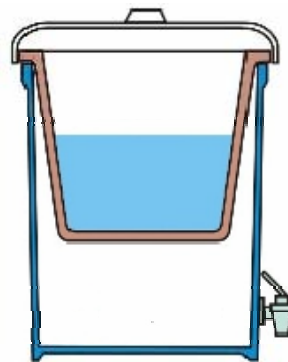


Figure 5. The Filtron Ceramic Pot (www.pottersforpeace.org)



Figure 6. The Filtron System by Potters for Peace (www.pottersforpeace.org)

For example, the Katadyn Ceradyn® candles, which have a nominal pore size of 0.2 μm , are impregnated with the metal for bacteriostasis. The filters can be used to treat up to 50,000 liters of water depending on the cleaning frequency, according to the manufacturers. The flux can be up to 1.5 liters/hour and is dependent on the turbidity of the raw water. However, field studies have shown that flux can be reduced to the point where users are not able to obtain enough water at all times. Results in a study in Bolivia show that 100% of the samples met the WHO guideline of less than 1 thermotolerant coliform (TTC) per 100 mL of water. Furthermore, the mean reduction of diarrhea prevalence during six months was 64% (Clasen *et al.*, 2004).

The cost of these ceramic filters has been shown to be around \$25 for a community in Bolivia. Assuming that 25 liters are treated per day, the operating cost is \$0.006 per day or 0.00025 per liter. Although this seems to be an affordable solution, the average price the users surveyed in the study would pay was \$9.25, which is well under the total cost of the filters (Clasen *et al.*, 2004).

Cloth Filters

Sari cloth has recently appeared in many articles, after studies were made in several villages in Bangladesh (Huq *et al.*, 1996; Bradbury, 2003; Colwell *et al.*, 2003). The studies analyzed how effective sari cloth could control the concentration of *Vibrio Cholerae* in drinking water. When eight layers of sari cloth were used to filter the water, cholera rates halved (Bradbury, 2003). However, four folds are recommended to reduce the probability of clogging and slow passage of water while guaranteeing adequate removal (Huq *et al.*, 1996).

Although viruses are too small to be filtered out by the fabric, research has shown that they attach to plankton that is too big to fit through the pores of the sari cloth and can therefore be removed. Experiments have shown that 99% of the *V. cholerae* cells attach to plankton or particulates. One of the dominant groups of the zooplankton community are copepods, which are found in both freshwater and saltwater (Huq *et al.*, 1996). Approximately 10^4 to 10^5 *Vibrio cholerae* viruses can attach to a single copepod (Colwell *et al.* 2003). This amount is enough to produce clinical cholera in an individual (Huq *et al.*, 1996). By simply folding the sari cloth, a filter with a pore size of approximately 20 μm is produced. This is enough to remove all zooplankton and most phytoplankton. Overall, cholera viruses could be reduced by half employing this technique (Colwell *et al.*, 2003). Although cloth filter is not a solution that addresses all the needs of a community when it comes to safe drinking water, it is an improvement.

2.2.2 Chemical Addition

Much of the research in the area of chemical addition for the treatment of water in developing countries has been focused on providing systems that provide steps similar to those found in a conventional water treatment plant in other parts of the world. Although alum and ferric salts have been proven in industrialized nations, many developing countries might lack access to such chemicals. Therefore, it is beneficial to explore the use of natural

coagulants or flocculants that can be locally available as well as those that have been proven to work in centralized water treatment plants.

2.2.2.1 Conventional Coagulants

Several types of systems in which chemicals are added to the water to be treated have been devised. Most of these systems are comprised of the addition of chemicals that are meant to coagulate the particulate matter that will then be settled. Disinfection normally follows this step, although in many cases disinfection has been the only water treatment utilized.

The World Health Organization has conducted studies in several parts of the world to establish the effectiveness of disinfection with chlorine. The participating families are supplied with a sodium hypochlorite solution that is produced locally and a narrow-mouth container for storage. This intervention has decreased the incidence of diarrhea in Guatemala by 44%, in Zambia by 48%, and in Uzbekistan by 68% (Rangel *et al.*, 2003). However, there are disadvantages to this type of approach like the ineffectiveness of chlorine against pathogens like *Cryptosporidium* and its ability to form disinfection by-products when the receiving water has a high content of organic matter. Currently in the United States and many other industrialized countries, the levels of disinfection by-products are being closely regulated since these compounds have been linked to cancer and other diseases after long-term exposure (Rangel *et al.*, 2003). Also, in many communities, the public refuses use a form of chlorine for disinfection because of the adverse effect on the water's taste and odor (Mintz *et al.*, 2001).

In industrialized nations, Chlor-Floc (CF) and iodine tablets are used in emergency situations. The 600 mg CF tablets provide flocculating agent and 8 mg/L of residual free chlorine for 1 liter of water if used at temperatures between 10-25°C. At temperature less than the specified range, two tablets are recommended for the same amount of water. The mixing time should be at least 1 minute and the contact time is specified between 12-20 minutes depending on the temperature. The use of a cloth filter is recommended for

these CF tablets to further reduce the turbidity and presence of microorganisms. The iodine tablets, on the other hand require a contact time of at least 35 minutes in order to provide 8 mg/L residual iodine (Powers *et al.*, 1994).

Systems that involve the addition of other chemicals to simulate the process that takes place at a conventional water treatment plant have also been used in field studies (Rangel *et al.*, 2003). The Center for Disease Control (CDC) and the Procter and Gamble Company have developed a system named Pur® Water Purifier. This system incorporates a coagulant (ferric sulphate), an alkaline agent, flocculation aids, and a chlorine-based disinfectant (calcium hypochlorite). It is provided in sachets that are used to treat 10 liters of water (Souter *et al.*, 2003; Crump *et al.*, 2004). The advantage of including a flocculation-coagulation step is that organic matter, heavy metals, and even large pathogens can be removed through the agglomeration of smaller particles forming larger ones (Rangel *et al.*, 2003). Therefore, this product is particularly useful when the source water is both highly contaminated and turbid (Crump *et al.*, 2004).

The process begins with the addition of the sachet to 10 liters of water which then has to be stirred for 30 seconds and then allowed to settle for 5 minutes. This stirring and settling process is repeated two more times (Souter *et al.*, 2003). After this, the water is ran through a 100% white cotton flannel filter and stored. Although there is chlorine residual that aids in preventing additional contamination, the storage vessel should have a narrow mouth and a spigot to avoid dipping contaminated containers in the clean water (Rangel *et al.*, 2003). The Pur® Water Purifier system provides a residual chlorine concentration between 2-3.5 mg/L depending on whether a low-dose or high-dose formulations are used.

The Pur® Water Purifier has been shown to provide a 4-log reduction for both poliovirus and rotavirus, an 8-log reduction for *E. coli*, and a 3-log reduction for *Cryptosporidium* oocysts. In addition, over 99% of the arsenic was removed. However, this data corresponds to laboratory trials which can

be significantly different from field data (Souter *et al.*, 2003). In field trials, the turbidity was reduced from an average of 19 NTU to 0.25 NTU with no value greater than 4 NTU. Arsenic levels were also reduced from an average level of 13 µg/L to under 0.3 µg/L. In addition, none of the 320 households used during the study had detectable levels of *E. coli* since all samples had less than 1 organism per 100 ml of water (Souter *et al.*, 2003).

This specific product outperformed another traditionally used coagulant, alum, in a study done in Kenya. Alum failed to reduce turbidity to a level below 5 NTU. However, it was more effective in the inactivation of *Vibrio cholerae* due to its ability to reduce the pH of the source water. Nevertheless, a sour taste was reported, which discouraged the public from using such chemical (Crump *et al.*, 2004).

2.2.2.2 Natural Coagulants

Natural coagulants are those derived from plants or animal material with little or no chemical processing. The main advantage to this type of coagulants is that they are environmentally friendly. They are also indigenous to many regions around the world, making local production possible while helping to reduce their cost.

Moringa oleifera

Moringa oleifera is a tree native to Northern India that has become widely grown throughout the tropics. The tree has been used not only as an aid in wastewater treatment, but has also been commercialized as a nutritional supplement.

Studies have shown that a COD removal greater than 50% can be obtained when using doses between 50-100 mg/L. When the *M. oleifera* is coupled with an alum dose of 10 mg/L, COD removal can increase up to 64%. However, this removal is mostly done during filtration since the flocs that are formed are strong but do not have good settling characteristics. Although the addition of alum will increase COD removal, it can also lead to a

greater filter head loss and almost three times the sludge production as compared to using just the natural coagulant.

Although this seed was studied for use in wastewater treatment, it has been used in water treatment as well (Bhuptawat *et al.*, 2006). In another study performed in Kenya, *M. oleifera* was used to treat surface water and yielded a turbidity removal of 50% on average when the raw water had turbidity ranging between 23-90 NTU. It was also shown that the optimum dose was 50 mg/L, which is comparable to that required for alum (Muyibi and Okuofu, 1995).

Prosopis juliflora

A study in Venezuela has employed a natural coagulant that is indigenous to the region called *Prosopis juliflora* (also known as mesquite bean). The studies used synthetic raw water containing potassium chloride (KCl), sodium bicarbonate (NaHCO₃), magnesium chloride (MgCl·6H₂O), and calcium carbonate (CaCO₃). The optimum dose was determined to be between 20 and 40 mg/L for raw water with turbidity of 30 NTU. The final turbidity was shown to be less than 5 NTU (Diaz *et al.*, 1999).

Cactus latifaria

Another natural coagulant used in the same study carried out in Venezuela employed another species called *Cactus latifaria*. The same synthetic raw water containing potassium chloride (KCl), sodium bicarbonate (NaHCO₃), magnesium chloride (MgCl·6H₂O), and calcium carbonate (CaCO₃) was used. It was concluded that a dose between 10 and 20 mg/L has been shown to be optimum for raw water with turbidity between 50 and 100 NTU and yields a final turbidity that is less than 10 NTU (Diaz *et al.*, 1999).

2.2.3 Solar Disinfection

Point-of-use solar heating, also called SODIS, is a technique in which water is simply poured in polyethylene terephthalate (PET) bottles and then

exposed to the direct sun light (Oates *et al.* 2003). In tropical and subtropical countries, the temperatures in these bottles can easily reach 45°C, which is the temperature above which thermal inactivation begins to take place (Mintz *et al.*, 2001). However, for adequate microbial inactivation 3-5 hours of solar radiation above 500 W/m² are needed (Oates *et al.*, 2003).

In a study conducted in Kenya, samples that were heavily contaminated with *Escherichia coli* were disinfected after 7 hours of exposure to direct sun light with a maximum water temperature of 55°C (Joyce *et al.*, 1996). This could be a method that could be implemented for particularly small communities, but it has the disadvantage that there is a long wait time period and that it can not be applied in environments where the water will not exceed the thermal inactivation temperature. Another disadvantage associated with SODIS is that it is ineffective in disinfecting water with a measured turbidity greater than 30 NTU (Oates *et al.*, 2003). Furthermore, SODIS has been shown to be ineffective against chemical contaminants present in the source water (SANDEC, 2003).

In order to improve the performance of SODIS systems, a reactor that utilizes a titanium dioxide (TiO₂) coating has been devised and named a solar photocatalytic disinfector (SPC-DIS). In this disinfector, the photocatalyst is isolated onto an acetate coated flexible insert that is then placed inside a borosilicate glass bottle. This type of system achieves bacterial inactivation below the detection limit in 75% of the time and requires 75% of the cumulative UV dose, as compared to conventional PET containers that do not contain the TiO₂ insert. In addition, it has been calculated that 550 J are required per liter of raw water to yield each 90% (1-log) reduction for bacteria. It is thought that the accelerated inactivation of microorganisms occurs through an advanced oxidative process that takes place within the SPC-DIS system. In addition to inactivating bacteria, the system is also capable of photodegrading isopropanol, which suggests the possibility that it might also degrade other organic compounds like pesticides (Duffy *et al.*, 2004).

2.2.4 Ultraviolet Disinfection

Point-of-use ultraviolet (UV) disinfection has been an alternative technology that has been developed recently. Studies indicate that wavelengths ranging from 240 to 280 nanometers (nm) can effectively kill microorganisms. This is done by damaging their DNA and preventing the microorganisms from replicating. Nevertheless, there are two drawbacks that need to be considered: the absence of residual disinfection (much like point-of-use boiling) and the need for extremely clear water. Often, water will need to be pre-treated before the UV light treatment phase can be initiated in order to remove larger organisms and particulates (Gadgil *et al.*, 1997).

UV systems incorporate a more advanced technology that might not be available in developing nations. Therefore, it is common to see it applied in point-of-use systems in industrialized countries as a final barrier for pathogens and contaminants. These systems are often coupled with carbon filters in order to reduce the suspended solids and the UV absorptivity. In a specific study, the carbon filter was shown to remove *Giardia lamblia* cysts and *Cryptosporidium parvum* oocysts while achieving a 3-log reduction. The UV disinfection portion achieved a 4-log reduction for poliovirus, hepatitis A, and rotavirus even when the flowrate was set to 150% of the water treatment capacity suggested by the manufacturer (Abbaszadegan *et al.*, 1997).

2.3 Chitin and Chitosan

In recent years, much attention has been given to the use of so called biopolymers for the removal of contaminants in water. The process through which biopolymers adsorb compounds is known as biosorption. Among its advantages are minimal cost of materials, easiness of operation, and selectivity over the alkaline metals (Baran *et al.*, 2006).

Chitin is a naturally-abundant biopolymer that can be extracted from the exoskeleton of insects, fungi, and crustaceans (Gupta and Kumar, 2000). It is postulated that it is the cell wall component that allows metal

biosorption (Benguella and Benaissa, 2002). Therefore, it has been found to have sorption properties that make it an ideal material for use specifically in water contaminated with heavy metals.

Furthermore, chitin can be chemically treated (through deacetylation for example) to generate derivatives, one of which is known as chitosan. This compound has also been used for adsorption of heavy metals because it can also provide binding sites along its structure. The deacetylation of chitin to form chitosan can occur to different extents and there is currently a lack of consistency as to exactly what degree of deacetylation will form chitosan. Therefore, the term chitosan is loosely used in literature, as will be the case in this document.

2.3.1 Chemical Composition and Properties

Chemically, chitin is a high-molecular weight linear polymer of *N*-acetyl-D-glucosamine known as *N*-acetyl-2-amino-2-deoxy-D-glucopyranose (Gupta and Kumar, 2000). It can also be thought of as a polysaccharide with (1-4)-2-acetamido-2-deoxy-D-glucose units that can be deacetylated (Lee *et al.*, 1997). The units are linked by β -D (1 \rightarrow 4) bonds.

Chitin is the second most abundant polymer in nature, after cellulose (Zhou *et al.*, 2004). The compound is quite similar to cellulose not only in its insolubility, but also in its low chemical reactivity. However, it contains a higher percent of nitrogen (6.89%) which makes it a useful chelating agent (Gupta and Kumar, 2000). In addition, its acetamido groups are non-specific chelators that can form hydrogen bonds with heavy metals, making them useful as adsorbents for this type of application. It has also been suggested that the amine nitrogen on each chitin monomer serves as the active site for ion coordination for metals (Lee *et al.*, 1997).

Another interesting characteristic of chitin is that it is a highly basic polysaccharide, unlike other polysaccharides that tend to be either neutral or acidic. Although it shares its hydrophobicity with cellulose, it is also highly insoluble in most organic solvents.

Chitin carries one amino group per glucose ring (See Figure 7), which allows for the availability of electron pairs for coordination. Consequently, it behaves as a Lewis base. The surface area of chitin has been found to be insignificant, indicating that solid chitin is practically nonporous (Benguella and Benaissa, 2002).

Physically, chitin is white, hard, and inelastic. SEM photographs (see Figure 8) have revealed that the compound is made of several thin sheets of material that are loosely bound together (Benguella and Benaissa, 2002).

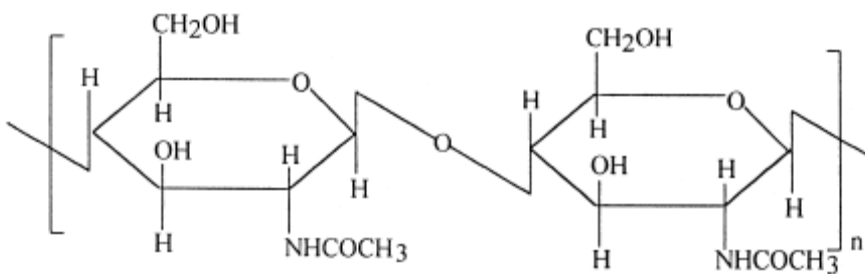


Figure 7. Chemical Structure of Chitin (Gupta and Kumar, 2000)

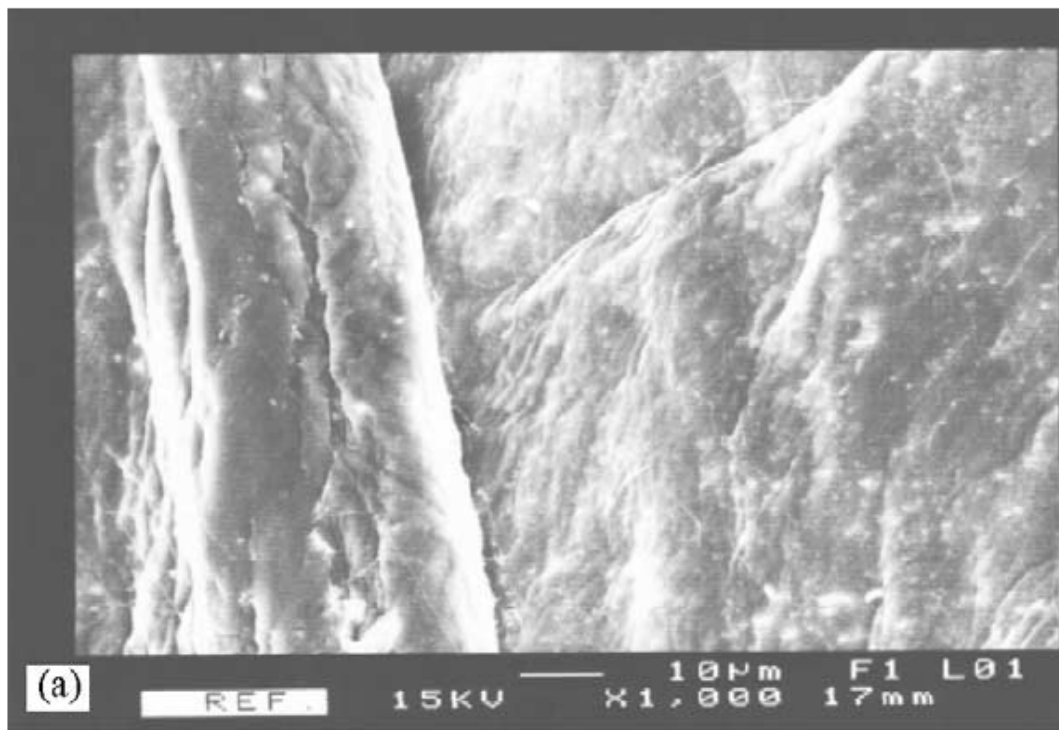


Figure 8. SEM Image of Chitin (Benguella and Benaissa, 2002)

Chitosan, which is formed through the *N*-deacetylation of chitin (See Figure 9), is soluble in very dilute acids like acetic acid and formic acid (Gupta and Kumar, 2000). This presents a problem since heavy metals cannot be easily removed from chitosan for regeneration by using acids. In this respect, chitin's resistance to acids makes it more favorable for successive regeneration for extended use (Zhou *et al.*, 2004). It has been categorized as a hydrophilic, natural cationic polymer that is an effective ion exchanger. This is explained by the presence of a large number of amino groups that can increase the adsorption capacity of chitosan with respect to that of chitin (Evans *et al.*, 2002).

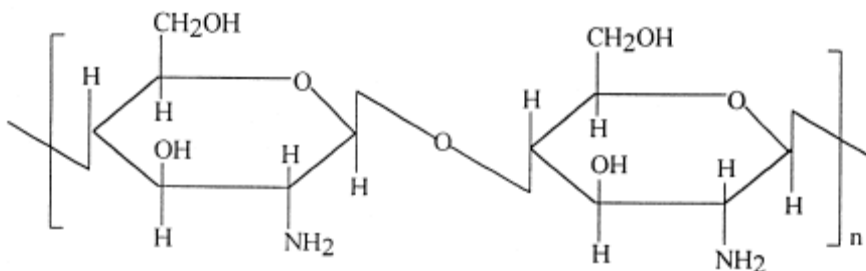


Figure 9. Chemical Structure of Chitosan (Gupta and Kumar, 2000)

Chitosan can be easily obtained in a powder form, while chitin is available in flakes as well. This is the only apparent physical difference between the two, although SEM images reveal that their structures are quite different (See Figure 10).

The processing method used for chitosan will ultimately affect its performance in the removal of heavy metals since it will influence its degree of deacetylation. This will in turn affect the pore distribution and accessibility within the solid matrix (Evans *et al.*, 2002).

The molecular weight of both chitin and chitosan has been determined by light scattering. For chitin, the molecular weight has been averaged (by weight) to be between 1.03×10^6 and 2.5×10^6 kDa. In the case of chitosan, the estimation tends to be vaguer since the degree of deacetylation will

influence the molecular weight of chitosan, but for 70% deacetylation the value will be between 1×10^5 and 5×10^5 kDa (Gupta and Kumar, 2000).

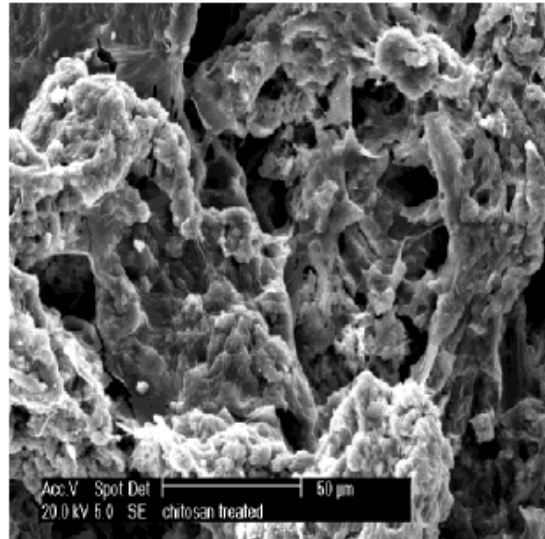


Figure 10. SEM Image of Chitosan (Rae and Gibb, 2003)

Chitin and chitosan are amino sugars whose characteristics make them efficient ligands. They are able to form stable complexes with metal ions. Chitosan can chelate metal ions in the following order: $\text{Cr}^{3+} < \text{Co}^{2+} < \text{Pb}^{2+} < \text{Mn}^{2+} \ll \text{Cd}^{2+} < \text{Ag}^+ < \text{Ni}^{2+} < \text{Fe}^{3+} < \text{Cu}^{2+} < \text{Hg}^{2+}$ (Burke *et al.*, 2002).

2.3.2 Sources and Applications

Chitin can be easily extracted from crab or shrimp shells as well as fungal mycelia. The first step is to remove proteins and dissolve the high amounts of calcium carbonate in a strong acid like hydrochloric acid. Then, the resulting chitin is deacetylated through alkali treatment (involving sodium hydroxide in most of the cases). This treatment occurs at 120°C and lasts between one and three hours. The chitosan that is produced is 70% deacetylated. There is currently a lack of consistency as to what degree of deacetylation is standard, so there are many types of chitosan available commercially (Gupta and Kumar, 2000).

For the production of 1 kilogram of 70% deacetylated chitosan, 6.3 kilograms of hydrochloric acid and 1.8 kilograms of sodium hydroxide are required. This makes the product economically feasible when considering that chitin accounts for about 23% of shrimp shell waste (Gupta and Kumar, 2000).

Both chitin and chitosan have been used in several applications like photography, cosmetics, artificial skin, food and nutrition, ophthalmology, chromatography, paper finishing, solid-state batteries, and drug delivery systems (Gupta and Kumar, 2000).

2.3.3 Adsorption Mechanism

The uptake of heavy metals by chitin and chitosan is thought to involve both pore diffusion through the solid matrix and adsorption. These two processes are affected by physicochemical conditions like pH, particle size, and agitation rate (Evans *et al.*, 2002). Specifically, it has been suggested that there are three phases that describe the diffusive transport of solutes in chitosan: 1) mass transfer of solute from the bulk solution to the particle surface across the boundary layer (also known as external diffusion), 2) intraparticle diffusion, and 3) adsorption at the interior sites. It has been found that either the first or second steps will be rate-limiting (McKay *et al.*, 1989). Of these two, it is thought that more often it is the intraparticle diffusion that will limit the rate.

External diffusion occurs through the boundary layer from the bulk solution to the surface of a solid. Within the boundary layer, diffusive mass transfer dominates over the turbulence encountered within the surrounding fluid. In cases where there are high mixing rates, external diffusion will not be the rate limiting step. However, when the mixing intensity is too low, the external diffusion rate is diminished creating a boundary layer resistance (Evans *et al.*, 2002).

A distinction as far as size and shape of the adsorbent should also be made. In the case of chitosan for the removal of iron (III), powder provides

the best results followed by microspheres and flakes. Although powder and microspheres can have comparable sizes, this last arrangement is cross linked through the amine groups available on the chain. This reduces the number of free amine groups, decreasing the number of binding sites (Burke *et al.*, 2002).

Since both chitin and chitosan have a small internal surface area and porosity, the removal of heavy metals is likely to occur through chemisorption onto the active surfaces of the polymer. With different types of heavy metals, the recurring observation has been that a small particle size increases removal. This suggests that the heavy metals adsorb onto the external surface and do not penetrate the particles (Rae and Gibb, 2003).

Although the adsorption mechanisms for both chitin and chitosan appear to be very similar for a variety of heavy metals, some will be adsorbed better by one of the two biopolymers.

2.4 Membrane Systems

Semi-permeable membranes were first introduced in 1927 as a means to filter water by the German company Sartorius. Ever since, the technology has become a favorite alternative for many industries due to the high quality of the effluent that can be obtained.

2.4.1 Overview

The basic principle in the use of semi-permeable membranes is that a driving force (pressure or suction) is applied across the membrane so that certain substances can be separated. Although this process was once considered only for desalination, it is currently used to remove bacteria and other microorganisms, particulate material, and organic material for both water and wastewater treatment (Lahlou, 2000).

The two basic objectives when using membrane systems are to increase rejection and increase flux. These challenges can be addressed in different ways. Smaller pore sizes in the membrane, for example, will most

than likely increase the rejection. As a result, contaminants that have a smaller molecular weight will be separated from the effluent. This will increase the water quality of the permeate. However, as membranes with reduced pore sizes are developed and implemented, it is also necessary to understand that these membranes may also require higher pressure levels to operate. This results in higher energy consumption. Therefore, in the case of developing countries, systems utilizing microfiltration or ultrafiltration might be more viable because they have lower pressure requirements.

2.4.2 Membrane Background Concepts

One of the most important concepts regarding membrane filtration is transmembrane pressure (TMP). TMP is the difference in pressure from the feed to the filtrate across a membrane barrier (USEPA, 2003). Therefore, the maximum allowable TMP across a membrane is an important factor since there can be greater operational flexibility associated with a higher allowable TMP. A factor affecting the TMP is fouling, which is the gradual accumulation of contaminants on the membrane surface (USEPA, 2003). This inhibits the passage of water and decreases productivity. The result is an increase in TMP and an associated flux decrease.

Flux is defined by the USEPA 2003 Membrane Filtration Guidance Manual as the throughput of a pressure-driven membrane filtration system expressed as flow of permeate per unit of membrane area. The following equation illustrates how flux is calculated:

$$J = \frac{Q_p}{A_m} \quad (1)$$

In this case Q_p represents the permeate flow rate and A_m represents the total membrane area. Flux will be reported in LMH (liters per meter squared per hour) throughout this document.

Another quantity that can be used to characterize the behavior of a membrane is specific flux (M). This gives an indication of the permeability of the material and can be calculated using the following equation:

$$M = \frac{J}{TMP} \quad (2)$$

Specific flux is then normalized for flux as well as for pressure to determine the changes in productivity specifically attributable to fouling (USEPA, 2003).

A factor affecting both TMP and flux is temperature. For example, if operation is to be kept constant and the temperature is lowered, the TMP needs to be higher to account for the increase in the viscosity of water (USEPA, 2003).

Another commonly calculated parameter is resistance of the membrane, which measures of opposition to the driving force that inhibits the flow of permeate across the membrane. Temperature will influence resistance since the viscosity of the water will increase will decreasing temperature. The following empirical equation (USEPA, 2003) may be used to approximate the value of viscosity at a given temperature:

$$\mu_T = 1.784 - (0.0575 \cdot T) + (0.0011 \cdot T^2) - (10^{-5} \cdot T^3) \quad (3)$$

In this case, dynamic viscosity has units of centipoises (cp) and temperature is in degrees Celsius.

Once the values for viscosity are obtained, total resistance can be calculated using the following equation (USEPA, 2003):

$$R_T = \frac{TMP}{\mu_T \cdot J} \quad (4)$$

This equation is used to calculate total resistance (R_T). Total resistance is the sum of the membrane's intrinsic resistance (R_M), which is calculated using clean water as the feed, and resistance due to fouling (R_F). Concentration polarization will also contribute to resistance and will be a function of operational parameters and physical properties (R_G). This type of model is called the resistance in series model. The following equation is often used to describe it (Cheryan, 1998):

$$R_T = R_M + R_F + R_G \quad (5)$$

2.4.3 Membrane Fouling

One of the most widely recognized problems that membrane filtration systems have is fouling, which consequently decreases permeability. Fouling is the gradual accumulation of contaminants on the membrane surface, inhibiting the passage of water and decreasing productivity (USEPA, 2003). This disadvantage has major repercussions in the cost and feasibility of a project since it affects the membrane permeation flux, the membrane area, and the washing conditions among other design factors (Kaiya *et al.*, 2000). There are several ways in which a membrane may fail due to fouling and there is yet much to research in order to understand the mechanisms that drive this phenomenon.

There are two basic types of fouling: reversible and irreversible. A type of reversible fouling is called the cake layer, which forms dynamically during the operation of the system as the deposition of particles blocks pores over the course of a cycle (See Figure 11). It increases removal efficiency for some pathogens and bacteria. Even in MF systems, virus removal has been reported and attributed to cake layer formation. However, it can also increase the TMP and cause the system to fail because of extreme reversible or even irreversible fouling (USEPA 2003).

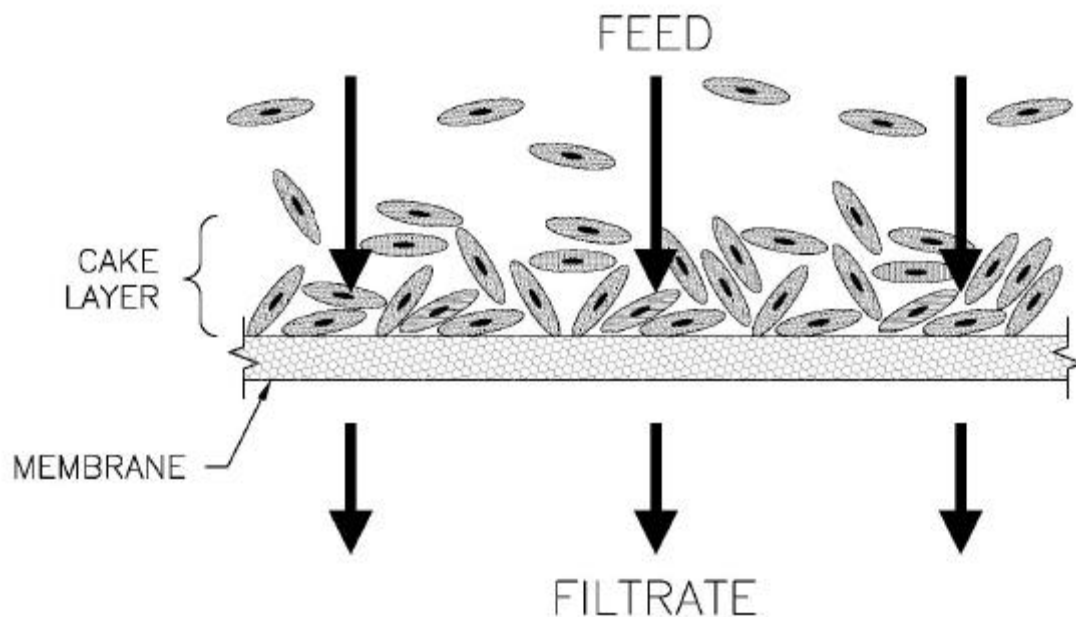


Figure 11. Deposition Mode Operation (USEPA, 2003)

The cake layer is an example of reversible fouling because it can be easily removed from the membrane by means of a physical process, like backwashing. Irreversible fouling, on the other hand, occurs when dissolved matter is adsorbed into the membrane pores and only chemical cleaning will restore the membrane to its operating conditions (Chang *et al.*, 2002). However, some researchers consider as irreversible fouling only that which eventually leads to failure and replacement of the membrane.

The flux selection is directly linked to the rate at which material is deposited on the membrane. For example, at a high flux, colloidal aggregation and heterogeneous deposits are observed. Then, rapid reversible fouling occurs through the formation and compaction of a cake layer. In addition, irreversible fouling also takes place more rapidly at higher flux rates (Chang *et al.*, 2002). The term critical flux has been defined as the pressure below which little or no fouling can be observed (Field *et al.*, 1995). The general hypothesis for MF, for example, is that to start there is a critical flux below which a flux decline does not occur. Operation below this level is called subcritical flux operation and it is expected to yield little or no fouling. In

addition, recent studies have shown that long periods of operation at very low fouling rates (close to the critical flux value) can produce an increase in transmembrane pressure that is initially slow and then becomes rapid and disastrous (Chang *et al.*, 2002). Determining the critical flux of a system is important because there can be significant technical and economical benefits. For example, the cost of cleaning the membrane can be reduced and its life span can be increased (Vigneswaran *et al.*, 2000)

There are several factors that influence the nature and extent of fouling on a membrane. The biomass characteristics are important because higher concentrations of extracellular polymeric substances (EPS) will contribute to fouling, discussed later on in this paper. Operating conditions are also an important factor that influences membrane fouling. The crossflow affects the mass transport of particles away from the membrane surface, thus affecting the resultant cake layer thickness. Interestingly, with small particles the crossflow velocity is directly proportional; while for larger particles, the crossflow velocity has no or even a negative effect on the permeate flux. Aeration is an operating condition that actually suppresses fouling by inducing a crossflow with air that removes the fouling layer. It also maintains the solids in suspension and scours the membrane surface (Chang *et al.*, 2002).

In drinking water systems, for example, organic matter leads to fouling by surface adsorption, which creates the cake layer, and by adsorption in the pores of the membrane (Kaiya *et al.*, 2000). In a study conducted by Vigneswaran *et al.* (2000), the critical flux of a system increased along with particle size. This implied that smaller particles have a higher tendency towards deposition on the membrane even if the flux is low. Therefore, a higher critical flux can be obtained for samples with larger particles.

On the other hand, wastewater treatment has to deal with other compounds that can cause fouling. Suspended solids, colloids, and dissolved molecules have relative contributions to the membrane filtration resistance of

65%, 30%, and 5%, respectively (DeFrance *et al.*, 2000). More specifically, membrane fouling has been found to be caused by extracellular polymeric substances (EPS). These substances can be produced by excretion of microorganisms, hydrolysis, and adsorption of organic matter from wastewater. EPS are composed of proteins, carbohydrates, humic substances and DNA and RNA (Chakrit *et al.*, 2005). Furthermore, in a study conducted at a municipal wastewater reclamation facility, it was determined that more than likely fouling had been caused by the insertion of organic macromolecules (like EPS) and small bacteria that would enter the membrane pores and build up on the pore walls. The cross sectional area of the membrane pores would then be reduced increasing resistance to filtration (Xing *et al.*, 2002).

There are several pretreatment and operation practices that can significantly reduce the rate of fouling, prolonging the life of the membrane. As a pretreatment practice, it is a common first step to screen the wastewater in order to remove any large suspended solids that might clog not only the membrane, but also the feed tube. In addition, powdered activated carbon (PAC) is added to increase permeability by improving the hydraulic properties of the cake. PAC addition also reduces the cake thickness by increasing the biosolids back-transport velocity (Chang *et al.*, 2002).

Reversible fouling can be corrected with one of two processes: backwashing or chemical cleaning. Backwashing is intended to be an intermittent process during which permeate is pumped back through the membrane into the feed channel to remove deposition. However, backwashing is not always effective, especially when pore blocking occurs. This is commonly due to inorganic materials, like calcite and struvite, which precipitate on the membrane surface and pore walls (Chang *et al.*, 2002). Chemical cleaning is performed with different compounds that target different areas. Permeate rinsing, for example, washes away the loosely attached deposition. Alkaline cleaning, which commonly uses NaClO, is used

to breach the matrix of organic macromolecules inside the membrane pores. Finally, acid cleaning, which commonly uses HNO_3 , dissociates metal ions from the organic matrix, breaks the matrix into pieces, and swaps away the fragmented foulants from the pores (Xing *et al.*, 2002). Chemical cleaning should in theory completely recover the membrane flux. The main disadvantage to using this process is that toxic or contaminated water is produced because most of the cleaning agents are caustic or contain detergents or oxidizing agents (Baker and Dudley, 1998).

2.4.4 Membrane Module Configurations

2.4.4.1 Hollow-Fiber Modules

These membranes are comprised of long, narrow, hollow tubes that might be made of a variety of polymers (See Figure 12). The fibers are commonly arranged vertically and potted in a resin on both ends (See Figure 13). These cassettes are then inserted into a pressure vessel. Fibers can also be arranged horizontally, although these systems are less common (USEPA, 2003).

There are two operational modes: inside-out and outside-in. In the first mode, the feed water flows through the center of the fiber and the pressure difference drives clean water radially through the membrane. The filtrate can then be collected on the outside. One disadvantage of this mode is that the potential for the center of the fiber to clog is very high. The outside-in mode, on the other hand, operates the opposite way. The cassettes are submerged in the feed water and the pressure difference drives the permeate to the center of the hollow fiber. With this type of operation, there is less potential for clogging and the available surface area for filtration is increased (USEPA, 2003).

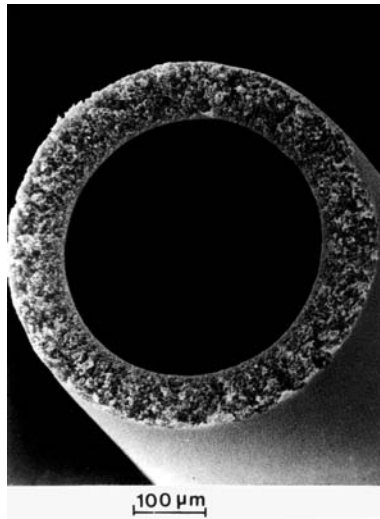


Figure 12. SEM Image of Hollow Fiber Membrane (Fraunhofer Institute, 2006)

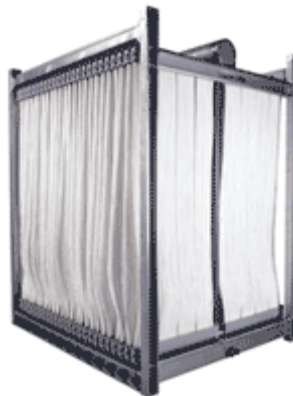


Figure 13. ZeeWeed® 500 Ultrafiltration Membrane (Zenon, 2007)

2.4.4.2 Spiral-Wound Modules

These modules are mostly used for nanofiltration and reverse osmosis applications to remove dissolved solids. Spiral-wound membranes consist of a set of two flat membrane sheets separated by a fabric spacer that is the permeate carrier. This is called a leaf. Three edges are then glued and the fourth edge is sealed around the perforated central tube. Each leaf is separated by a layer of plastic mesh, called a spacer, which serves as the feed water channel (See Figure 14). Each membrane element consists of

about 20 leaves that are then placed inside a tubular pressure vessel (USEPA, 2003; Baker, 2004).

The feed water enters the spacer channels at the end of the element in a parallel path to the central tube. The feed water then flows axially across the membrane surface, where the permeate is separated. This permeate flows spirally inward through the carrier and towards the central tube. The feed water that is not filtered continues to flow across the membrane surface and, as it flows, it becomes more concentrated. This concentrate exits the element on the opposite side from where the feed water entered (USEPA, 2003).

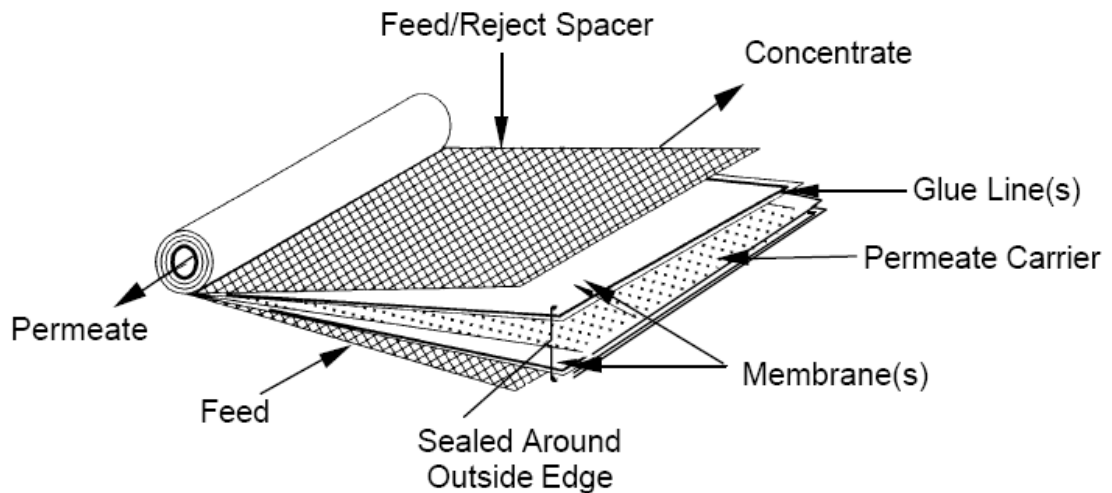


Figure 14. Spiral-Wound Membrane Module (USEPA, 2003)

2.4.4.3 Membrane Cartridges

These cartridges consist of a flat membrane sheet, feed spacers, and product spacers that are layered between two end plates (See Figure 15). The feed water flows parallel to the surface and the pressure difference drives the permeate across the membrane. The concentrate exits the module through the opposite way the feed water entered. The permeate flows through channels and is collected in a central manifold (Baker, 2004).

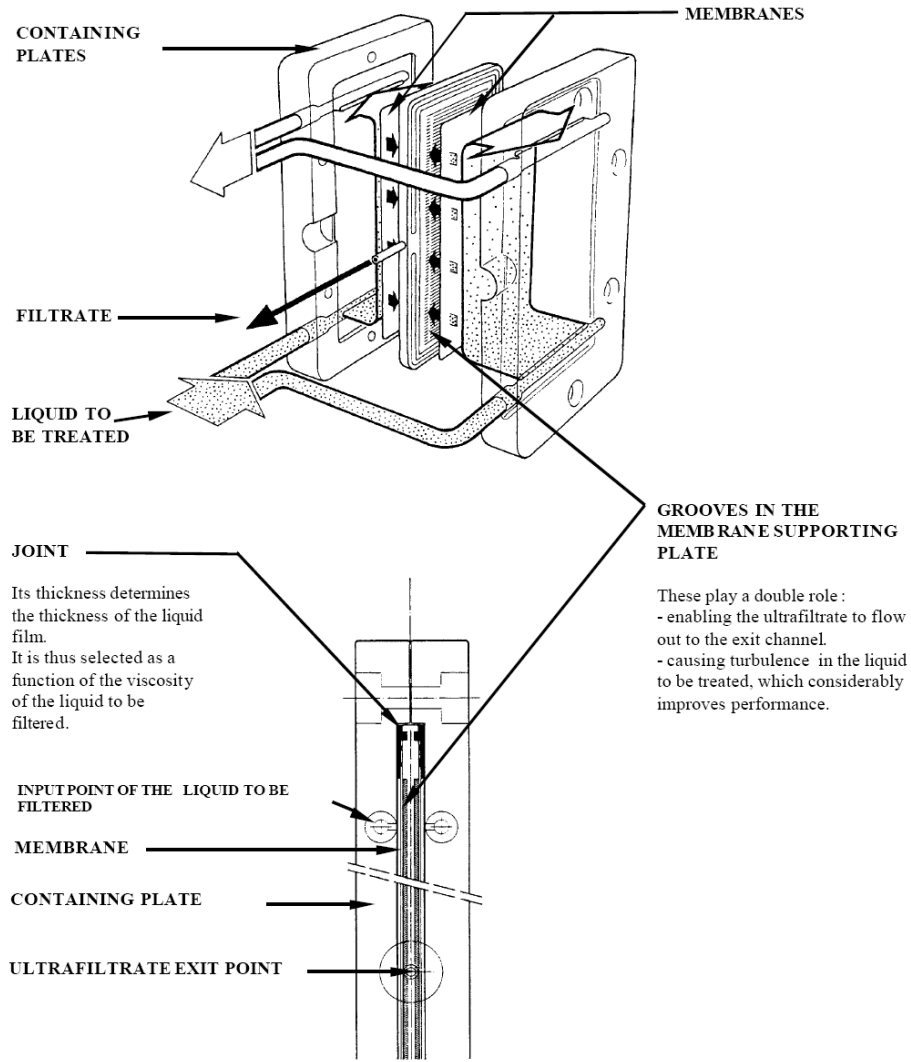


Figure 15. Plate and Frame Module (RHODIA Orelis, 2001)

2.4.5 Types of Membrane Filtration

Each type of membrane filtration basically differs in the pore size and its retention capabilities (See Figure 16). However, specific characteristics of the system, such as pH, temperature of the incoming stream, dissolved-solids content, molecular weight of the dissolved species, and the nature and loading of any suspended material will ultimately determine operational parameters (WE&T, 2003).

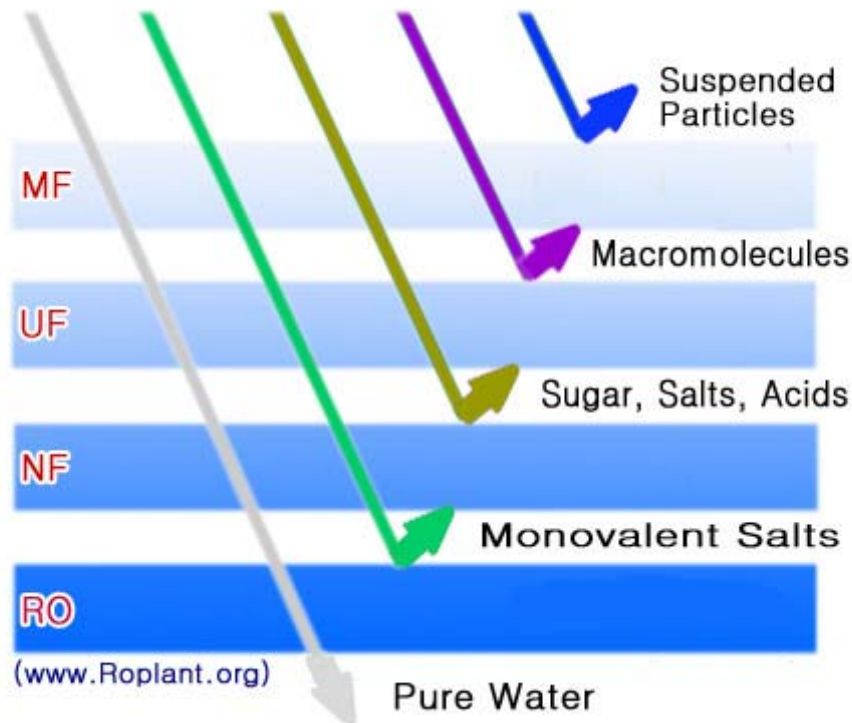


Figure 16. Simplified Filtration Spectrum (Roplant, 2006)

2.4.5.1 Microfiltration

Microfiltration (MF) is the separation process that employs membranes with a pore size of approximately 0.03 to 10 microns, a molecular weight cutoff (MWCO) greater than 100,000 daltons, and a feedwater operating pressure of approximately 100 to 400 kPa (15 to 60 psi). Some of the materials that can be removed through MF are sand, silt, clays, *Giardia*, *Lambia* and *Cryptosporidium* cysts, algae, and some bacterial species. Although MF is not an absolute barrier for viruses, it can be used in combination with disinfection to control these microorganisms (Lahlou, 2000).

There are several options when it comes to choosing the type of MF membrane: spiral wound, tubular, and hollow capillary fiber. Spiral wound membranes are not commonly used because of the flat-sheet nature of the membrane, which makes it difficult to keep the surface clean. Contrary to spiral wound membranes, tubular and hollow capillary fiber membranes allow

for backwashing. This process becomes extremely important when membrane fouling occurs. Backwashing for MF membranes can be done using liquid and gas and it is commonly fully automatic. When backwashing does not correct the fouling problem, chemical cleaning is required (Lahlou, 2000).

One of the most important advantages of MF is that there is little pretreatment needed for hollow-fiber systems when particles and microorganisms are the target contaminants. However, prefilters are commonly used to remove large particles that may plug the inlet.

Coagulants or powdered activated carbon (PAC) can also be added to enhance the removal of viruses and dissolved organic matter and to prevent fouling (Lahlou, 2000). MF membranes are generally made of ceramic and polymeric materials and are used not only to separate wastewater effluents, but also for processing liquids in the food, beverage, pharmaceutical, and chemical industries (WE&T, 2003).

2.4.5.2 Ultrafiltration

Ultrafiltration (UF) uses a pore size of approximately 0.002 to 0.1 microns, a MWCO of approximately 10,000 to 100,000 daltons, and an operating pressure between 200 and 700 kPa (30 and 100 psi). UF can be used to remove pathogens (although it is not an absolute barrier for viruses), higher-molecular-weight disinfection byproducts, and humic material (Lahlou, 2000).

UF is a pressure-driven process which allows most ionic inorganic species to pass through, while retaining discrete particulate matter and nonionic and ionic organic species. Due to the chemical and hydrolytic stability of UF membranes, pretreatment requirements are low. For example, pH needs to be adjusted to decrease the solubility of the species in the feed so that it may be filtered out. In addition, like in most systems, water containing dissolved iron and manganese ions need to go through an adequate oxidation process prior to the membrane step in order to avoid

precipitation during the backwash procedure. Another pretreatment practice that is not necessary but can be useful is to use PAC or coagulants to remove natural organic matter (NOM) and reduce the surface of membrane needed (Lahlou, 2000).

There are many advantages to using a UF system that include low chemical consumption (coagulants flocculants, disinfectants, and pH adjustment), good and constant quality of the treated water in terms of particle and microbial removal, process compactness, and simple automation (Lahlou, 2000). Besides being used in water and wastewater treatment facilities, UF is also used to separate flows as diverse effluent streams from dye houses and pulp and paper mills. In addition, in the dairy industry, it aids in protein concentration and juice clarification (WE&T, 2003). UF membranes are quite popular in Europe, where they take up a third of the market (Spear, 2004).

2.4.5.3 Nanofiltration

Nanofiltration (NF) membranes have a pore size of approximately 0.001 microns, a MWCO of 1,000 to 100,000 daltons, and an operation pressure of about 600 kPa (90 psi) but it can be as high as 1,000 kPa (150 psi). NF can remove almost all cysts, bacteria, viruses, and humic materials (Lahlou, 2000). It has also been used to remove color and human organic matter (WE&T, 2003). However, there are also some complications that arise from the ability of UF membranes to remove smaller species, like decrease in alkalinity and possible precipitation of ions associated with hardness. Since there is a decrease in alkalinity, the product water can be corrosive. Hardness ions can precipitate on the membrane, making pretreatment necessary.

It has been said that NF reduces the gap between UF and reverse osmosis (RO). However, the energy required for NF is still so high that it has hindered its advancement as a treatment alternative (Lahlou, 2000). It has also been observed that these membranes operate according to the

principles of diffusion, instead of sieving like MF and UF membranes. NF membranes have been used in applications related to demineralization and concentration (WE&T, 2003).

2.4.5.4 Reverse Osmosis

Reverse osmosis (RO) can effectively remove all inorganic contaminants, radium, natural organic substances, pesticides, cysts, bacteria, and viruses. However, this effectiveness is limited by high pressures that exceed 1400 kPa (200 psi) for operation (WE&T, 2003).

However, there are many advantages to RO systems besides their ability to remove nearly all contaminants and dissolved non-ions. For example, they are relatively independent of flow and the total dissolved solids (TDS) level. This makes them suitable to small systems that have a high variation of water demand. Their operational simplicity and automation are also favorable for their use in small systems (Lahlou, 2000).

On the other hand, there are several limitations to RO as well. There are high capital and operating costs, which can be even higher due to extensive pretreatment. Also, the membranes are more prone to fouling by salts, contaminants, and biofilms as compared to other alternatives. Perhaps one of the most evident disadvantages to RO systems is the production of a brine solution which contains all the contaminants at elevated concentrations (Lahlou, 2000). The cost of the disposal of the brine solution (which can represent up to 30% of the water to be treated) can be costly depending on the quantity and degree of treatment required.

RO systems have been desalination operations and in the food industry for concentrating fruit juices, teas, coffee, and sugar solutions (WE&T, 2003).

2.4.6 Membrane Materials

Traditionally, filter media have been made of cotton, wood, and cellulose. However, the growing demand for finer degrees of filtration has driven the industry to explore alternative materials (Sutherland, 2003).

Ceramic Membranes

Ceramic membranes have been developed by several companies for UF and MF. They are commonly made from aluminum, titanium, or silica oxides. The main advantages of this type of membrane are that they are chemically inert and resist high temperatures, which make them suitable for food, pharmaceutical, and biotechnology applications (Baker, 2004). Ceramic membranes have not been widely used for water treatment since they are considerably more expensive (USEPA, 2003).

Polymeric Membranes

One of the most widely used materials is polymers. Thermoplastic polymers, for example, are even available in extruded fiber or filament form that can be arranged to suit the filter medium. A lot of the focus has been turned to nanofibers, which are being manufactured from organic polymers (like nylon, polyester, aramid, and acrylic), biological polymers (like protein and collagen), and even activated carbon. Each of these materials is then used to make membranes that yield very high porosities (Sutherland, 2003).

Some of the polymers that have been used to manufacture membranes include cellulose acetate (CA), polyvinyl fluoride (PVDF), polyacrylonitrile (PAN), polypropylene (PP), polysulfone (PS), and polyethersulfone (PES). Each of these materials has different properties in terms of surface charge, hydrophobicity, pH and oxidant tolerance, strength, and flexibility. For example, CA membranes are susceptible to degradation and must be operated within a narrow pH range (between 4 and 8). However, they are resistant to chlorine doses of 0.5 mg/L or less. On the other hand, polyamide membranes can operate in a wider pH range but have an extremely limited tolerance to strong oxidants like chlorine (USEPA, 2003).

Non-woven media has attracted a lot of attention lately and it has changed greatly in the past 40 years. For example, needlefelts have been used for different types of filters, as their tensile strength and fiber shedding

characteristics have improved. Surface treatments, like resin and thermal bonding, can now be applied to improve the fiber retention properties. The most recent development has been in the so-called spun bonded materials, which are excellent for fine filtration (Sutherland, 2003).

2.4.7 Potential for Water Reuse

One of the advantages of membrane technology is the potential for water reuse. Therefore, many scientists have suggested that this technology could be the answer to attaining water sustainability. It has been proven that effluent from membrane bioreactors can be directly reused since bacteria, some viruses, and organic and inorganic constituents are removed (Torrens, 2001). Although public perception will be an obstacle in promoting this type of practice, it is a step in the right direction to encourage water reuse for activities such as irrigation. In this way, developing countries with scarce water resources move towards sustainability.

2.4.8 Limitations for Use in Developing Countries

Membrane filtration is a novel technology that is still being developed in industrialized nations. Its application in developing countries would require substantial modifications that could address the needs of the populations.

One of the major concerns of applying membrane technologies in developing countries is that there is a lack of technical expertise. Although membrane processes have become more efficient, they are still complex and require a certain level of understanding for their operation. Not only is it necessary to have trained personnel that can run the system daily, but it is also convenient to have a technician on hand that can troubleshoot any problems that may arise.

Although decades of research have removed major hurdles in the development of better membrane materials, membranes continue to be fragile and require careful handling. Furthermore, membrane usage continues to involve some type of pretreatment that would add a level of

complexity to the system. It is then necessary to develop new membrane materials that require less care and are more durable.

Another cost concern arises when considering that the household needs to have access to electricity in order to power a pump that creates enough pressure or vacuum on the system. Electrical costs are often the highest maintenance expenditure in water and wastewater treatment plants. Since in many areas having electricity is considered a luxury, energy-intensive alternatives do not provide a sustainable solution.

Perhaps the most significant limitation for the use of traditional membranes in developing countries is cost. This cost not only includes the initial capital cost, but also the cost of maintenance and operation. For example, a household membrane PVDF element, capable of delivering up to 0.75 gallons per minute, can cost between \$390 and \$1600 (Applied Membranes, 2003). Membrane production is a complex process that requires machinery and technical expertise. Since neither of these is present in many areas, local production becomes impossible. This would then require that the material is imported, increasing the cost even more. This is not desirable because in the event of the need for a replacement, the system might be inoperable for several days.

In order to provide relevant membrane technologies as a solution to the problem of access to safe drinking water and basic sanitation in developing countries, it is necessary to modify the systems that are often used in developed areas of the world. This creates a need for a technology that requires minor technical expertise, is durable and resistant, operates with low energy requirements, is affordable, and utilizes a material that is widely available and can potentially be manufactured locally.

2.5 The Scrap Tire Problem

It is estimated that 240 million tires were discarded in the United States in 1990. However, only 17% of the tires are recovered as rubber or heat while the rest are landfilled, piled, or disposed of illegally (USEPA,

1991). As a result, scrap tires have become a solids waste management challenge since they account for 12% of all solid waste produced (Conesa *et al.*, 2004).

2.5.1 Chemical Composition and Properties

The main components of tires are vulcanized rubber, rubberized fabric that contains reinforced textile cords, steel, or fabric belts, and steel-wire reinforced rubber heads.

The most widely used type of synthetic rubber used in the industry is styrene-butadiene rubber (SBR), although natural rubber is still used in tires. The structure of the tire consists of a complex elastomer consisting of block copolymers of styrene and butadiene monomers (Rangarajan *et al.*, 1999). Natural rubber must be vulcanized in order to be useful since in its natural state it is soft and tacky. The rubber undergoes a chemical process in which cross links between the *cis*-polyisoprene chains are formed (See Figure 17), making the rubber much harder (Solomons and Fryhle, 2004).

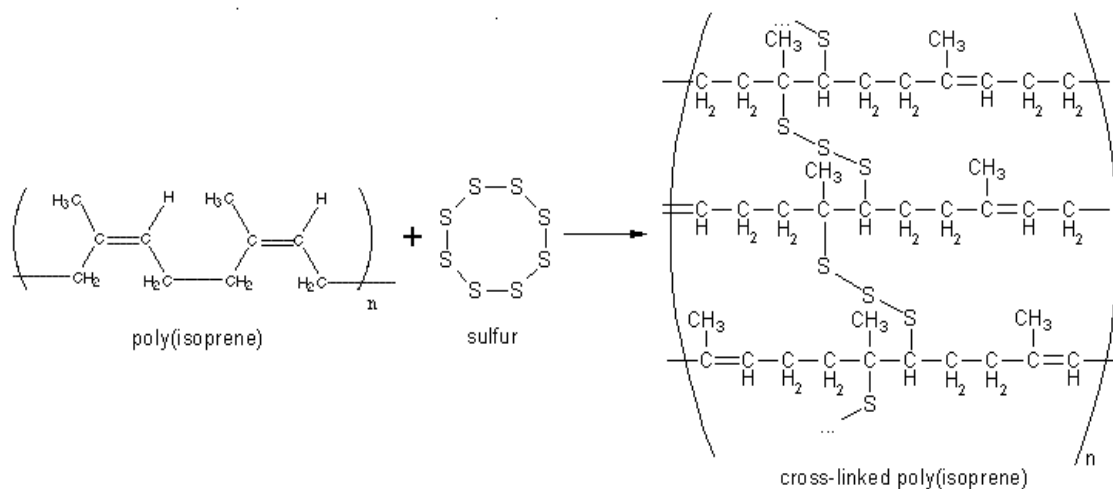


Figure 17. Vulcanization with Sulfur as Curing Agent (Affordable Housing Institute, 2007)

The cure agents are typically either sulfur or peroxide, with the former one being the most commonly used. The process makes the rubber harder, durable, and more resistant to chemical degradation. Some of the other

elements added to tires are dry pigments or fillers (like carbon black and silica), softeners and extenders, plasticizers, activators, accelerators and retarders, protectants, flame retardants, and structural materials (USDOE, 2000).

Carbon black (CAS 1333-86-4) is almost pure elemental carbon in the form of colloidal particles that is formed during the incomplete combustion of hydrocarbons. This material is in the top 50 industrial chemicals manufactured worldwide, based on annual tonnage (ICBA, 2004). Carbon black is added because it strengthens the rubber and gives it resistance to abrasion. It is by mass the largest amount of additive in tire rubber (Snoeyink and Weber, 1967). Parameters such as nitrogen sorption surface area (typically 150 m²/g), adsorption of dibutyl phthalate (typically greater than 120ml/100g), and particle diameter (typically 40-80 μm) have been measured and proved to be similar to the values for activated carbon (USDOE, 2000). The main difference between carbon black and activated carbon is that the former one has less internal surface area (Snoeyink and Weber, 1967). As a result, carbon black is said to have between 1.1% and 4.4% the sorption capacity of granular activated carbon (Kim *et al.*, 1997).

Although it might seem as if the similarities between carbon black and activated carbon would explain the sorption ability of scrap tire material, this is not the case. A study by Kim *et al.* (1997) showed that carbon black only has 20-60% the sorption capacity of ground tire. Based on this study, it has been suggested that carbon black does not seem to play a significant role in the sorption of organic compounds onto tire rubber.

2.5.2 Annual Waste Tire Generation Estimates

Finding data regarding waste tire generation in developing countries is a challenge since the disposal of this material is not widely regulated. However, data does exist for industrialized nations. For example, the estimated annual waste tire generation in the state of California alone is 40.2 million (CIWMB, 2007). For the United States, the annual estimate during

2005 was 299 million waste tires (RMA, 2006). This estimate does not include retreaded tires or used tires that were exported.

2.5.3 Methods for Scrap Tire Disposal

Scrap tires can be disposed of in many ways, including landfilling and stockpiling, recycling, and energy recovery. It is a common mistake to consider the use of scrap tires as recycling. For example, tire-derived fuel is not recycling because there is no end-product. It is, however, considered an energy recovery activity (RMA, 2006).

Figure 18 shows the different markets for scrap tire disposal in the United States during 2005.

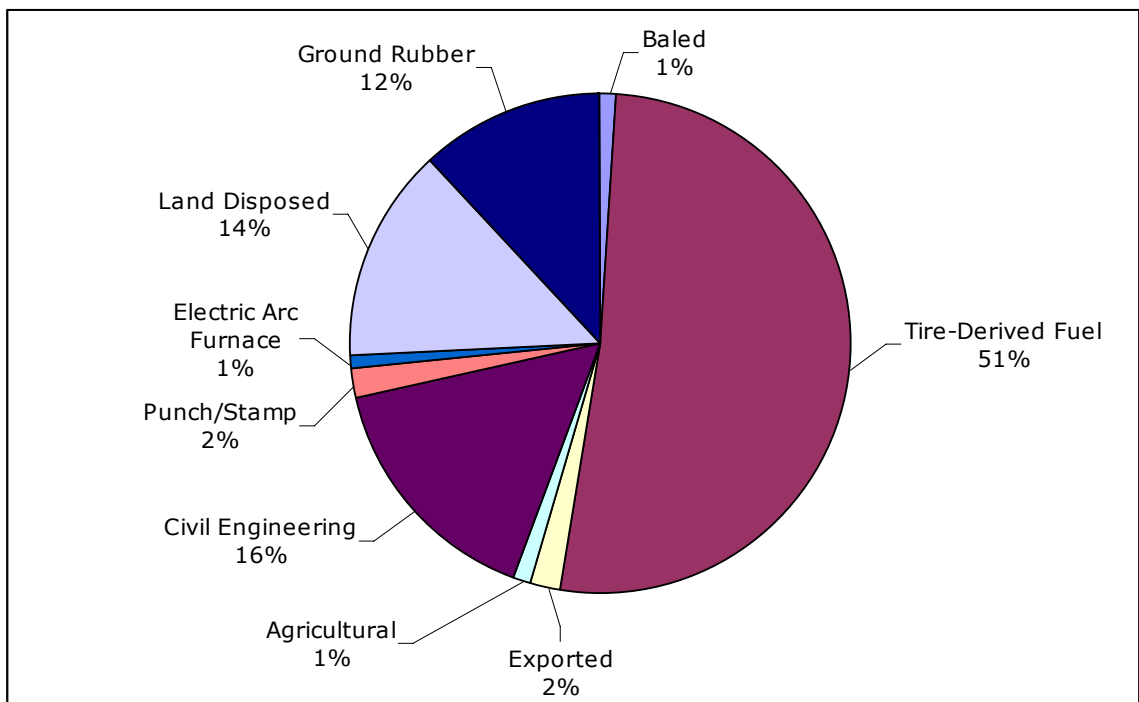


Figure 18. Scrap Tire Disposition in the U.S. in 2005 (Adapted from RMA, 2006)

2.5.3.1 Landfilling and Stockpiling

Landfilling tires is not an efficient or sustainable way of disposal because of the large volume requirements due to the tires' shape and relatively incompressible nature. Also, the scrap tires become a perfect

environment for the reproduction of rodents (USDOE, 2000). The only advantage of this type of disposal is that there are no processing costs involved. However, regulations in many states are becoming more stringent in this matter.

Stockpiling is a dangerous situation because they can be a breeding ground for mosquitoes. This is due to their shape and impermeability, which enables water to be retained within the tires. In addition, stockpiling also poses a threat as a fire hazard. Tires have a calorific value of 37,600 kJ/kg (14,000 BTU/lb) while coal has a calorific value of only 27,200 kJ/kg (12,000 BTU/lb). Tires are also mostly void space, with this fraction being around 75%. These two characteristics make it difficult to extinguish the fire with water or cut the oxygen supply (USDOE, 2000).

Scrap tire fires are a threat not only to human health and animal and plant life, but are also expensive to clean up. The cost of a scrap tire fire in Everett, Washington in the 1980s was 3.3 million dollars (Liu *et al.*, 1998).

2.5.3.2 Recycling for Energy Generation

Although scrap tires constitute about 12% of all solid waste, their size, shape, and physicochemical nature are obstacles for their recycling (Conesa *et al.*, 2004). Reprocessing scrap tires becomes complicated because of the additives and stabilizers that are added to improve the performance of the tires (Wojtowowicz and Serio, 1996).

Several options for recycling have been considered in order to take advantage of the high calorific value of tires. Some of these processes include combustion, pyrolysis, and irradiation.

Combustion

The use of tire-derived fuel has increased during the past decade due to the soaring energy prices, which have motivated industries to use alternative fuels. Combustion of tires is used to supplement coal and other

fuels in cement kilns, the pulp and paper industry, industrial boilers, and utility boilers (RMA, 2006).

For cement kilns, tire-derived fuel must be used in facilities where the demand is low since the alternative fuel cannot exceed 30% of the total; otherwise, the cement's curing process is affected. An advantage in this specific application is that the tires can be whole or processed. A reason for using whole tires is that they are cheaper and that their shape can provide an easier way to feed and weigh them (USDOE, 2000). However, using tire chips also helps promote the recycling of steel components for other industries. The main disadvantage for using whole tires is that these have a lower heating value (RMA, 2006). Although the use of tire-derived fuel has increased in recent years, concerns regarding the potential emissions and the lack of research on their effect on human health continue to emerge (USDOE, 2000).

Pyrolysis

During pyrolysis (also known as destructive distillation, thermal depolymerization, thermal cracking, coking, and carbonization), the tires are thermally degraded into smaller and less complex molecules. This is a complicated process since rubber is a poor thermal conductor and consequently requires large amounts of energy as compared to other materials. There are three main products: pyrolytic char, oil, and gas. Pyrolytic char may contain carbon black, ash, clay fillers, sulfur, zinc oxide, calcium and magnesium carbonates, and silicates. Pyrolytic oils may contain both heavy and light oils, as well as toluene and benzene. Finally, pyrolytic gases are composed of paraffins, olefins, and non-condensed light oils. These are not expected to have a high impact on air pollution because they are burnt as fuel, which decomposes the pyrolytic gas into water, carbon dioxide and monoxide, sulfur dioxide, and nitrogen oxides (if complete combustion is assumed). However, volatile organic compounds and particulates may be

emitted through leaks. Approximations for these fugitive emissions have not yet been estimated (USDOE, 2000).

2.5.3.3 Destruction Using Microwaves

When tires are irradiated with microwaves, the product is a material that can then be compressed into a fine powder while allowing the metal parts to be recovered. However, a gray gas, whose composition has not yet been analyzed, is also produced. This represents a health concern since the irradiation of scarp tires could potentially produce toxic fumes (USDOE, 2000). Even if this concern were to be ignored, this alternative is energy intensive as does not provide a sustainable solution to the problem.

2.5.3.4 Recycling for Ecological Applications

Because of the similarities found between carbon black and activated carbon (a material commonly used as an adsorbent), researchers have been considering the possibility of using scrap tires for removal of contaminants in water. Nonpolar organic compounds like benzene, toluene, and tetrachloroethylene are attracted to other nonpolar materials, like the SBR found in tires (Edil *et al.*, 2004). Several studies have agreed that waste tires have the ability to remove heavy metals, hydrogen sulfide, and organic compounds (Kim *et al.*, 1997; Kershaw *et al.*, 1997; Meng *et al.*, 1998; Shin *et al.*, 1999; Rangarajan *et al.*, 1999; Edil *et al.*, 2004; Alam *et al.*, 2004).

2.5.3.4.1 Sorption: Organic Compounds

The process of sorption of organic molecules by solids can be further subdivided into two different processes: adsorption and absorption. During adsorption, the substance attaches itself to the surface of the solid without diffusion. The process of absorption, on the other hand, involves the interpenetration of the solute into the sorbent phase (Kershaw *et al.*, 1997).

Particle Size

If sorption of organic compounds takes place only on the surface of the rubber, the effect of particle size can be an important factor. However, analyses have shown that partition coefficients of different sized particles are not significantly dissimilar. This clearly indicates that the sorption of organic compounds onto ground tires is not dependent upon the external surface of the tires. Perhaps a more important factor is the location within the tire from which the granules are made. For example, it has been shown that there is a significant difference in partition coefficients between granules of the sidewall and tread parts of the tire. This occurs because different polymers are used for each of these parts. As a result, tire chips (which contain other tire components like steel wire and fabrics) will have less sorption capacity than tire granules (Kim *et al.*, 1997).

Cross-linking

In an experiment done by Rangarajan *et al.* (1999), pure SBR completely dissolved in organic solvents like TCE and octane. However, crosslinked SBR and tires merely swelled in the presence of the solvents. This proved that cross-linking is an important characteristic that will preserve the mechanical integrity of a good sorbent. The nature of the solvent is also an important characteristic because its polarity is directly related to the amount that is sorbed. For example, alcohols will sorb less than TCE because of their hydrophilicity and hydrogen bonding that enables them to have a higher preference for water. During the same study, the desorption kinetics were also studied in order to establish how feasible it was to remove the solvent from the rubber for regeneration purposes. The results indicated that regeneration of the tire elements by desorption of pure organics could be accomplished fairly easily even recovering the solvent (Rangarajan *et al.*, 1999).

Octanol-Water Partitioning Coefficient

Data has been found to support the hypothesis that organic chemicals will have an affinity to bind to ground tire rubber (Gunasekara *et al.*, 2000). Another important finding is that the partition coefficients of organic compounds onto tire rubber can be related to the octanol-water partitioning coefficients (K_{ow}). This is useful because these last values can easily be found in literature for many substances. It has been observed that the logarithmic values of the tire partition coefficients are directly proportional to the octanol-water partition coefficients. The diffusion coefficient, on the other hand, does not appear to have a simple relationship to physical and chemical properties like molecular weight or size (Kim *et al.*, 1997).

2.5.3.4.2 Sorption: Inorganic Compounds

A study by Kim *et al.* (1997) tested for the competition between organic and inorganic compounds because these last ones have also been known to sorb onto rubber. However, it was found that the mechanism through which organic compounds are sorbed onto the tire material is different from the one used by the inorganic compounds (Kim *et al.*, 1997). For mercury, it is thought that there is a reaction that involves different compounds found in tires like sulfur, carbon black, or zinc (Gunasekara *et al.*, 2000). Rowley *et al.* (1984) tried to explain this mechanism and identified it as an ion-exchange type of reaction involving primarily the exchange of zinc (II). Although the adsorption of mercury onto tire rubber has been shown to be a slow process (taking days for rubber as compared to hours for metal hydroxides), the technique is effective if the pH is kept in an acidic to neutral range (Meng *et al.*, 1998).

2.5.3.4.3 Ballast Water Treatment

Crumb rubber has been investigated as an alternative treatment option for ballast water because of the advantages it exhibits as compared to typical filter media. These advantages include its elasticity and light weight,

higher filtration rates, lower head loss, longer filtration run time, and better effluent quality. These improved characteristics are associated with the low density of rubber, which allows for much lower backwash water rates than common media like sand or anthracite. Furthermore, pilot test results show that crumb rubber filtration can reduce up to 70% of phytoplankton and 45% of zooplankton (Tang *et al.*, 2006).

2.5.3.4.4 Constructed Wetlands

The main issue with the use of crumb rubber for this application has been its potential for degradation due to oxidation, heat, light, and mechanical conditions. However, none of these problems were encountered in pilot studies in wetlands so the stability of the tire chips is not questioned. Tire chips are thought to be an alternative for gravel in constructed wetlands because they have a bulk porosity of approximately 54%, as compared to only 32% for gravel. A higher value for porosity results in a longer detention time for the wastewater, which allows for more treatment. Furthermore, it appears that constructed wetlands filled with tire rubber chips can perform as well as those filled with gravel as far as removal of BOD₅, TSS, VSS, NH₄, and fecal coliforms. Although tire chip performance is similar to that of gravel, their cost and ease of transportation make this type of media good alternative (Richter and Weaver, 2003).

2.5.3.4.5 Landfill Leachate Treatment

Scrap tires are used for different purposes in landfills. These include using them in cap closures, as permeable backfill in gas venting systems, as material for daily cover, as permeable aggregate for leachate collection, and in operational layers.

A study investigated the use of tire chips as a drainage layer for the leachate collection system of a landfill. The study showed that when the tire chips were used, the level of volatile organic compounds was much lower

than when gravel was used due to the sorption onto the polymeric material (Edil *et al.*, 2004).

2.5.3.4.6 Septic System Drain Fields

Although tire-derived aggregate has not been approved for this type of use in every state, its popularity has increased over the past years. Part of its popularity is that it has a lower density as compared to traditional materials, making it more affordable in terms of required labor. Contrary to using stone, the recycled aggregate provides a much higher void volume. A disadvantage is that the pieces must have uniform size for this application, which implies further processing (RMA, 2006).

2.5.3.5 Recycling for Engineering Applications

2.5.3.5.1 Roadways

Crumb rubber provides key characteristics that make it an ideal material for roadway construction like light weight, low earth pressure, good thermal insulation, better dampening for properties for running vehicles, and good drainage properties. However, there are concerns related to fires with this kind of application (Adhikari *et al.*, 2000).

Shredded waste tires have been used to reinforce sand to provide higher shear strength. This is particularly useful for highway fills (Foose *et al.*, 1996). Increased durability and fatigue resistance are other characteristics that recycled rubber provides (Adhikari *et al.*, 2000).

2.5.3.5.2 Embankments

Although the use of tire chips for embankments had become widely acceptable, about a decade ago this practice began to be questioned. As with roadways, the risk of fires due to exothermic reactions was a concern (Adhikari *et al.*, 2000). However, sand-rubber mixtures were found to inhibit these exothermic reactions and consequently began opening a new market

for this recycled material. This solution was simple and provided virtually a material that is virtually incompressible and does not cause cracking or erosion (Yoon *et al.*, 2006).

2.5.4 Ground Rubber Applications

The use of ground rubber for different types of applications is a cycle of demand and sustainability. This cycle typically undergoes seven phases: introduction, incubation, acceptance, increased demand, market saturation, gradual decrease, and stasis. This behavior was seen with playground applications and is currently being seen with sports turf applications. It has then been suggested that crumb rubber producers need to constantly seek the next target market (RMA, 2006). The markets that currently account for most of the ground rubber applications in the United States are shown in Figure 19. It has been suggested that of all the current markets available for ground rubber, molded and extruded products have the greatest potential for expansion due to the variety of applications (RMA, 2006).

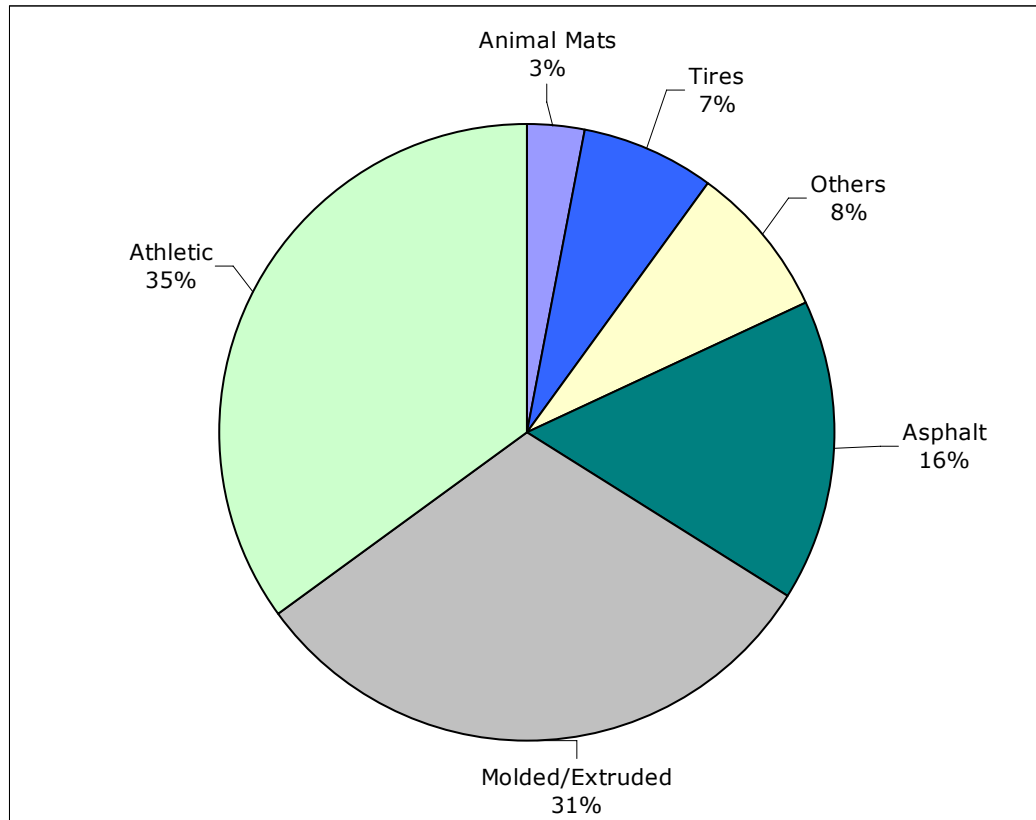


Figure 19. U.S. Ground Rubber Market Distribution in 2005 (Adapted from RMA, 2006)

2.5.4.1 Sports Turf

The main disadvantage of this application is that it requires that all metal parts are removed from the tires. However, the product provides many advantages. For example, there have been problems associated with heavy foot traffic that can be reduced with the use of recycled rubber. Among these are inhibition of plant growth and impact-related injuries for athletes. Pilot studies have indicated that the use of crumb rubber can significantly reduce soil hardness and water content in non-compacted field tests (Groenevelt and Grunthal, 1998). Another study proved that nitrate leaching could be significantly reduced with the use of rubber, although the method of nitrate mitigation remained unclear. There were no reported adverse effects on turf grass establishment, density, quality, or color (Lisi *et al.*, 2004). Although the concentration of zinc has been observed as a disadvantage, the levels are

not so high that they produce toxicity in turf grass (Groenevelt and Grunthal, 1998). It has been suggested that adding crumb rubber beneath sand-based root zones can be implemented along with other proven methods to reduce nitrogen contamination of water bodies (Lisi *et al.*, 2004).

2.5.4.2 Molded and Extruded Products

Ground scrap tire can be combined with an adhesive material, such as urethane or epoxy, to manufacture a variety of molded and extruded products. These products include carpet underlay, flooring material, dock bumpers, patio floor material, railroad crossing blocks, and roof walkway pads (RMA, 2006).

Ground rubber can also be combined with other polymers to fabricate injection-molded and extruded products, like soaker hoses for irrigation. Aside from the sports turf market, it is thought that the molded and extruded rubber product market has the greatest potential to expand. This is due to the high quality and relatively competitive prices of the products. However, there is a lack of publicly available information and knowledge on the methods to compound recycled rubber with other polymers (RMA, 2006).

A widely commercially-available extruded product manufactured using recycled scrap tire rubber is soaker hoses used for irrigation. This method utilizes drip irrigation in order to make the process more efficient by eliminating losses due to direct evaporation and wind. The soaker hoses are made of porous rubber and a binder, allowing for water to seep once pressure is applied. However, the market for this specific product is restricted since its applications are limited.

2.6 Problem Identification

Many regions of the world face a crisis that involves lack of access to safe drinking water and basic sanitation. In most cases, these areas are impaired by reduced financial resources and scarce technical expertise. For

this reason, it is essential that new technologies address these issues in a sustainable manner to provide long-term solutions.

Membrane filtration provides many advantages for its application, but such systems require modifications that make them more suitable for developing areas. In an effort to provide a new membrane filtration system that is aimed at helping such regions in their fight to establish safe drinking water and sanitation, several requirements were identified. The goal is then to design a technology that is applicable in these regions, which has been termed *ECOL-Mem*. Each of the letters of the abbreviation *ECOL* stand for a characteristic that is required.

The letter *E* stands for “environmentally-friendly”. The goal is to use a material that has been recycled in order to provide a second use in the life cycle of a product. Since solid waste management has become a concern in many parts of the world, utilizing a waste material would help solve two problems at the same time. Another aspect of assessing the environmental impact is to aim to reduce the energy dependence, which is a factor that is linked to other characteristics of the membrane as well.

The letter *C* stands for “capacity building”. In trying to generate solutions for problems in less favored areas, it is important to consider that these need to focus on the long-term. It is possible to donate membrane filtration systems currently used in industrialized nations, but without helping the population build its own capacity, this solution cannot be sustained. Considering the scarce technical training, applicable technologies must be easy to operate and must withstand misuse.

The letter *O* stands for “obtainable”. The material with which the membrane is manufactured must be readily available locally. This not only helps reduce cost but also simplifies replacement. In the case of manufacturing, it must be simple enough to be replicated in different areas of the world.

The letter *L* stands for “low cost”. The system as a whole must not only have a low capital cost, but also a low operational cost. Assuming that

the material that is to be used as a membrane is recycled, the cost could be driven down once widespread manufacturing is available. Operational costs could be reduced by using a system with low pressure requirements so that it can be run with the use of hand pumps or other devices. The possibility of being able to make use of gravity to drive the system would also be an advantage. Furthermore, the durability of the product reduces the need for frequent replacements.

2.7 Research Objectives

The overarching objective of this research effort is to design a system that can be applied in developing countries to ensure access to safe drinking water and basic sanitation. Since membrane filtration with traditional materials is not adequate for use in developing areas, alternatives needed to be explored. Therefore, the objective for this specific study was to evaluate a possible membrane material that to determine whether or not it met the specific criteria described in the previous section (Section 2.6).

The material evaluated as a possible *ECOL-Mem* candidate was a porous rubber tubing (PRT) that contains 65% recycled crumb rubber. The product is recycled, durable, and could potentially be less expensive than traditional membrane materials if considering its life cycle analysis. Although it might not be currently available in all areas, widespread manufacturing is possible since the raw material (waste tires) is available virtually everywhere. This would increase availability and further reduce cost.

To our knowledge, PRT has never been used in this type of application. Therefore, it was necessary to evaluate its intrinsic filtration characteristics and the quality and quantity of water it was able to produce.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Porous Rubber Tubing (PRT)

The porous rubber tubing (PRT) used is commercially available in home improvement and discount superstores. It is intended to serve as a soaker hose for drip irrigation.

The first patent on record for PRT was issued under the name Underground Irrigation Porous Pipe (Turner, 1977). However, there have been other patents filed directly related that have proposed modifications to improve the PRT (Mason, 1985; Mason, 1986; Prassas and Bard, 1994). For example, the addition of carbon black has been suggested to reduce degradation by ultraviolet radiation (Prassas and Bard, 1994).

3.1.1.1 Porous Rubber Tubing Manufacturing

PRT is manufactured by using a mixture containing reclaimed tire rubber and a binder, like polyethylene (PE). During the extrusion process to form the pipe, the water present in the extrudate vaporizes and produces small pores.

The first patent for porous rubber tubing intended for underground drip irrigation was filed by Turner in 1977. In this document, previously vulcanized rubber (such as that recovered from scrap tires) was to be ground to a size smaller than a 30-mesh screen. The product mix, which was to be extruded, was comprised of 70% rubber granules and 30% thermoplastic binder (Turner, 1977). This last mix contained 70% high density

polyethylene (HDPE), 14% polyvinyl chloride (PVC), 15% acrylonitrile-butadiene-styrene (ABS) copolymer, and 1% attaclay (Turner 1977; Tock and A'hern 1993).

However, a study done by Tock and A'hern (1993) revealed that the process described by Turner could not yield a PRT with the leaking rate required for drip irrigation. Furthermore, there were unacceptable variations from lot to lot.

A new patent was filed by Mason (1985), who claimed that the amount of water present in the extrudate is directly related to the porosity of the final product. The moisture content was to be kept between 0.75% and 1.5% by weight. Also, the variability of the moisture content was to be reduced so that it did not vary by more than 10% throughout a batch. It was also discovered that Turner's process produced PRT with variable pore formation because of the presence of volatile compounds that evolved into carbon dioxide at high temperatures. This problem was resolved by heating the composition to a temperature high enough to remove the volatiles before forming the pellets (Mason, 1985).

The new patent claimed a pelletizable mixture that included elastomer in crumb form, a binder resin, a slip agent, and a lubricant. This would allow the production to take place anywhere standard extrusion equipment was available. Figures 20 shows the proposed pelletizer for the PRT/binder mixture and Figure 21 shows the proposed PRT extruder.

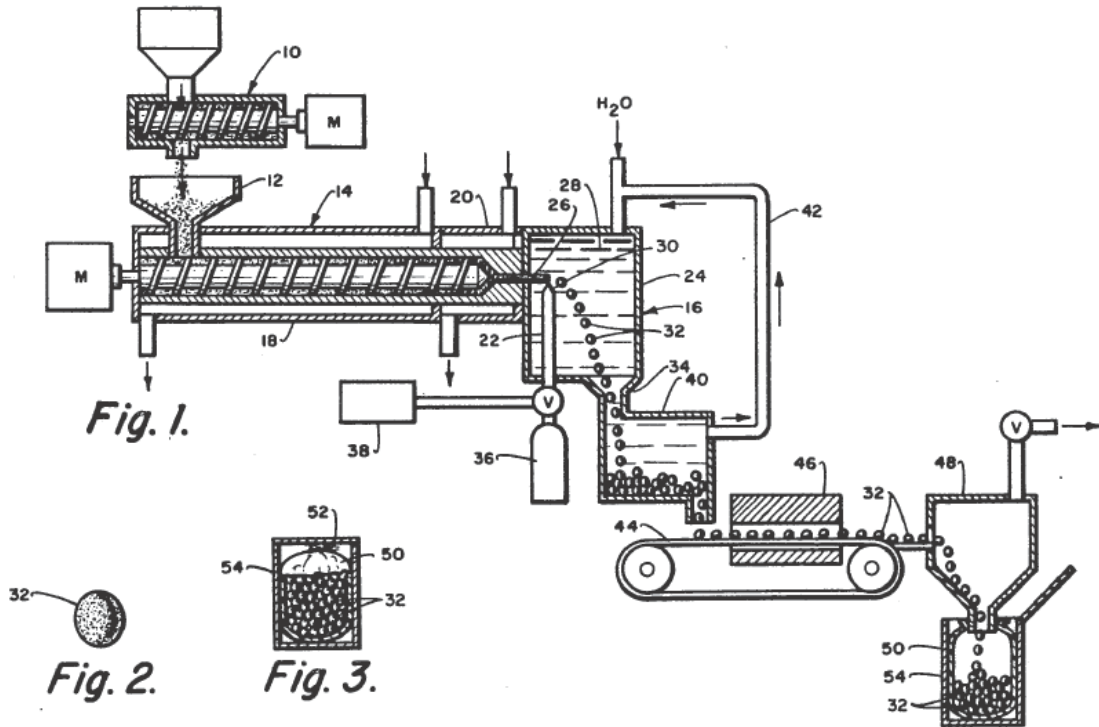


Figure 20. Crumb Rubber/Binder Pelletizer (Mason, 1986)

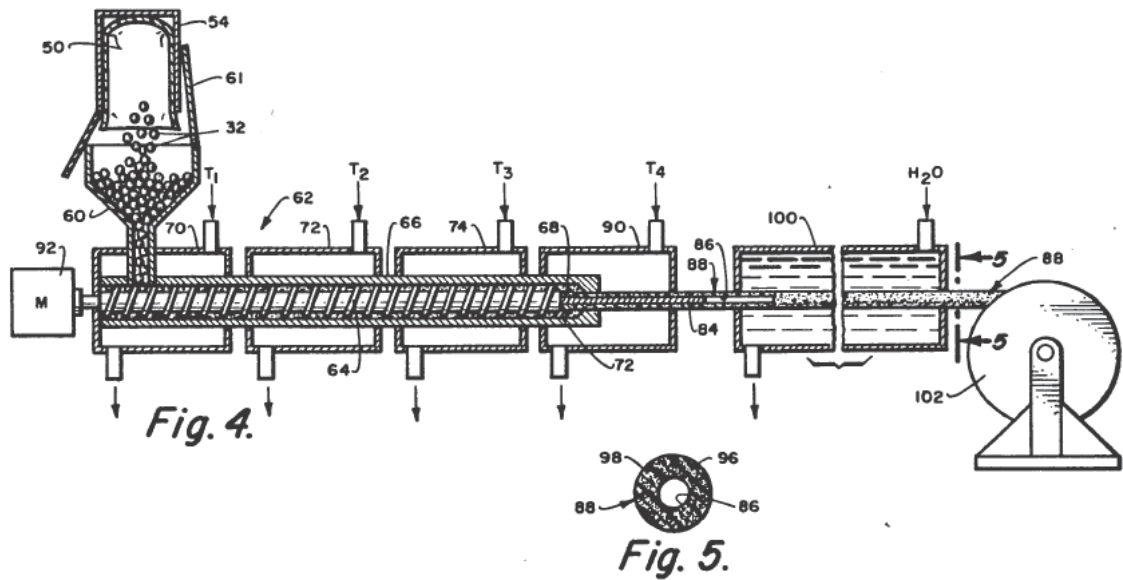


Figure 21. PRT Extruder (Mason, 1986)

The elastomer could be prevulcanized crumb rubber, such as that obtained from scrap tires, with particles between a 20-mesh and a 60-mesh size. The optimum binder was suggested to be composed of 60% to 70% of high density polyethylene and 30% to 40% of low density polyethylene (LDPE). The slip agents were added to aid in extruding the rubber binder mixture. Although the use of talc was recommended, other finely divided minerals like clays, silicas, carbonates, or micas could also be used. The suggested lubricant was a metal stearate that could be calcium, magnesium, or zinc stearate (Mason, 1985).

The PRT was optimized by the addition of an ultraviolet stabilizer that made the product resistant to degradation by sunlight in a patent by Prassas and Bard (1994). The patent described that ultraviolet radiation produces free radicals resulting in chain scissions or the creation of other radicals that can degrade polymer chains. This degradation can be prevented by the addition of carbon black pigment to transparent resins. Although the recycled rubber particles already contain around 30% carbon black, this was not contributing to the binder phase. This meant that the carbon black was not available for absorption of ultraviolet light, allowing the radiation to penetrate the binder film. The patent suggested the addition of 0.1% to 3% by weight of carbon black to the binder resin, which provided both ultraviolet and thermal stabilization (Prassas and Bard, 1994). Currently, PRT is produced by combining the patents listed for Turner (1977), Mason (1985), and Prassas and Bard (1994).

3.1.1.2 Porous Rubber Tubing Preliminary Evaluation

Although PRT is available in a wide variety of diameters and manufactured under various brand names, two specific brands and diameters were used in this investigation. The following table summarizes the characteristics of the tubing tested.

Table 2. Characteristics of Porous Rubber Tubing Used

	Mini Soaker	Bulk Soaker
Nominal Diameter	1/4 inch	1/2inch
Inside Diameter	3/16 inch	7/16 inch
Outside Diameter	5/16 inch	5/8 inch
Wall Thickness	1/8 inch	3/16 inch
Length of Roll	25 feet	50 feet
Brand Name	Better Homes and Gardens	Moisture Master
Manufacturer	Aquapore Moisture Systems, Inc.	Colorite Plastics Company

There is variation between the different PRT brands but the two that were tested contained 65% recycled tire rubber. Microscopic differences between the two types of PRT tested can be seen in the following scanning electron microscopy (SEM) images. SEM also revealed an uneven surface and a wide pore size distribution for both samples (See Figures 22, 23, 24, and 25). Refer to Appendix C for more SEM images.

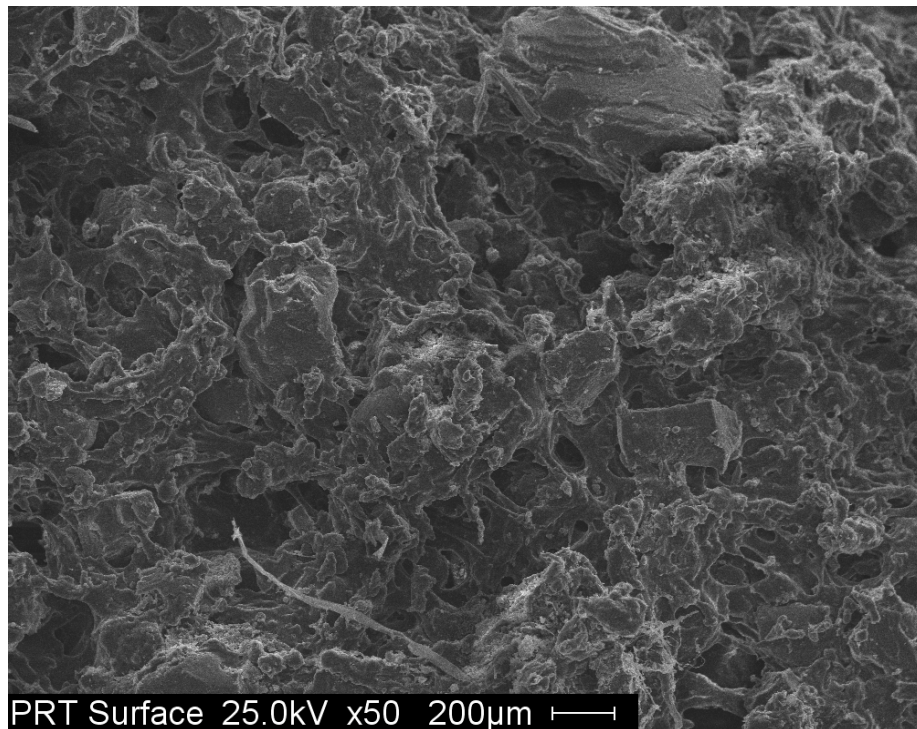
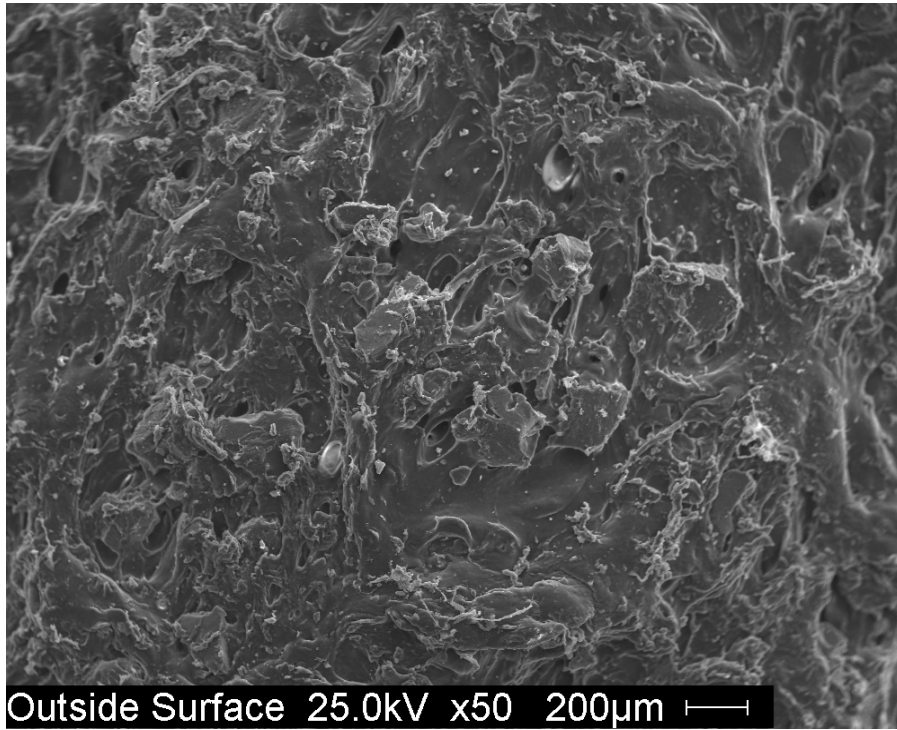
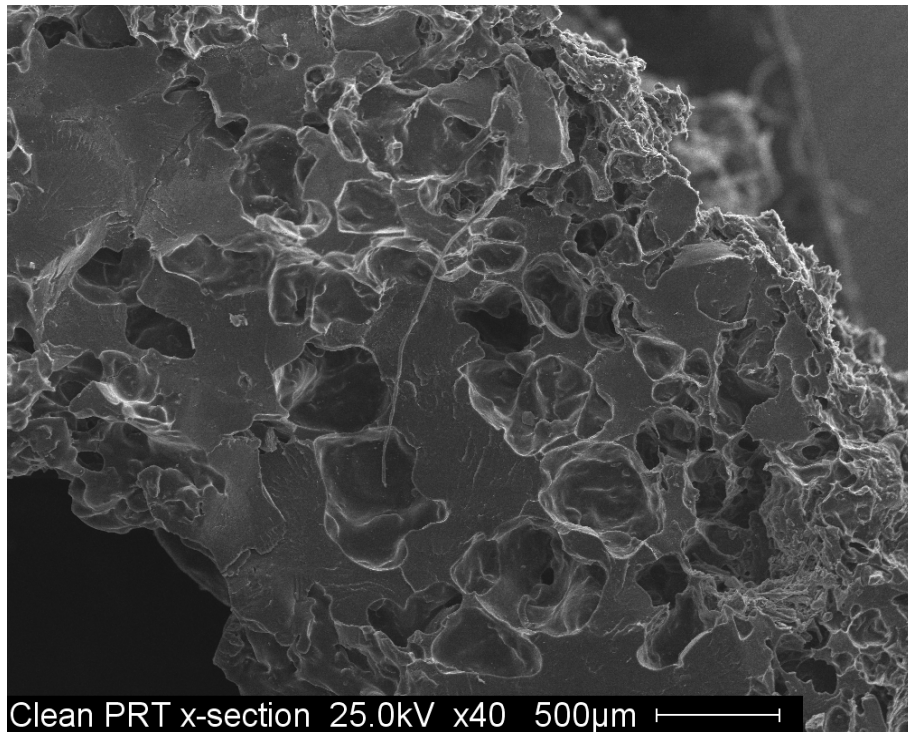


Figure 22. SEM Image of 1/4" Diameter PRT Surface



Outside Surface 25.0kV x50 200 μ m
Figure 23. SEM Image of 1/2" Diameter PRT Surface



Clean PRT x-section 25.0kV x40 500 μ m
Figure 24. SEM Image of 1/4" Diameter PRT Cross Section

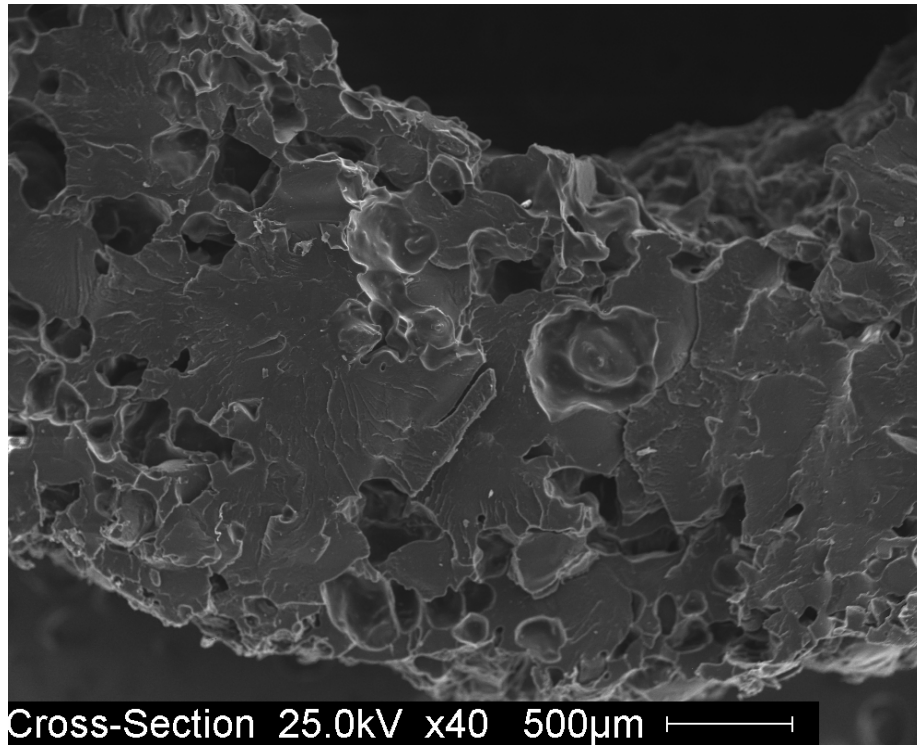


Figure 25. SEM Image of 1/2" Diameter PRT Cross Section

3.1.2 Bentonite

Bentonite (CAS 1302-78-9) is a type of clay that was used to simulate turbid river water. The specific bentonite used in this research was laboratory grade and obtained from Fisher Scientific (Catalog No. B235-500). SEM images show an angular particle shape, although this observation was not confirmed with sphericity calculations (See Figure 26). Sieve analysis was attempted once again used to determine particle size distribution, but the particle size was below size 200 (75 μm). Therefore, this type of analysis was not valid. SEM images were used to approximate a particle diameter of 10 μm .

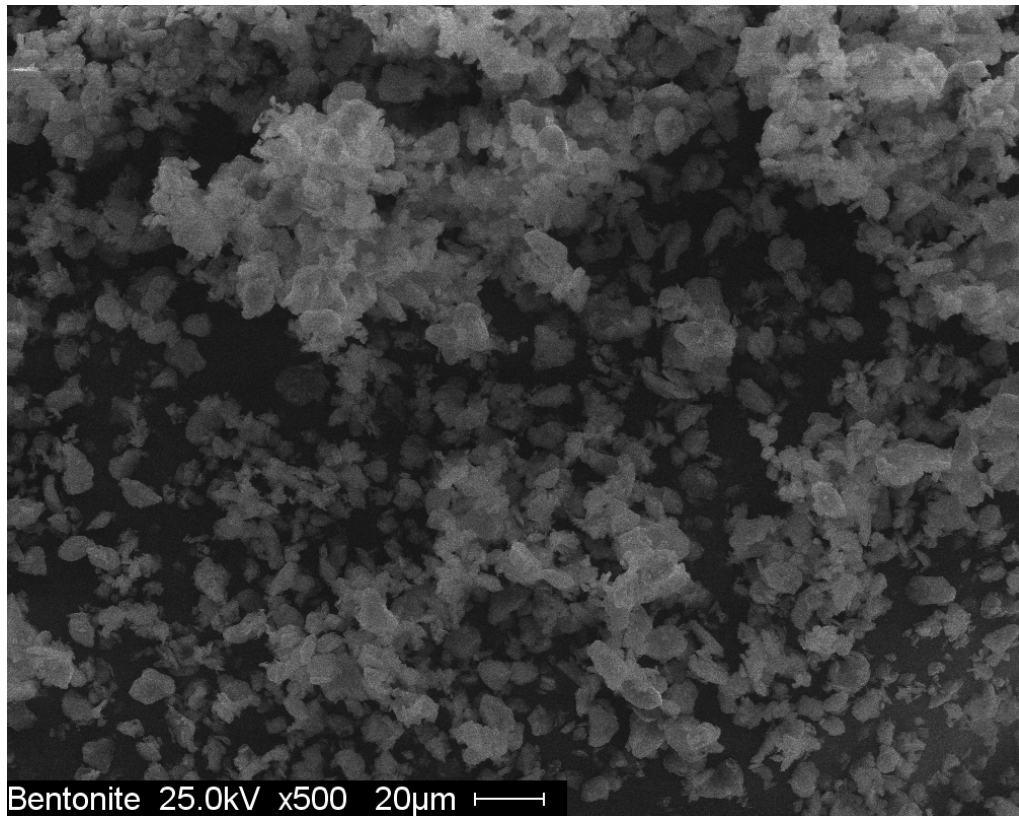


Figure 26. Scanning Electron Microscopy of Bentonite

3.1.3 Anaerobic Digestion Sludge

The anaerobic digestion sludge was diluted to different concentrations in order to simulate source water that had been contaminated due to a lack of basic sanitation practices. This sludge was obtained from the Glendale Wastewater Treatment Facility in Lakeland, Florida.

3.1.4 Chitin

The chitin used in this research was obtained from Fisher Scientific and supplied by MP Biomedicals, Inc. (Catalog No. 101334). According to the supplier, the polymer is unbleached and practical grade (CAS 1398-61-4). Although it is found in fungi, yeasts, marine invertebrates, and arthropods, its listed source are crustacean shells. The chitin's molecular formula is $C_{30}H_{50}N_4O_{19}$ (see Figure 27) with a molecular weight of 770.8 g/mole (MP Biomedicals, Inc., 2006). SEM images revealed a flaky structure (See Figure 28).

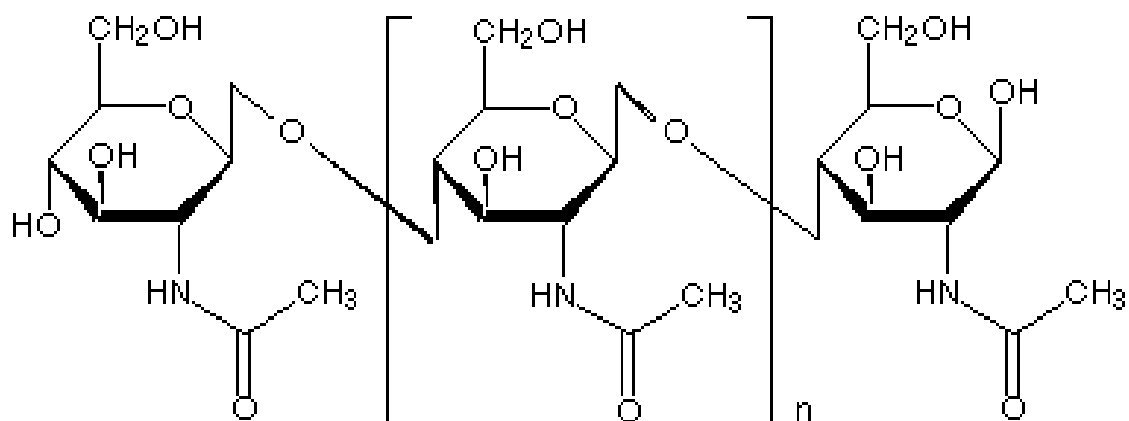


Figure 27. Chemical Structure of Chitin, Unbleached (MP Biomedicals, Inc., 2006)

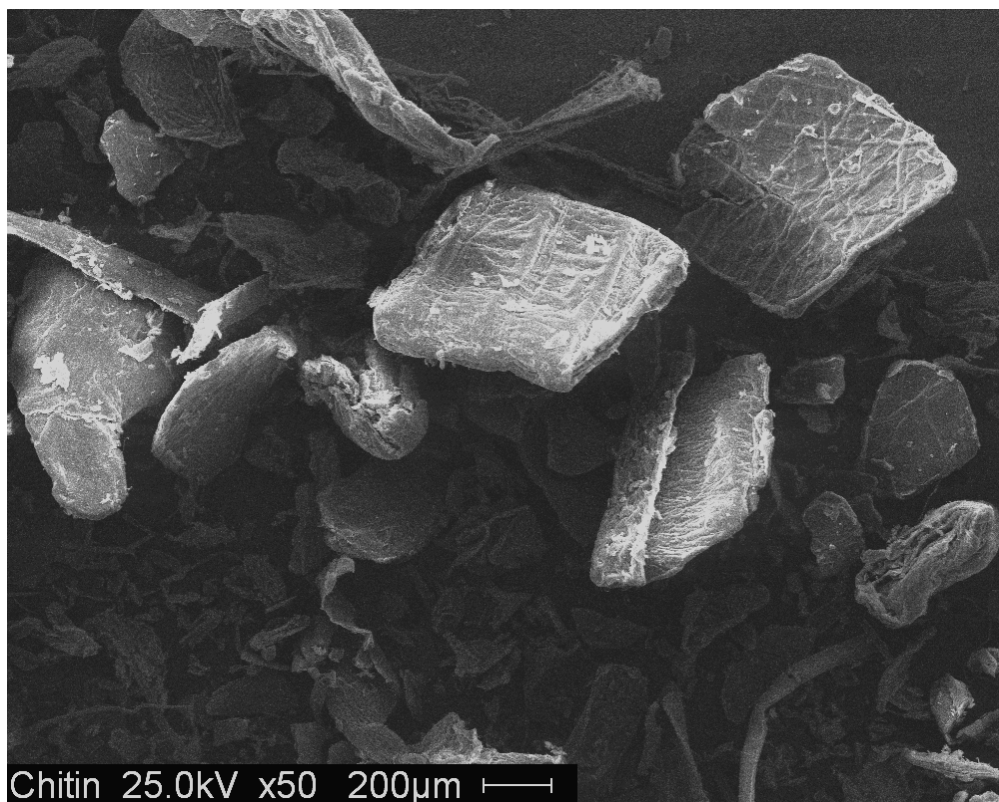


Figure 28. Scanning Electron Microscopy of Chitin

Sieve analysis was done on the chitin to determine the particle size distribution. Figure 29 shows the particle size distribution curve that was

obtained. The uniformity coefficient (C_U) and coefficient of gradation (C_Z) were calculated using the following formulas (Das, 2002):

$$C_U = \frac{D_{60}}{D_{10}}$$
$$C_Z = \frac{(D_{30})^2}{D_{10} \cdot D_{60}} \quad (5)$$

These equations yielded a uniformity coefficient equal to 3.5 and a coefficient of gradation equal to 1.51. The particle size distribution curve was also used to estimate that approximately 80% of the particles have a size greater than 200 μm . This information suggests that in the event of chitin addition; most of the flakes would be retained by the PRT.

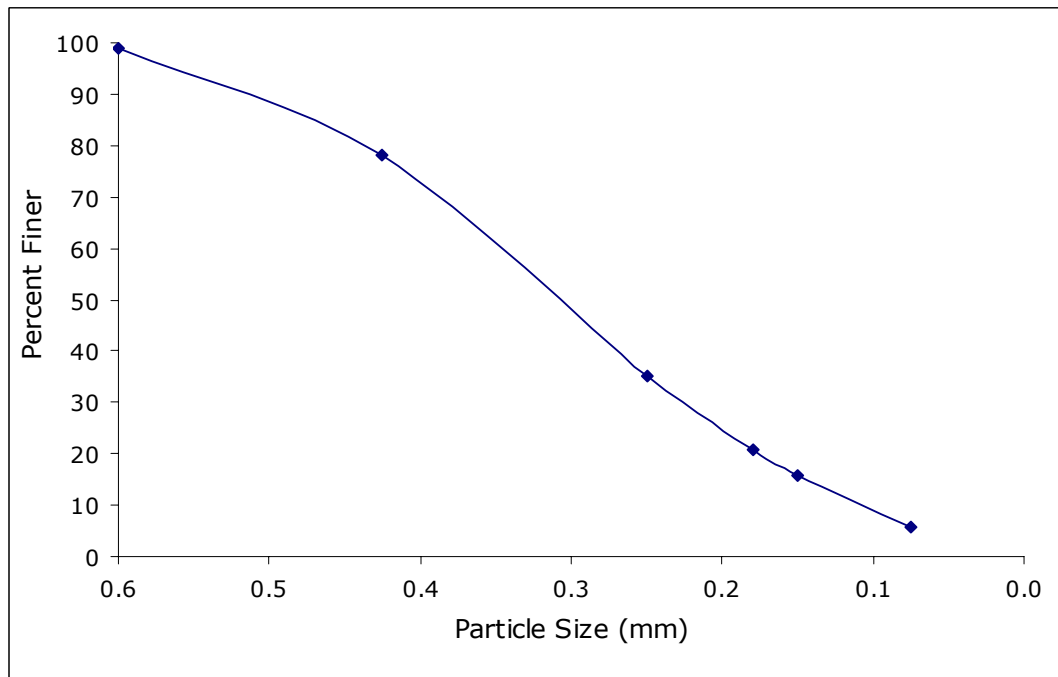


Figure 29. Particle Size Distribution Curve for Chitin, Unbleached

3.2 Testing Apparatus

3.2.1 Cassette Setup

Thirteen PRT segments, measuring approximately 5 inches each, were arranged vertically and connected with plastic T fittings and tubing. They were arranged together in a circular shape and attached to glass stirring rods to provide weight and prevent the cassette from floating during backwash (See Figures 30 and 31).

The PRT cassette had a total length of approximately 1.65 m (65 in) and provided 0.856 m² (9.21 ft²) of surface area for filtration. The purpose of this configuration was to make it easily transferable to other reservoirs for testing or chemical cleaning.

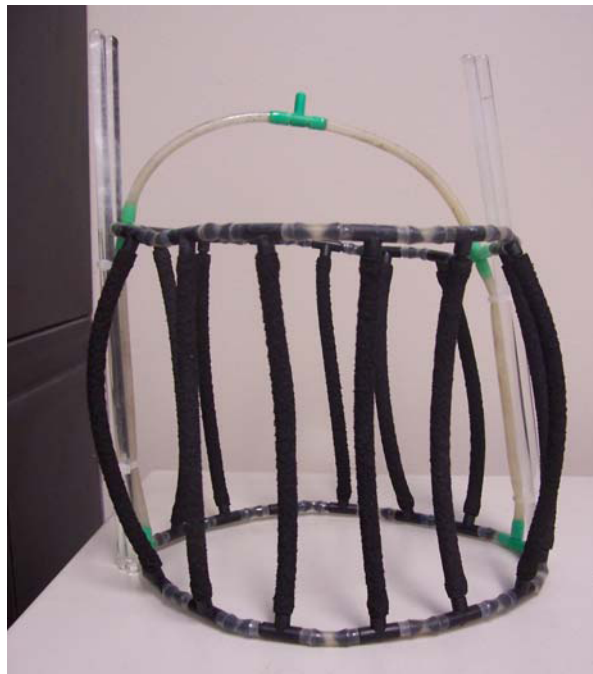


Figure 30. PRT Cassette

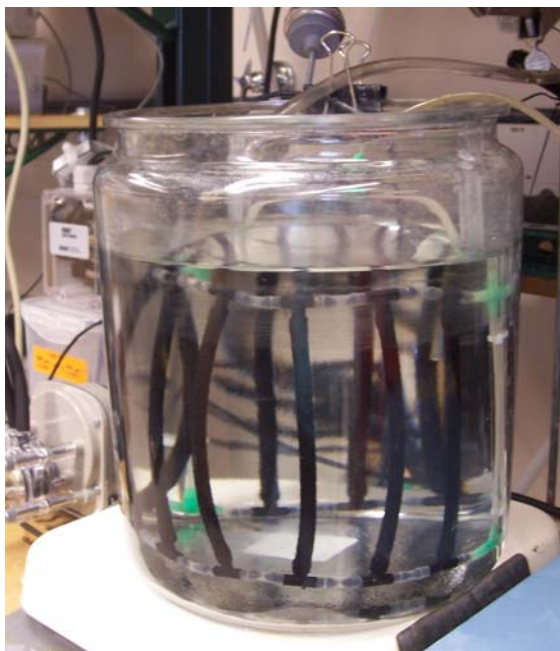


Figure 31. PRT Cassette in Feed Reservoir

3.2.2 System Setup

The system used for testing was basically comprised of a reservoir, a pump, and a data logging system. This section will focus on the description of the first two elements, while data logging will be described in Section 3.2.3.

The reservoir was a glass container that was filled with 6.75 L of feed solution, whether it was tap water or any of the testing surrogate source waters used throughout the investigation. This volume provided approximately 7 inches of liquid height measured from the bottom of the reservoir. The reservoir was placed on heavy duty magnetic stir plate (Bellco Glass Bell Stir) and mixed with a stir bar. Although other mixing and feed reservoir configurations were tested (See Appendix B), it was concluded by observation that a magnetic stirrer and a round container could provide the most efficient and uniform mixing. A magnetic stirrer was capable of keeping the particles in suspension to provide uniform feed water characteristics. Glass was chosen as the material for the reservoir since it is inert.

The PRT cassette was placed in the reservoir and connected to a vacuum gauge, a pressure transducer (Cole Parmer Model 68075), and a

pressure gauge. The pressure sensors were connected to the suction end of a peristaltic tubing pump (Cole Parmer Model 7553-70) using Norprene tubing (Masterflex® 06404-24). The negative pressure generated by the pump provided the TMP required for filtration with the PRT. The pump was run at a setting of 4 for most of the tests, which corresponded to a flow rate of 432 mL/min (for calibration data refer to Appendix A). This flow rate was measured without connecting to the PRT cassette and using tap water.

The permeate from the PRT then flowed into a wire rain meter which was used to record the flow rate. Further description of this setup will be given in Section 3.3. Finally, the permeate flow was recycled back to the feed reservoir. Because the system was designed for testing membrane performance, permeate recycling was necessary to maintain a constant head level in the reservoir. In an actual treatment configuration, the permeate would be collected for use, rather than being recycled into the feed reservoir. See Figures 32 and 33 for full system setup and Appendix D for pictures of all the system parts.

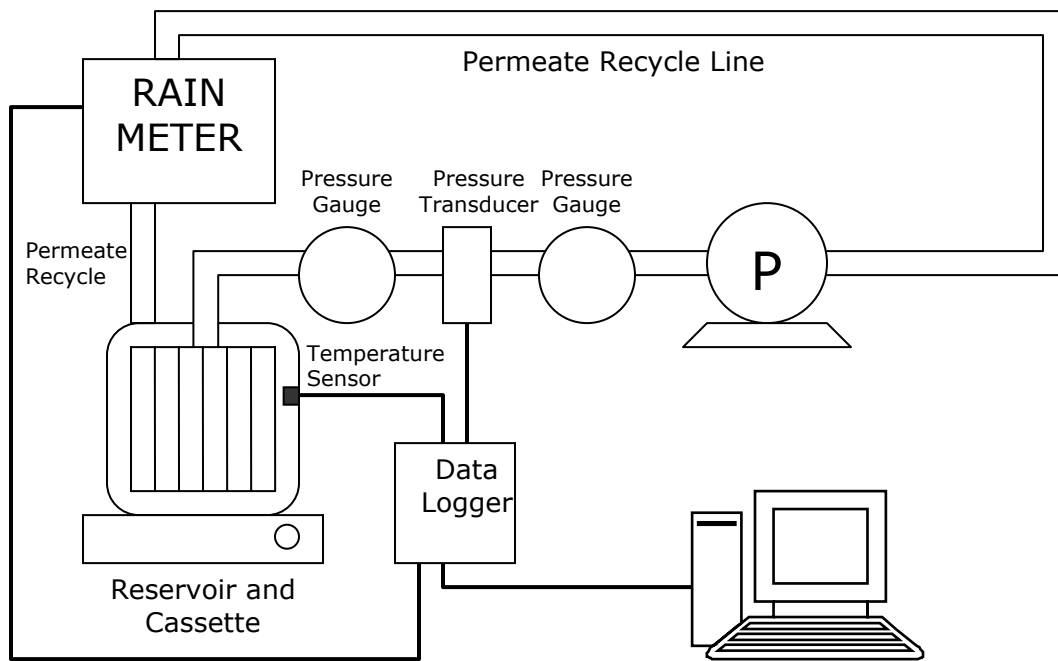


Figure 32. System Setup Diagram



Figure 33. System Setup Picture

3.3 Data Logging

Two different devices were used for data logging throughout the study. They were both supplied by Onset Computer Corporation (Bourne, MA) and only differed in the maximum number of sensors supported. The first device used was a HOBO Weather Station (Model H21-001) which had a capacity for a maximum of 15 sensors. The other device was a HOBO Micro Station (Model H21-002) which had a capacity for up to 4 sensors.

Both of these devices could be connected to a computer through a serial port cable. The software used was BoxCar Pro 4.3 (Onset Computer Corporation). Logging intervals were usually set to 1 minute, but could be easily increased when high solids feed was being filtered.

Once the data was downloaded onto the hard drive of the computer, it was exported to Microsoft Office Excel. A spreadsheet was prepared to calculate average permeate flow, feed water temperature, and gauge pressure readings. Other parameters like TMP, resistance, and flux were also calculated using this spreadsheet.

3.3.1 Pressure Measurements

A pressure transducer (Cole Parmer Model 68075) was connected to the setup as described in Section 3.2.2. Both a pressure gauge and a vacuum gauge were used to calibrate the device (See Appendix A). The transducer was wired to a 12-bit Voltage Input Adapter (Model S-VIA-CM14) supplied by Onset Computer Corporation. This adapter was then connected to either the weather station or the micro station.

3.3.2 Temperature Measurements

The temperature measurements were done using an 8-bit temperature sensor (Model S-TMA-M002) provided by Onset Computer Corporation. This sensor was connected directly to either data logging device.

3.3.3 Flow Rate Measurements

Flow rate measurements were done using a wire rain meter (Model WS-7048U) provided by LaCrosse Technology. This meter was wired to a pulse input adapter (Model S-UCB-M006) which was connected to either data logging device.

Wire rain meters have been traditionally used to collect precipitation data. They are resistant to water damage, which makes them optimum for this type of application. The meter has a collection area which funnels into a tipping bucket. Each time the bucket fills up, it sends a pulse signal. Since the rain gauge was not compatible with the data logging devices, it was necessary to use the adapter mentioned previously.

The wire rain meter was calibrated prior to using it in the study. This was done to account for splashing occurring during elevated inflows. Calibration data can be found in Appendix A.

3.4 Analytical Methods

The PRT was subject to high solids concentration so that the permeate flux after only a few minutes was severely reduced. This limited the amount

of permeate that could be collected for both total solids and turbidity measurements. Therefore, turbidity measurements are not available for every point and will only be given as an indication of the overall trend in the system over the run time. The total solids data consists of only one sample per test since the permeate flux did not allow for collection of multiple samples.

3.4.1 Total Solids

Total solids measurements were performed according to Section 2540B (Total Solids Dried at 103-105°C) of *Standard Methods* (APHA, 1995) Procedure listed in Section 2540 B and termed "Total Solids Dried at 103-105°C". These samples were collected directly from the reservoir for the feed samples or prior to the rain meter device for the permeate samples. The percent removal from the feed to the permeate was then calculated.

3.4.2 Jar Testing

The jar test is widely used to simulate a full-scale coagulation and flocculation process and it is used to determine optimum coagulant doses (Viessman and Hammer, 2005). The apparatus consists of six agitator paddles that operate at the same rotational speed and six containers that have a volume of 1 L each. The containers were filled with 1 L source water and stirred gently as the flocculant was added. At this point, the rotational speed was increased to 150 rpm to provide flash mixing for 3 minutes. The apparatus was then turned off and the paddles were removed from the water to allow for floc formation and settling. Observations related to floc size and settling characteristics were then recorded.

3.5 Scanning Electron Microscopy (SEM)

The samples imaged were first dried if they had been previously in use in the system. They were later frozen by using liquid nitrogen and fractured.

A sputter coater (Anatech Limited Hummer X) was used to coat the fractured samples with a thin film of gold.

A scanning electron microscope (Hitachi Model S-800) was used to image the PRT. The instrument's measurement accuracy is $\pm 5\%$, but can be as high as $\pm 15\%$ if the sample is insulating. All images shown here indicate in their caption the voltage used (either 10kV or 25 kV). The room temperature was maintained between 15-25°C and the humidity level was kept below 60%.

3.6 Total Carbon Analysis

Total carbon analysis was used to determine whether the PRT was leaching into different types of water (RO water, NF water, tap water, low and high pH). This can be a concern for public health since the PRT contains various substances and is derived from a waste material.

For the leaching experiments, a Total Organic Carbon Analyzer (Shimadzu TOC-VCSH) was used. The instrument was calibrated using a KHP solution (See Appendix A for calibration curve) and ultra pure air as the carrier gas to eliminate any possible contamination. The samples used had a volume between 30 and 40 mL. The value reported was an average of the three most precise readings.

3.7 Procedures

3.7.1 Backwashing

Backwashing was initially done by reversing the flow of the pump so that air flowed from the inside of the PRT to the feed water. This allowed for unclogging of the pores. The duration of this procedure was normally 5 to 10 minutes when it was intended to extensively clean the PRT in between runs. However, backwashing optimization trials were also performed. In these cases, the procedure lasted anywhere from 15 seconds to 5 minutes.

The system was also tested during several days using a continuously-operating mode that included a set of four 3-way pinch solenoid valves (Cole Parmer EW-98302-46) arranged as shown in Figure 34. These valves were connected to a terminal block (National Instruments CB-37FH 778673-01) that was connected to a computer through a shielded input/output cable (National Instruments SH37F-37M 778621-01). The interface was an industrial digital output module (National Instruments PCI-6516 779082-01). Using LabVIEW 7.1, a program was created to activate the solenoid valves at specified intervals.

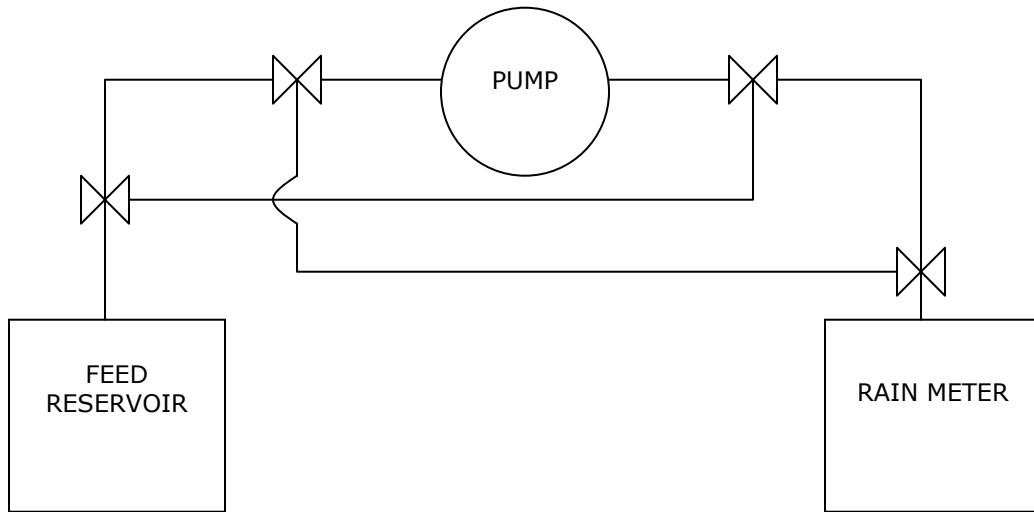


Figure 34. Solenoid Valve Placement for Automatic Backwashing of Continuously-Operated Cycles

This system allowed for the continuous operation of the pump in the same direction while providing backwashing as well. Once the solenoid valves were activated, the direction of the fluid within the tubing was reversed so that the permeate that was already contained was returned to the feed reservoir. Once all the permeate had been evacuated from the tubing, air would backwash the PRT membrane. As with the manual cycles, the backwashing fluid consisted of a combination of both permeate and air.

3.7.2 Physical Cleaning

Physical cleaning was only done after a complete run was finished. It consisted of brushing the PRT cassette with a dilute Alconox® solution. The cassette was then rinsed with tap water.

3.7.3 Chemical Cleaning

The chemical cleaning was done after runs using feed water with high solids concentrations or whenever backwashing did not restore the flow rate to at least 90% of its initial clean water value. The procedure included the physical cleaning described in the previous section as well as running the dilute Alconox® solution through the system. This not only cleaned the PRT, but also the entire system tubing. Once this procedure was finished, tap water was used to test the PRT cassette and determine whether or not the pore blockage had been eliminated.

3.8 Calculations

The calculations described in the successive sections were all integrated into the spreadsheet previously mentioned. This spreadsheet was also used to illustrate relationships between the different parameters. All calculations were done using accepted equations described in Chapter 2 (Background). Calculations done that are specific to the PRT cassette system will be described in detail in this section.

3.8.1 Transmembrane Pressure (TMP)

Transmembrane pressure is the difference in pressure between the feed (P_F) and the permeate (P_P). The feed pressure corresponds to the hydrostatic pressure and the permeate pressure was that measured by the transducer (P_g). Therefore, the following formulas were used:

$$\begin{aligned} \text{TMP} &= P_F - P_P \\ \text{TMP} &= \rho g \left(\frac{1}{2} L + h \right) - P_g \end{aligned} \quad (6)$$

In this case L represents the length of the PRT segments and h represents the height of the water column above the PRT cassette. The following diagram better explains this concept.

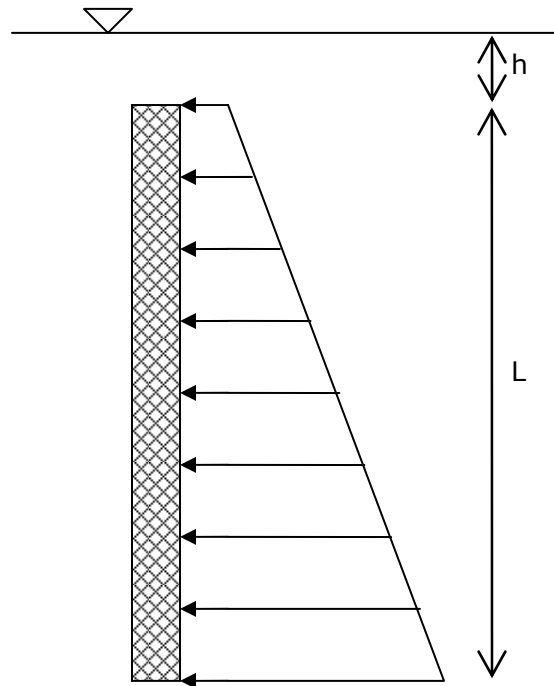


Figure 35. Explanation of TMP Calculation

The system that was used for this study kept both the values of h and L constant. The PRT had a segment length (L) of 5 inches and the height of the water column (h) was 2 inches. This provided a total liquid height of 7 inches.

3.9 Phases of Study

The evaluation of PRT as a suitable candidate for *ECOL-Mem* consisted of both laboratory work and was divided into the following phases of study:

- Determining the intrinsic membrane properties using clean water.

- Quantifying rejection and operational performance by challenging the membrane with bentonite and sludge solutions as simulated feed waters.
- Quantifying rejection and operational performance upon addition of chitin in a flocculation-enhanced filtration setting.
- Providing a preliminary life cycle analysis (LCA) to assess the possible environmental impact of PRT as a membrane material.

CHAPTER 4

EVALUATION OF PROPERTIES, PERFORMANCE, AND SUITABILITY

4.1 Intrinsic Membrane Properties

The purpose of this phase was to investigate the properties of the PRT when in operation with clean water. This aided in better characterizing the effect of certain types of model contaminants in the feed water. Furthermore, testing was done to quantify the variability of the PRT in terms of flux and permeability.

The PRT system was tested for several hours using tap water under different pump settings (See Appendix A for calibration curves). The water level was kept constant by using the same feed water reservoir and the same volume of water in order to have consistent results. The recorded parameters were temperature, flow rate, and pressure. Using this data, TMP, flux, and resistance were calculated using the equations shown in the Chapter IV.

4.1.1 Operation under Varying Pump Settings

This section will include data with reference to flux, TMP, and resistance, which were obtained from measured parameters such as flow rate, gauge pressure, and temperature. The pump setting produced direct effects that followed trends that had been predicted, establishing that the PRT performed consistent with the behavior of traditional membranes.

The trend shown in Figure 36 is that a higher pump setting yields higher flux. It was expected that a higher pump setting would exert a higher vacuum on the system and also a higher TMP. Since the TMP is the driving force of a membrane system, increasing its value generates a higher permeate flux. This was evident in the Flux vs. Time Graph (Figure 34).

Although the values for the two lowest pump settings remained somewhat constant during 3 hours, the value for the highest pump setting decreased. This could be due to impurities in the water, since tap water was used for all experiments.

A similar trend was experienced with TMP, although unexpected results arose during the first part of the run. The system took a longer time to stabilize its pressure so that two of the curves (the one for PS3 and the one of PS4) intersect at about 0.75 hours (See Figure 37). However, after the system stabilized, at this intersection point, the curves continued to increase slowly and follow the same pattern as the curve for PS2. The difference between the initial and stabilized pressures is minor. However, since tests were run with tap water, there could be impurities in the feed that can cause pressure buildup.

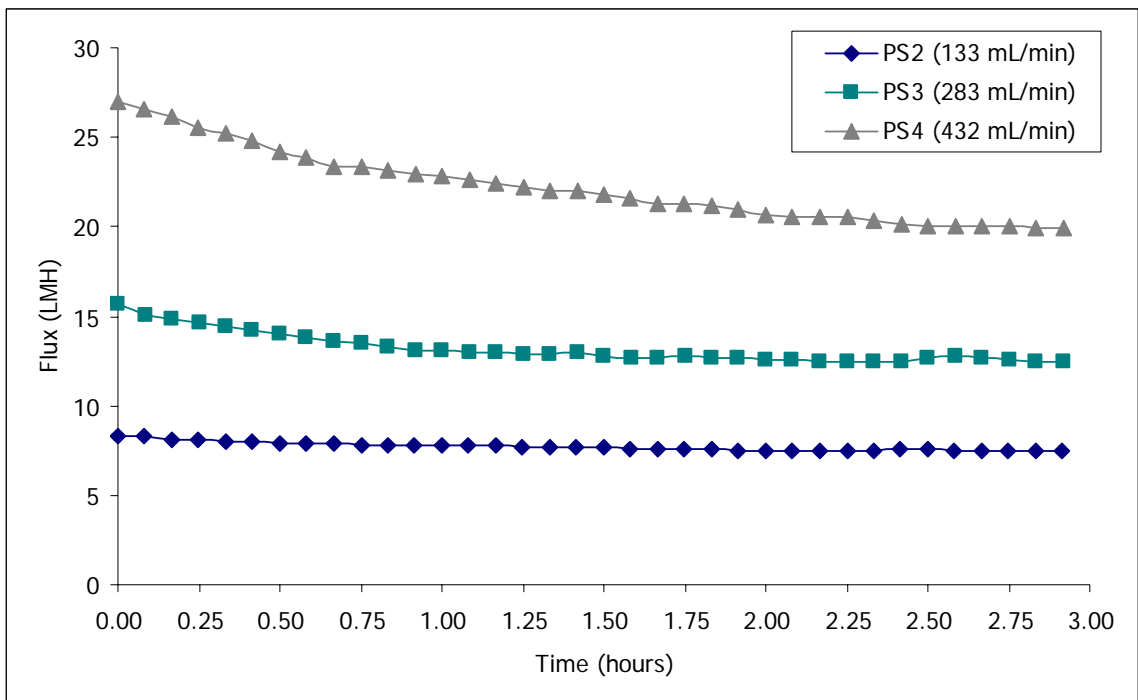


Figure 36. Flux vs. Time for Clean Water with Different Pump Settings

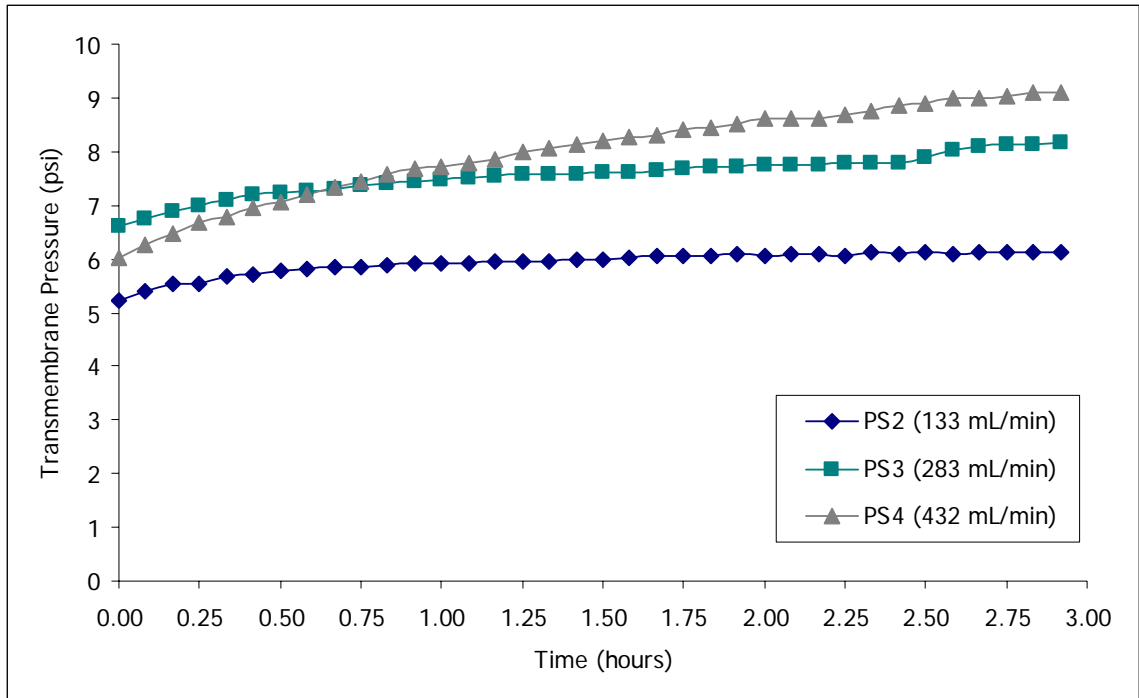


Figure 37. TMP vs. Time for Clean Water with Different Pump Settings

The resistance values were highest for a slower pump setting and smallest for the fastest pump setting (see Figure 38). This type of behavior was not expected since the decrease in TMP would be counteracted by a decrease in permeate flux. The final result should have been that the resistance remained the same for all trials since the viscosity and the characteristics of the feed water remained constant as well. A possible explanation for this behavior is that the pump setting in fact alters the structure of the PRT membrane. A higher vacuum would then open the pores, thereby lowering the resistance. This effect can be noticed in the PRT since the material has a thicker wall, a larger filtration matrix, and higher elasticity than traditional membranes.

The specific flux vs. time graph (Figure 39) has the same profile as the flux vs. time graph (Figure 36). However, it gives an indication of the permeability of the membrane taking into consideration both area and applied vacuum.

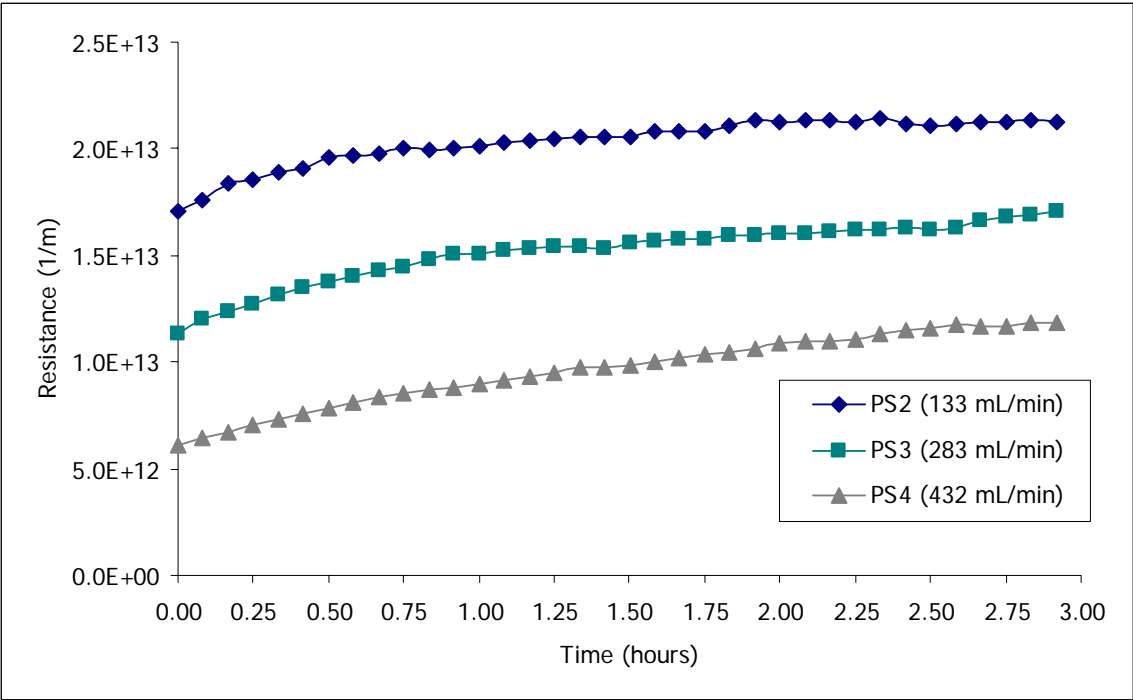


Figure 38. Resistance vs. Time for Clean Water with Different Pump Settings

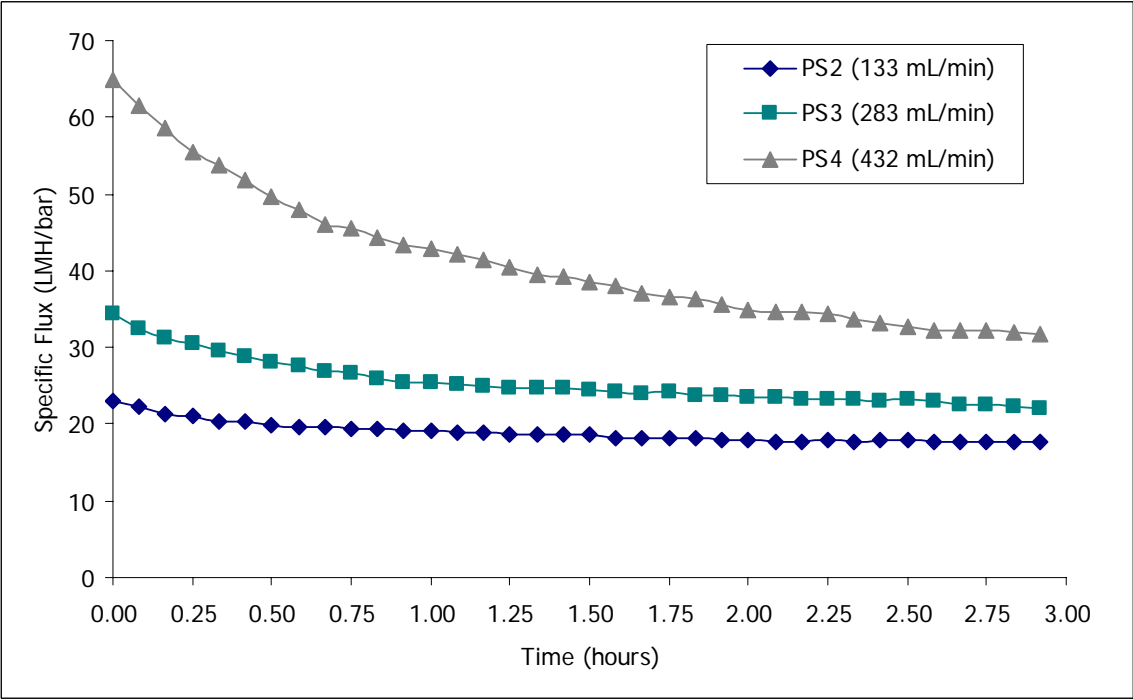


Figure 39. Specific Flux vs. Time for Clean Water with Different Pump Settings

Figure 40 illustrates the relationship between flux and TMP and shows that these two have a linear relationship. The slope of the trend line shown is related to the inverse of the relationship by a factor equal to the viscosity of the water. Using this slope, the average resistance for the PRT when tested with clean water was calculated to be $6.74E12 \text{ m}^{-1}$.

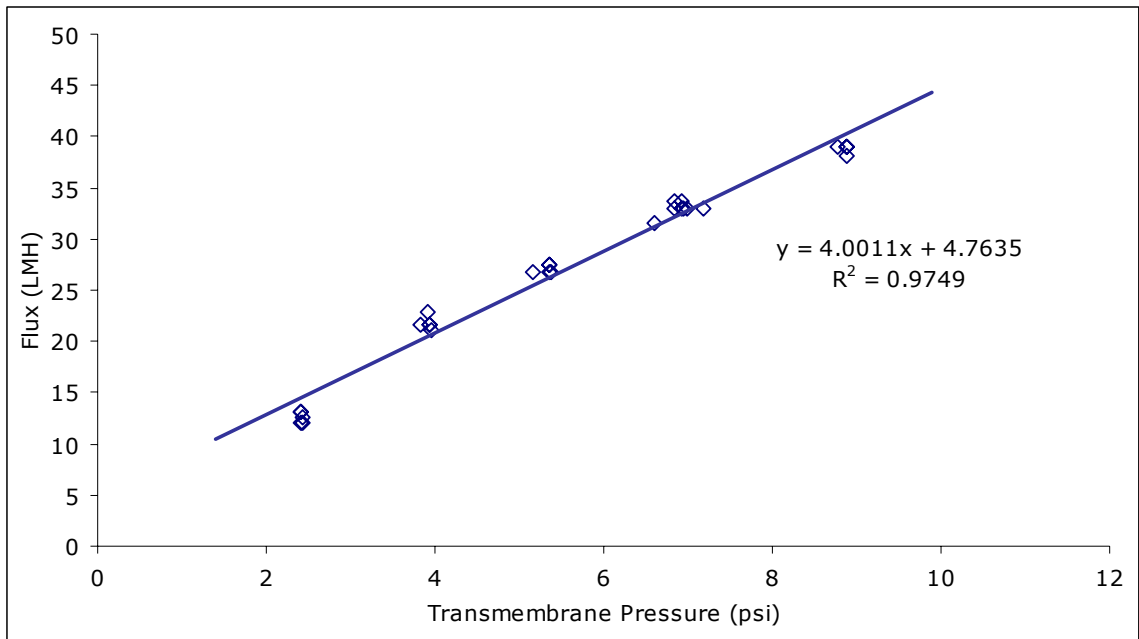


Figure 40. Flux vs. TMP for Clean Water

4.1.2 Variability in PRT

Clean water tests were performed using PRT from the same manufacturer but various lots. Visual inspection revealed differences in the material's stiffness, roughness, and density. Lot 2 was used for the majority of the data collected for this study. When Lot 2 was no longer available, Lot 1 was used. Since both of these lots had similar permeate flux values, it was assumed that they were representative of each other. Lot 3, however, was significantly different both by visual inspection and through SEM imaging. It was then decided that Lot 3 would not be used for further comparative testing.

Figure 41 shows that there is significant variability in the material's flux data from one lot to another. For example T3 appeared to be smoother

than the other two lots. Differences in extrusion temperature and composition of the PRT could account for the variability. Attempts were made to challenge T3 with solids (bentonite and sludge), but this membrane appeared to be more susceptible to the presence of particles since the flux under such loadings was negligible. One sample collected using sludge as the feed solution yielded no measurable difference in total solids from feed to permeate. No further testing was done using this specific lot, since it could not provide acceptable flux and did not effectively improve permeate water quality.

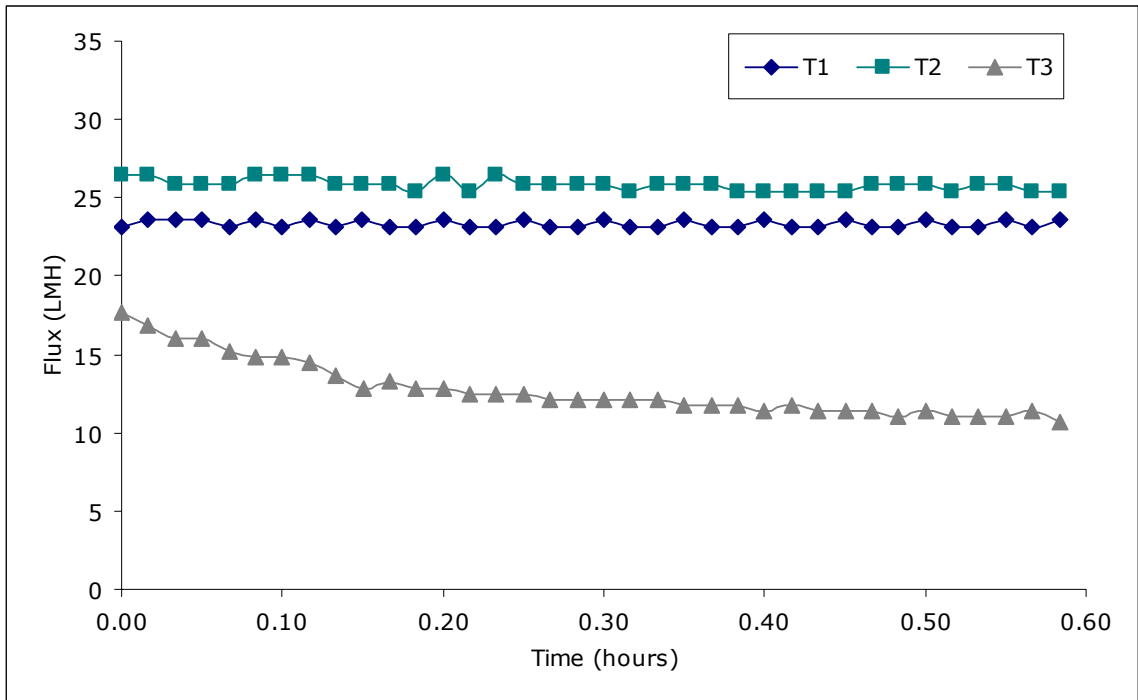
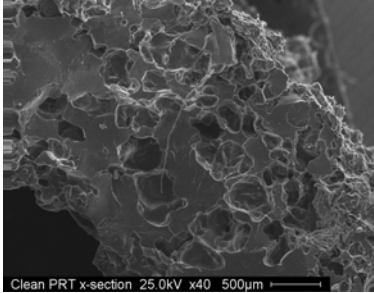
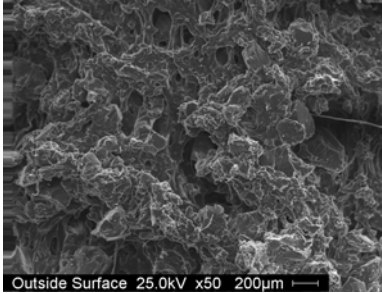
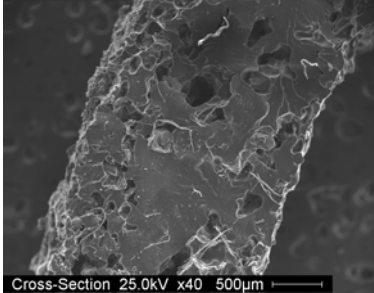
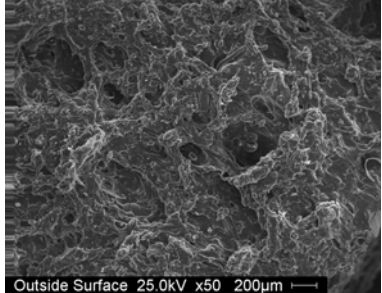


Figure 41. Flux vs. Time for Different PRT Cassettes

Table 3. Differences Between T1/T2 and T3

Sample	Visual Inspection	Cross Section SEM	Outside Surface SEM
T1 and T2	Rough surface	 <p>Clean PRT x-section 25.0kV x40 500µm</p>	 <p>Outside Surface 25.0kV x50 200µm</p>
T3	Smooth surface, dense packing	 <p>Cross-Section 25.0kV x40 500µm</p>	 <p>Outside Surface 25.0kV x50 200µm</p>

4.2 Filtration Characteristics

This section will focus on the results of challenging the PRT with different solutions, which were meant to simulate contaminated source waters. In addition, the effect of chitin addition on tap water was also investigated in order to establish if there was a significant decrease in flux. This would help establish if the chitin flakes were an adequate flocculant for use in conjunction with the PRT.

All testing done from this point was done using a pump setting of 4. This setting was selected because it provided an adequate range of permeate flux to be measured by the rain meter device. Furthermore, it protected the integrity of the pumps that were used.

As an indication of the effectiveness of the PRT in removing contaminants, total solids tests were used. Although the total solids concentration is not the only parameters that should be considered in evaluating a water system, it was decided that this method would provide an indication of rejection that could be used for preliminary evaluation. Furthermore, solids represent impurities in the water such as particles. These particles can harbor pathogens, rendering downstream disinfection processes less effective. Hence, total solids were used as a key indicator of PRT filtration performance.

4.2.1 Bentonite Feed Water

The purpose of adding bentonite to the water contained in the reservoir was to simulate turbid surface water (e.g., rivers and lakes). Turbidity, as well as solids, may help harbor pathogens and act as a barrier when utilizing methods like solar disinfection (SODIS). Therefore, it was important to understand the behavior of PRT in the presence of clay.

Permeate Quantity Results and Discussion

Bentonite solutions containing different concentrations were tested using the PRT cassette. The flux data indicated that as the clay concentration

increased, the PRT fouled faster (See Figure 42). It was also established that although there were significant differences during the first 0.5 hours in terms of flux for the different trials, ultimately the steady state flux values were similar.

Another relationship that can be used is that between cumulative permeate filtered through the membrane and flux because it gives an indication of solids loading on the PRT. In Figure 43, it can be seen that as more volume of permeate passes through the membrane, more solids get deposited on the material's surface while the flux declines.

In addition, almost 20L of permeate can be produced per hour when the bentonite concentration equals 714 mg/L. This is an important amount since the United Nations Development Programme (2006b) has established that this is the required amount of water per capita per day for hygiene and consumption.

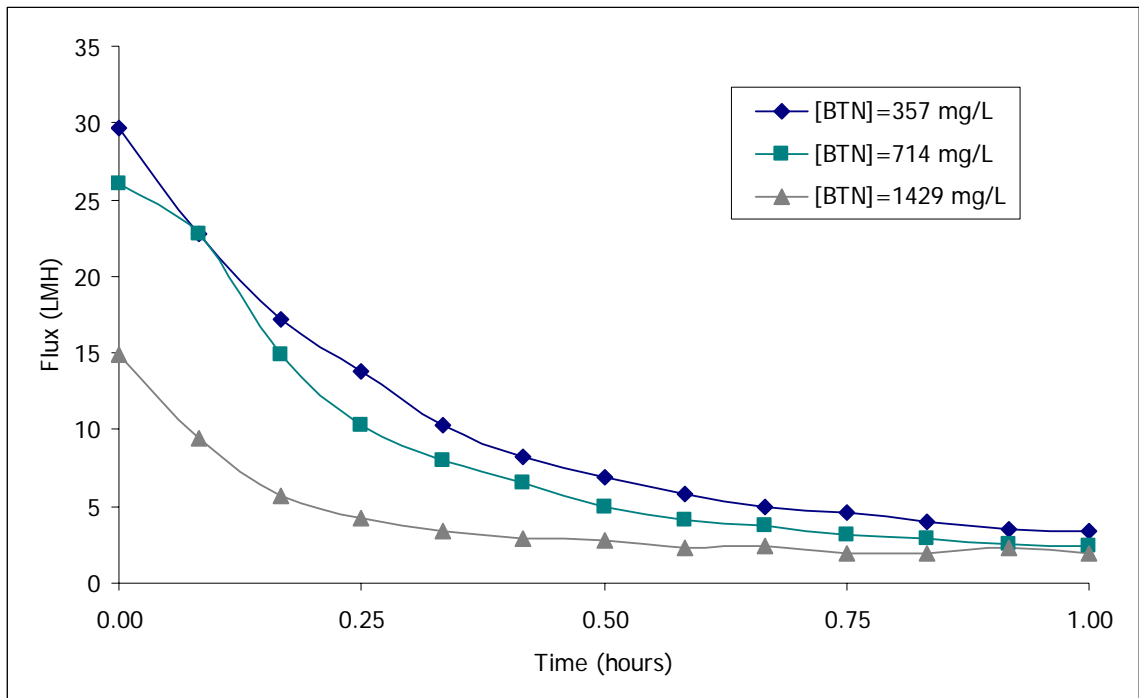


Figure 42. Flux vs. Time for Different Bentonite (BTN) Concentrations

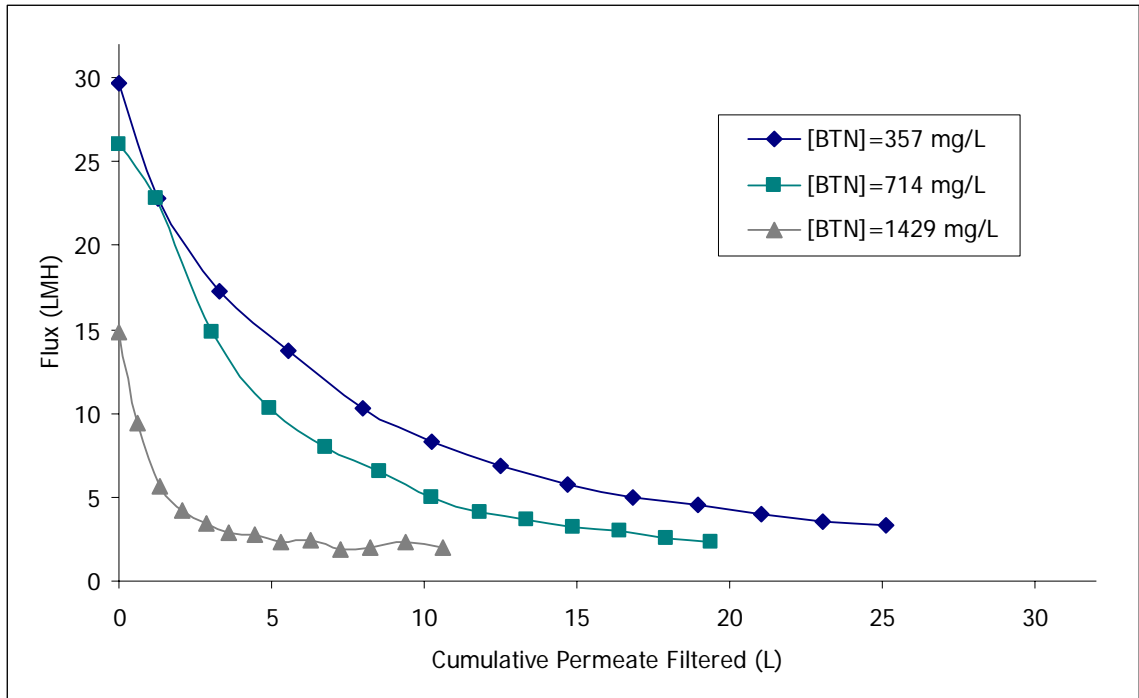


Figure 43. Flux vs. Cumulative Permeate Filtered for Different Bentonite (BTN) Concentrations

In the case of bentonite, TMP was similar for the two lowest concentrations, while it experienced a significant increase at the highest concentrations (See Figure 44). This type of curve suggests that TMP can be related to clay concentration, but not in a linear manner. However, the general trend was that a higher bentonite concentration in the feed water would generate a higher initial increase in the TMP. This occurs because a higher concentration feed will deposit more solids on the surface of the membrane as it flows through, increasing the total membrane resistance.

Following the same trend as TMP, higher resistance was encountered when the feed water contained a higher concentration of bentonite (See Figure 45). The series labeled as R_m represents the intrinsic membrane resistance that was obtained during clean water operation (See Section 4.1.1) and is shown as a means of comparison. The general trend is that the membrane is less permeable at higher solids concentrations because the cake layer build up decreases the amount of permeate that is able to flow through the PRT.

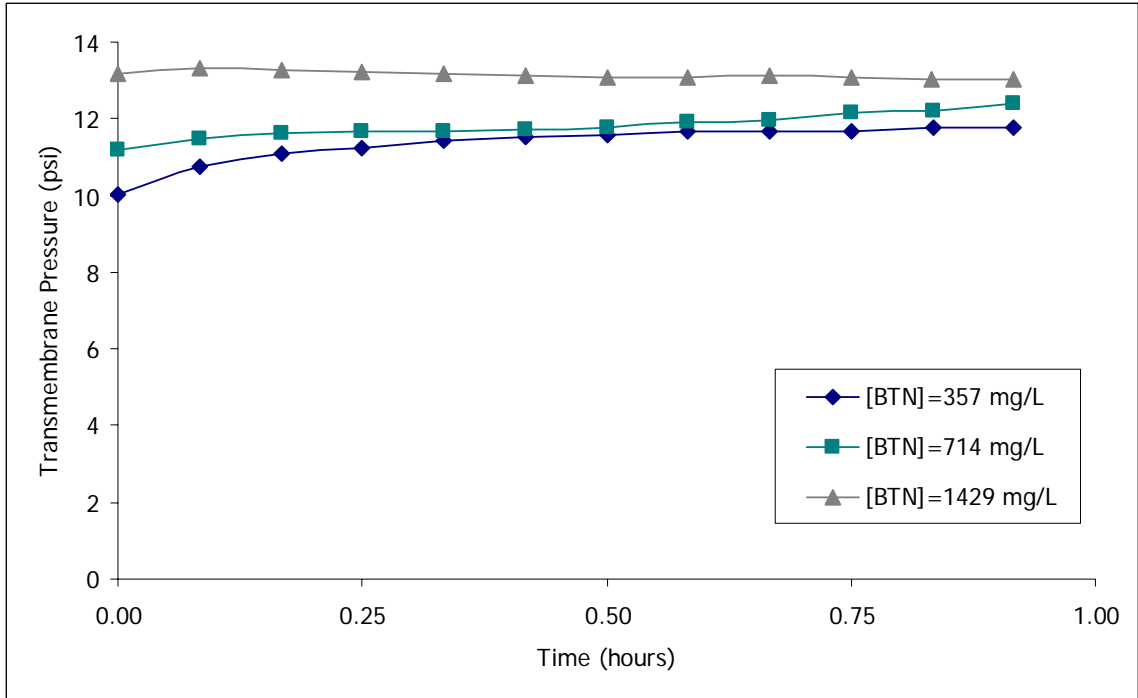


Figure 44. TMP vs. Time for Different Bentonite (BTN) Concentrations

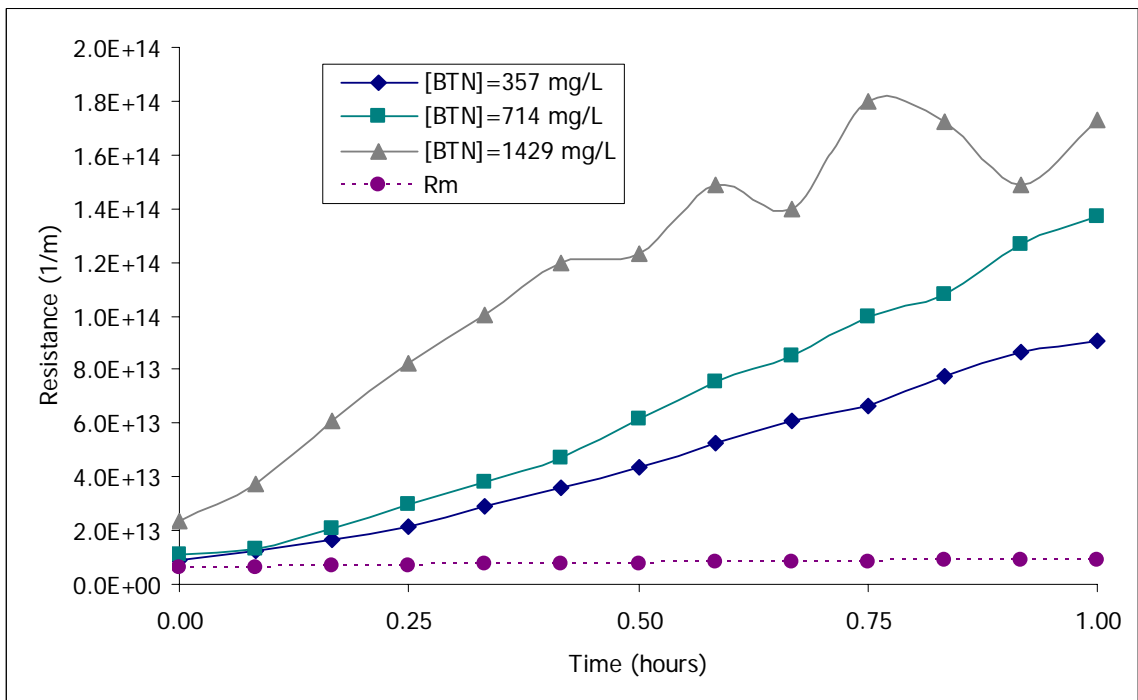


Figure 45. Resistance vs. Time for Different Bentonite (BTN) Concentrations

Figure 46 illustrates the relationship between resistance and cumulative permeate filtered. A higher amount of permeate filtered is also related to a higher amount of contaminants mass (in this case bentonite) that has flowed through the membrane. Therefore, the resistance will increase as the cumulative volume filtered increases. The graph then represents the extent to which the membrane fouls so that the feed solution containing 1429 mg/L of bentonite fouls faster than that containing 357 mg/L.

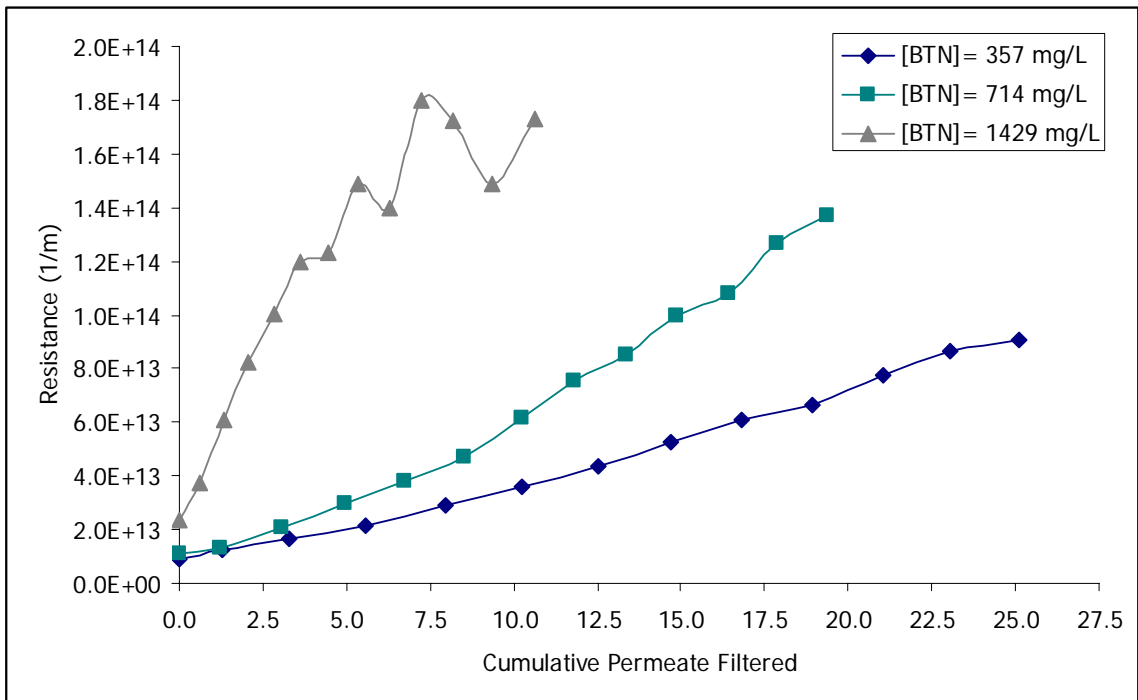


Figure 46. Resistance vs. Cumulative Permeate Filtered for Different Bentonite (BTN) Concentrations

Permeate Quality Results and Discussion

Different bentonite solutions were tested to characterize how clay particles could be rejected by the PRT membrane. These solutions had total solids concentrations of 750 mg/L, 1000 mg/L, and 1600 mg/L.

All concentrations tested yielded permeate water quality that was slightly better than that of the feed samples (See Figures 47, 48, and 49). This meant that the PRT was not effectively able to reject clay particles. This

type of behavior was expected since the pores that were seen using SEM imaging were around an order of magnitude larger than the bentonite particles (refer to Figures 24, 25, and 26). The percent removal that could be credited to the PRT membrane remained under 20% for most of the trials (See Figure 50), revealing that improvements were necessary in order to significantly enhance total solids removal for this type of application.

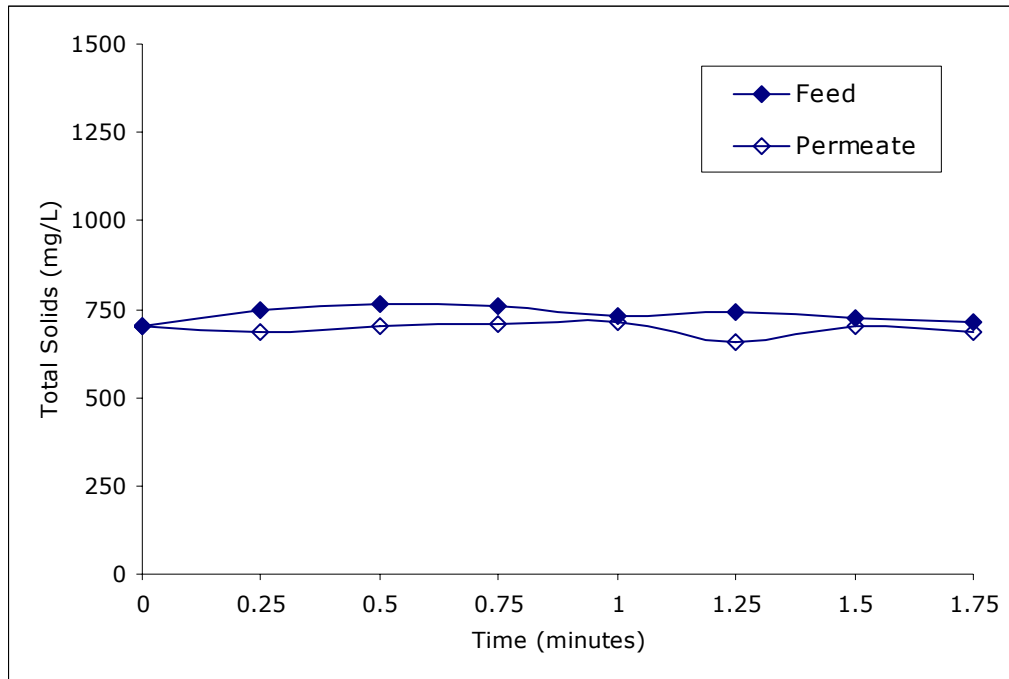


Figure 47. Total Solids Concentration Comparison for Solution Containing 750 mg/L of Bentonite

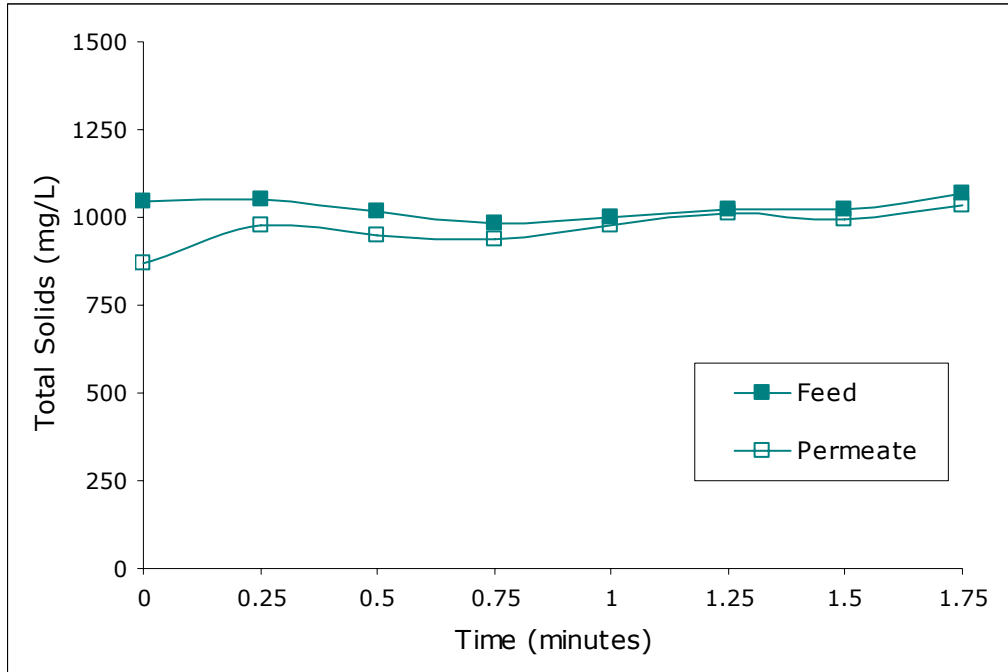


Figure 48. Total Solids Concentration Comparison for Solution Containing 1,000 mg/L of Bentonite

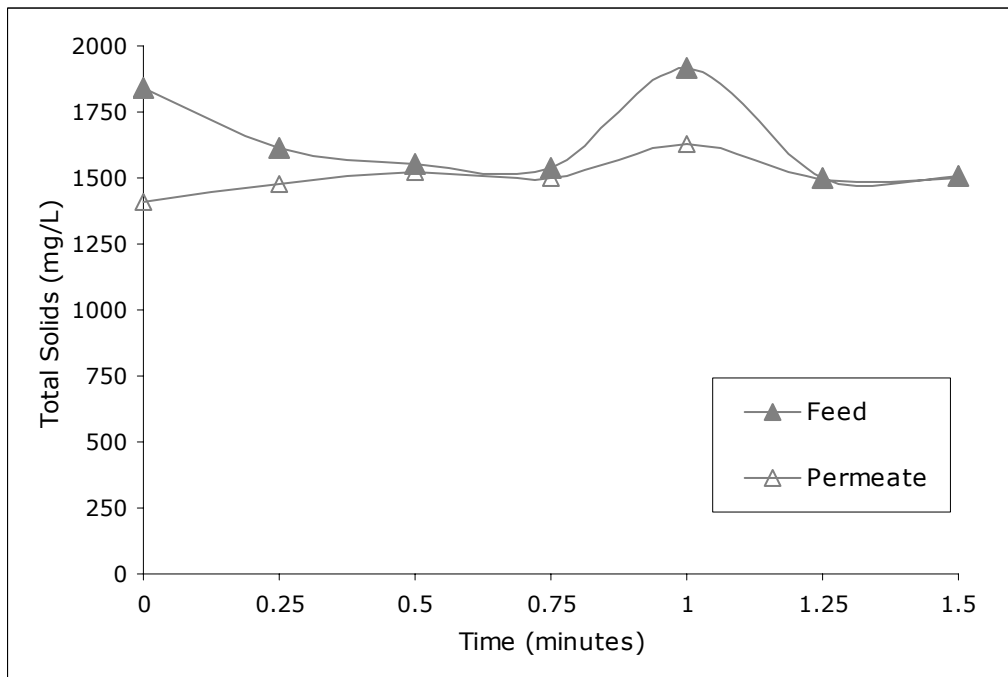


Figure 49. Total Solids Concentration Comparison for Solution Containing 1,600 mg/L of Bentonite

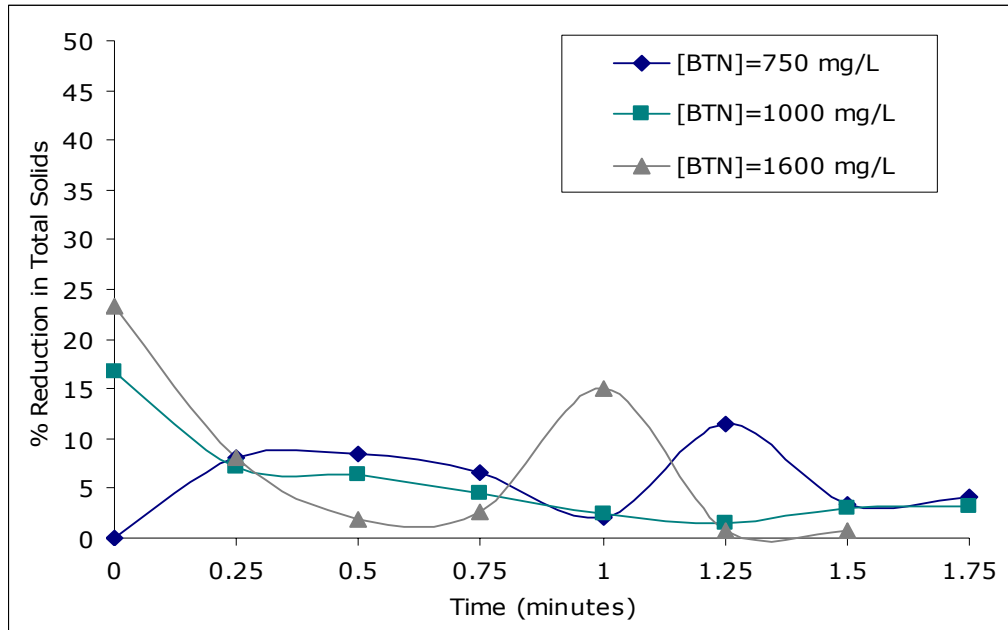


Figure 50. Percent Reduction in Total Solids for Various Bentonite Solutions

Backwashing and Recovery

The data that has been presented so far has shown continuous runs that last between 1 and 3 hours for different tests. The runs are ended after a few hours because the fouling becomes so severe that the permeate flux is difficult to quantify because it is particularly low. However, the membrane can be recovered in most cases when the fouling is reversible and due to a cake layer. This is often the case with bentonite clay. Therefore, trials were conducted to establish an approximate operational interval as well as a backwashing interval.

The chosen concentration was 1,400 mg/L because it was important to verify that the mechanism through which bentonite fouls the membrane, even at a high concentration, consists mostly of the formation of a cake layer and not pore blocking or other forms of irreversible fouling. Although different combinations of operation interval and backwash interval were tested, only the most efficient will be presented within this section. All other data can be found in Appendix E. The two combinations of operational and backwashing intervals that were most efficient in terms of permeate flux are summarized in Table 4.

Table 4. Backwashing Combinations

Run	Operational Interval (min)	Backwashing Interval (min)
1	30	1
2	15	1

Longer runs were tested, but they resulted in operation of the membrane after severe fouling had occurred. In this case, the permeate flux was almost negligible for an extended period of time, making the combination less efficient. Runs with operational intervals below 15 minutes were not tested because they would have backwashed the membrane before it was required. Different backwashing intervals were used. However, for both runs it was determined that one minute was the optimum value. Shorter intervals yielded lower permeate flux recovery values while longer backwashing intervals did not benefit the recovery and contributed to longer down time.

The following graphs show how the permeate flux is recovered after backwash for both runs.

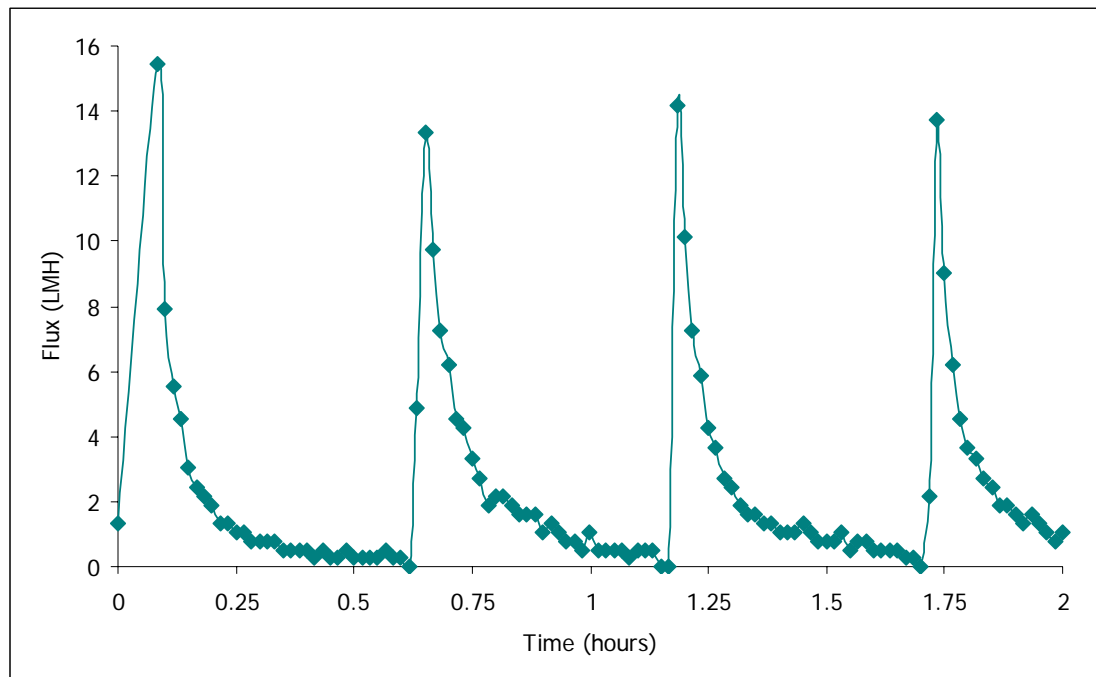


Figure 51. Permeate Flux Recovery After Backwash for Run 1.

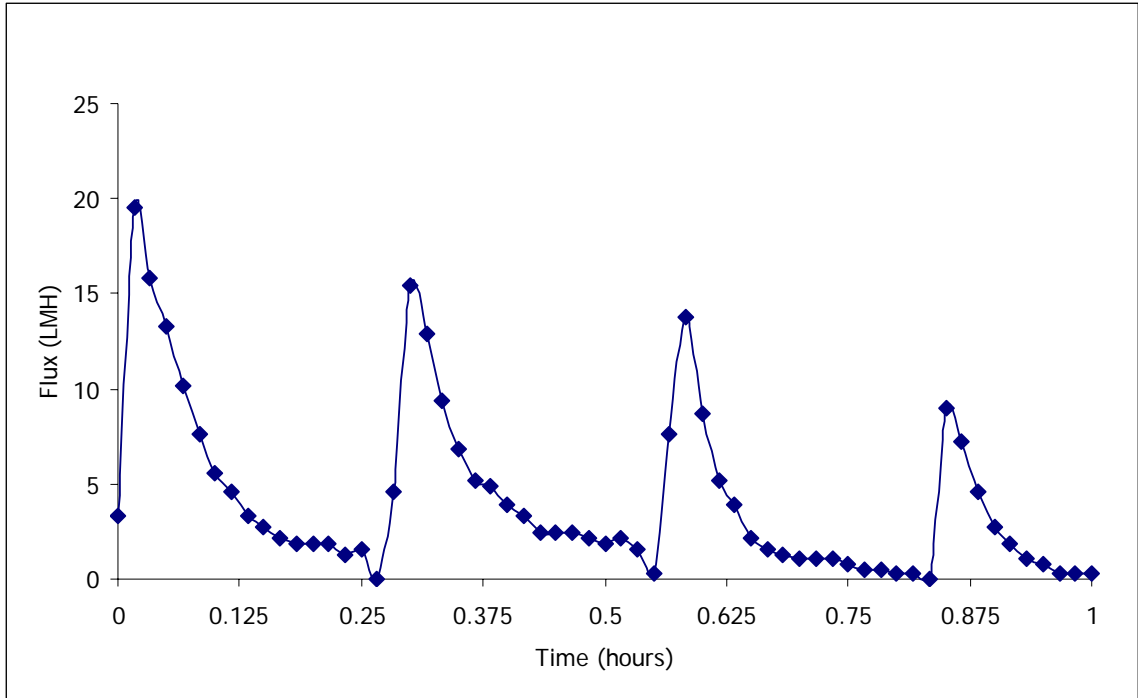


Figure 52. Permeate Flux Recovery After Backwash for Run 2.

It was not expected that run 2 recovered to a higher extent than run 1, as shown in Figures 51 and 52. A possible explanation is that the cleaning procedure was not been done correctly in this specific case, so that there was residual fouling from previous runs. However, this does not comprise other data since this is an isolated case. It is expected that, if repeated, run 1 would result in the same type of recovery as run 2.

A continuously-operated system was also tested in addition to manual backwashing. In this case, solenoid valves were used to reverse the flow through the PRT without reversing the pump direction. The system operated with a bentonite concentration of 714 mg/L. The membrane filtered the feed water during 0.5 hours and ran the backwash cycle during 1.5 minutes. Figure 53 shows the flux data during 4 hours and Figure 54 shows the corresponding TMP data during the same period of time. The continuously-operated system proves that permeate can be obtained on a long-term basis and is not limited to short running intervals.

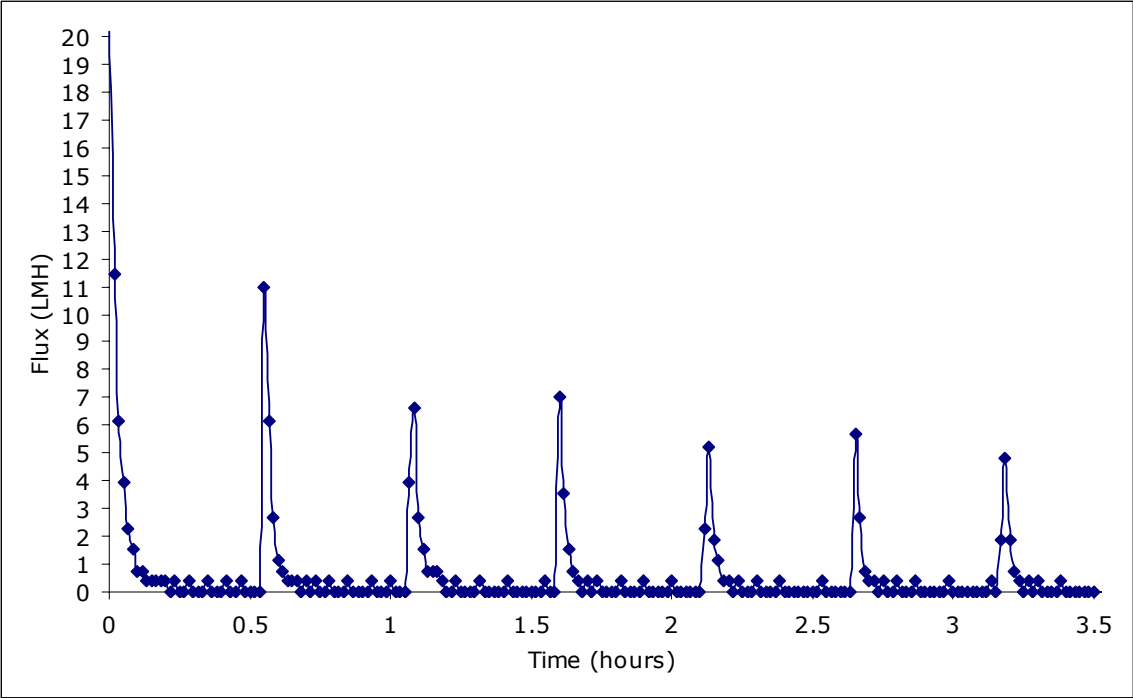


Figure 53. Permeate Flux Recovery Profile for Continuously-Operated System

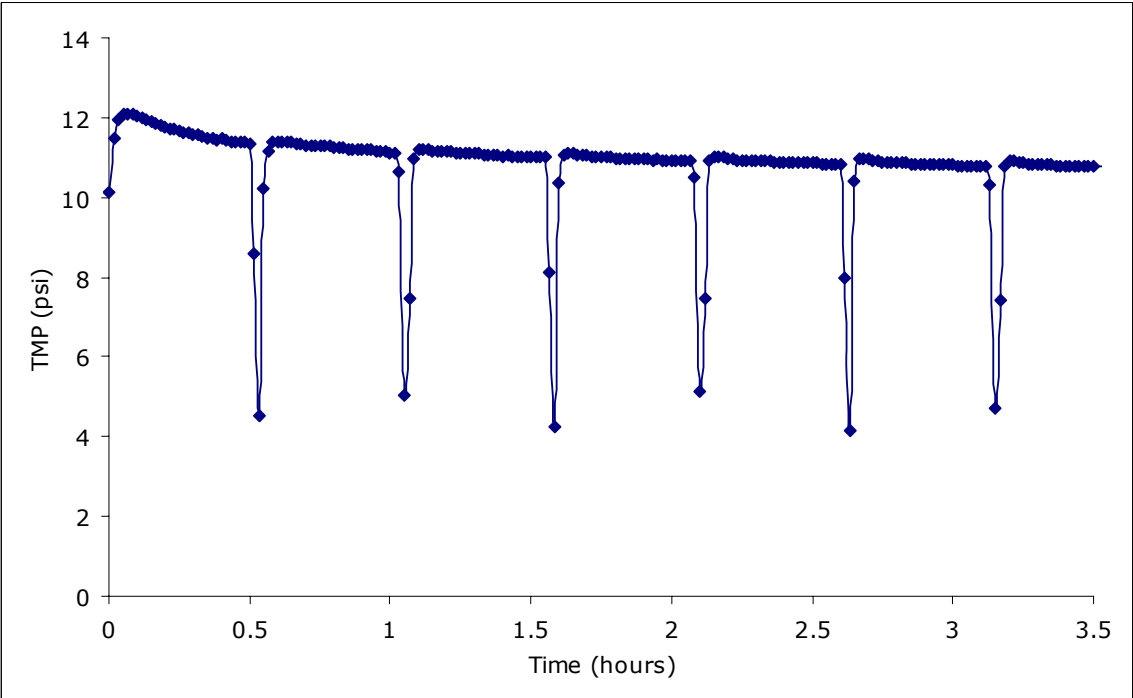


Figure 54. TMP Profile for Continuously-Operated System

4.2.2 Sludge Feed Water

The purpose of adding sludge to the water contained in the reservoir was to simulate impaired source water. This would be typical of areas where access to basic sanitation is lacking, which leads to contamination of the source for potable water in many cases. The characteristics of the solids in this simulated source water are different from the solutions containing bentonite. In this case, particles can be seen by the naked eye and although the turbidity is far from ideal, it is much lower than that of bentonite solutions. The presence of solids can be indicative of pathogens and can also act as a barrier when utilizing disinfection methods.

Permeate Quantity Results and Discussion

Sludge solutions containing different concentrations were tested using the PRT cassette. The flux data indicated that as the total solids concentration increased, the time to reach equilibrium flux decreased (See Figure 55). It was also established that although there were significant differences in the initial flux for the different trials, ultimately the equilibrium flux values were quite similar and below 1 LMH.

Comparatively, Figure 56 shows that much less volume can be obtained from the PRT when using sludge instead of bentonite. In the case of 15 mg/L, less than 5.5 L can be obtained in one hour.

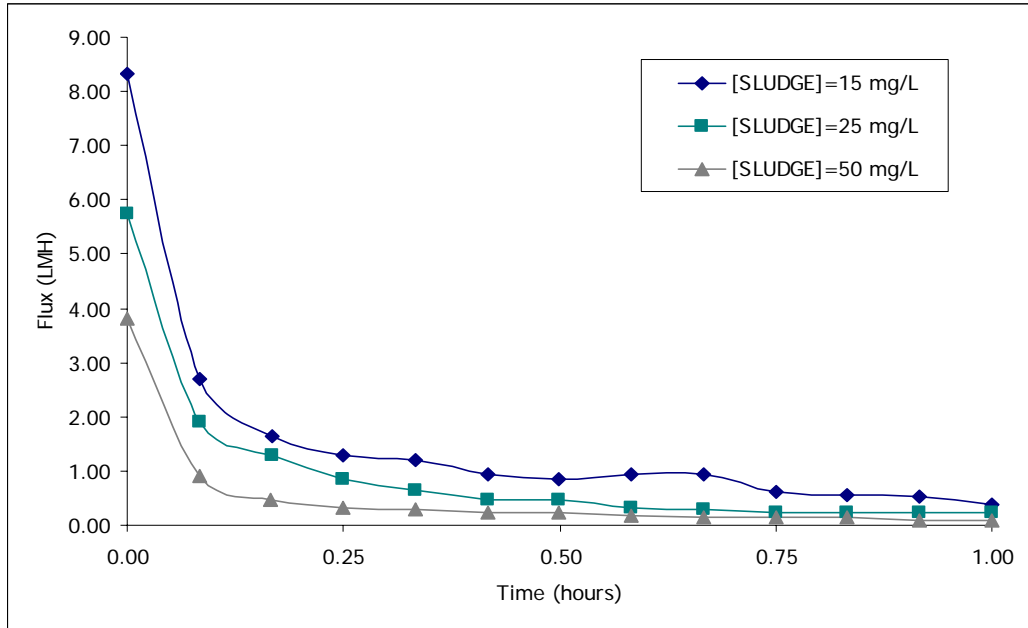


Figure 55. Flux vs. Time for Different Sludge Concentrations

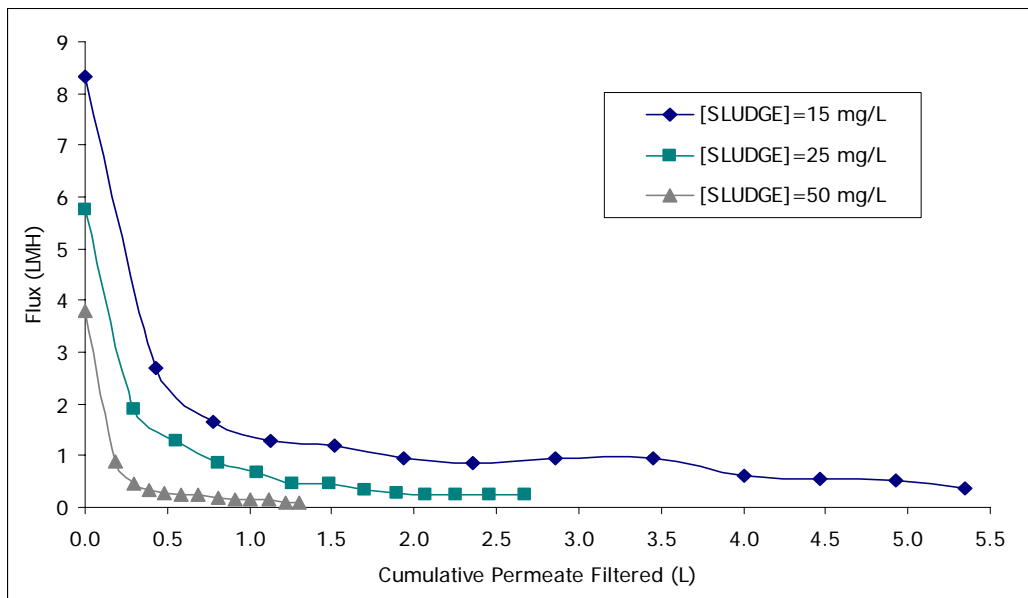


Figure 56. Flux vs. Cumulative Permeate Filtered for Different Sludge Concentrations

In the case of sludge, TMP was similar for the three concentrations tested (See Figure 57). The value was consistently kept below 12 psi and stabilized around 11.5 pounds psi for all trials. The behavior of the curve suggests that solids loading may not significantly impact TMP at low

concentrations. Since doubling the concentration did not double the value of the TMP, it can be assumed that the relationship is not linear. However, if higher solids loadings were tested, the TMP would have to significantly increase to account for the increased concentration. This occurs because a higher concentration feed will deposit more solids on the surface of the membrane as it flows through, increasing the TMP.

Following the same trend as flux, higher resistance was encountered when the feed water contained a higher concentration of bentonite (See Figure 58). This means that the membrane is less permeable at higher solids concentrations because the cake layer build up decreases the permeate flow. Once again, R_m represents the intrinsic membrane resistance that was measured using clean water (See Section 4.1.1) as a means to explain that the resistance due to the presence of sludge is the most severe form of fouling.

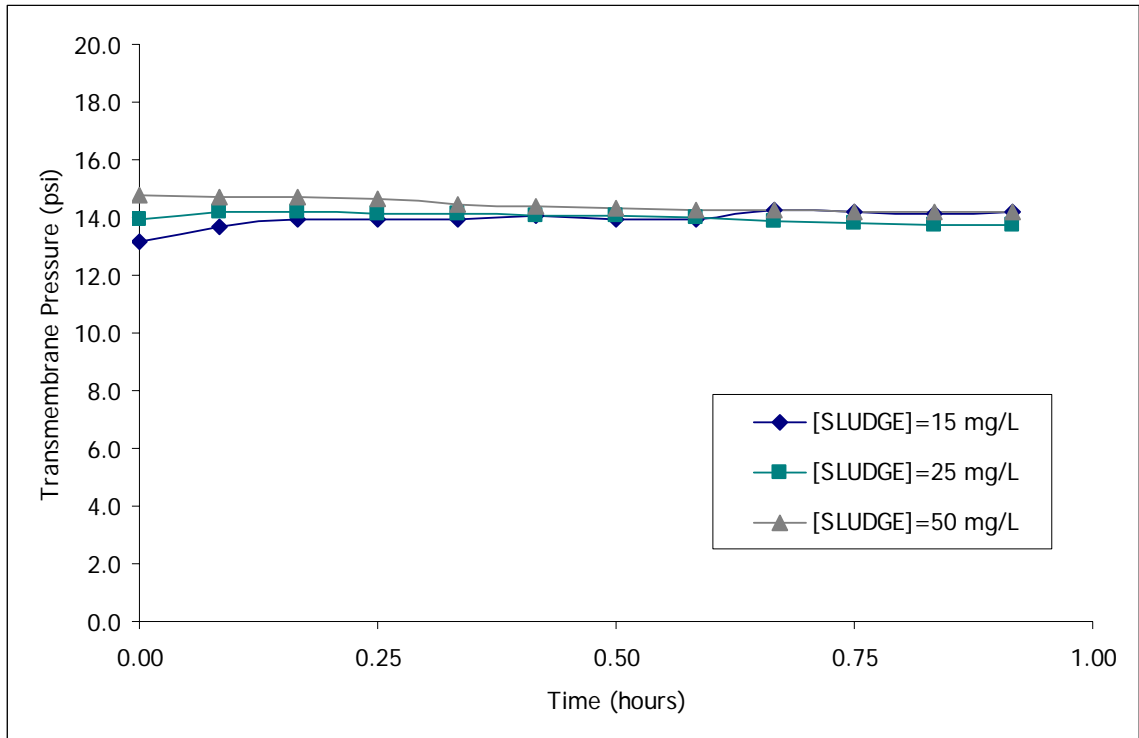


Figure 57. TMP vs. Time for Different Sludge Concentrations

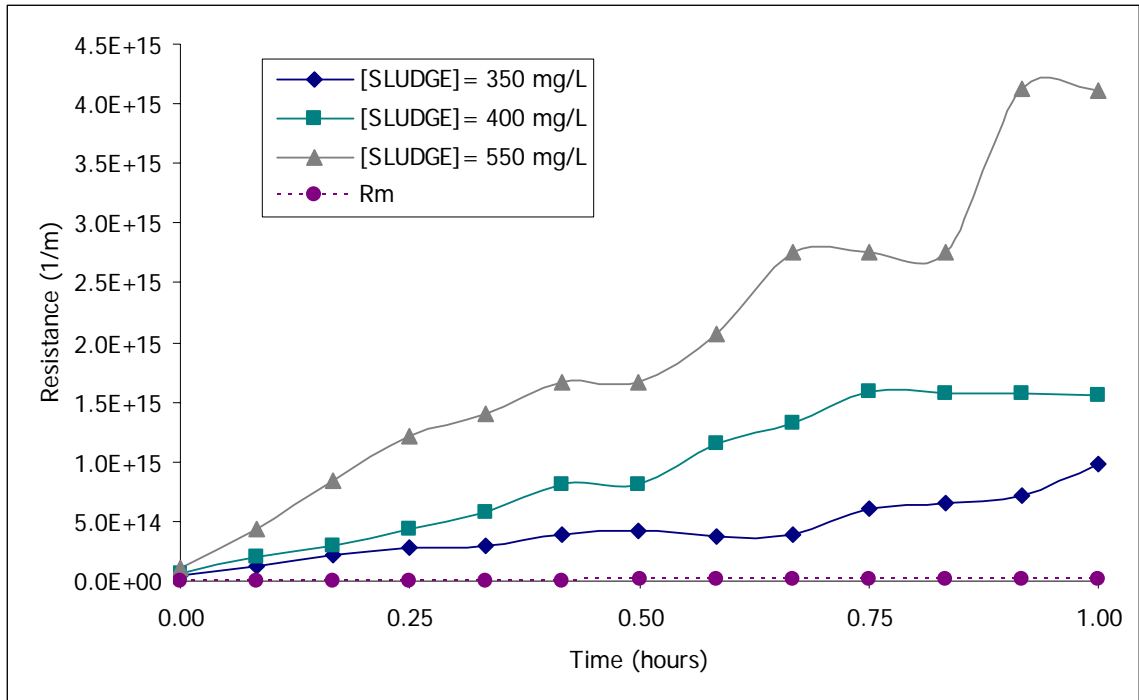


Figure 58. Resistance vs. Time for Different Sludge Concentrations

Figure 59 represents the relationship between resistance and cumulative permeate filtered. The trend seen with bentonite feed water is followed by sludge feed water as well. However, the extent to which fouling occurs is much greater and can be seen when comparing the resistance values for the two types of feed water. In the case of the sludge solutions, the resistance is over an order of magnitude greater than with bentonite solutions. Also, the membrane experiences fouling to a higher extent when the total solids concentration is increased as seen by the reduced amount of cumulative permeate filtered and the steep slope of the curve.

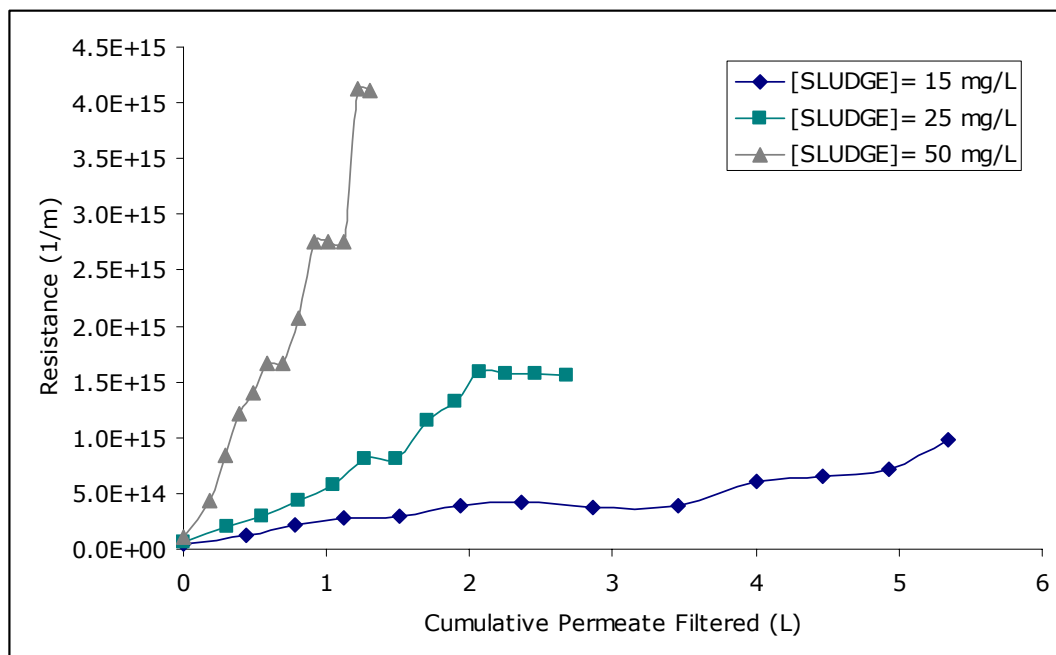


Figure 59. Resistance vs. Cumulative Permeate Filtered for Different Sludge Concentrations

Permeate Quality Results and Discussion

Sludge concentrations were prepared by diluting anaerobic digestion sludge in tap water. The characteristics for each solution are summarized in Table 5. The purpose of using different sludge solutions was to establish the rejection capacity of the PRT when exposed to various solids loadings. In general, a lower solids loading yielded permeate with a greater percent removal of solids. However, permeate water quality did not remain constant.

Table 5. Summary of Sludge Solutions Tested with PRT

Solution	Volume of Anaerobic Sludge	Volume of Tap Water	Average Total Solids Concentration (Feed)
1	400 ml	6.75 L	350 mg/L
2	450 ml	6.75 L	400 mg/L
3	620 ml	6.75 L	550 mg/L

Figure 60 corresponds to a feed solution with a concentration of 350 mg/L of total solids. This test yielded the most consistent permeate water

quality and provided the highest percent removal of the three solutions tested (see Figure 63). Figure 60 corresponds to a feed solution with a total solids concentration of 400 mg/L. In this case, the permeate water quality followed the exact same trend as the feed water quality with a solids removal that remained under 20%. Figure 62 corresponds to a total solids concentration of 550 mg/L, which resulted in the lowest percent removal (refer to Figure 63).

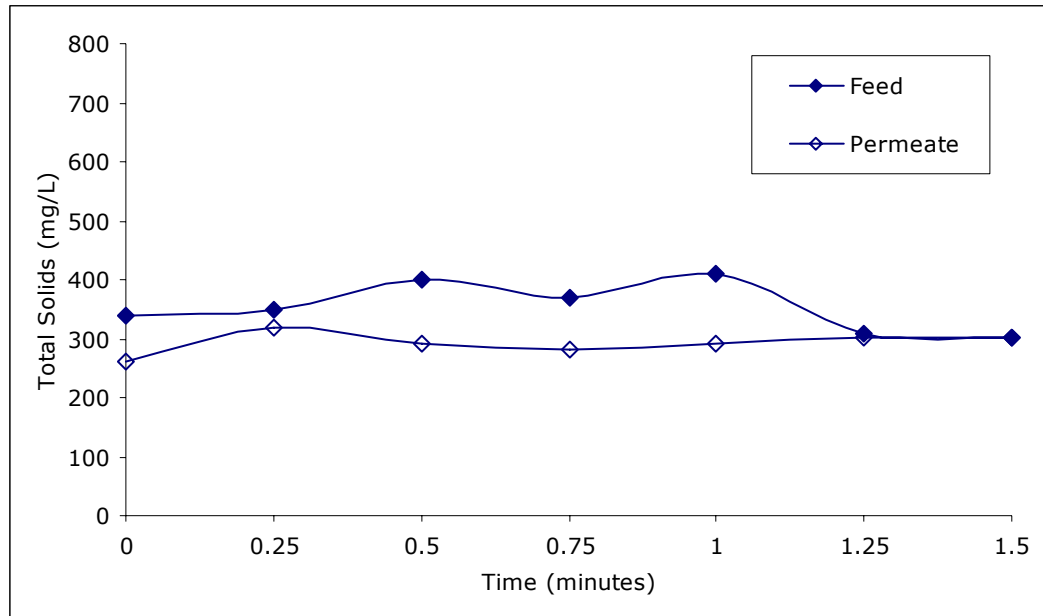


Figure 60. Feed and Permeate Total Solids Concentration for Solution 1 (Sludge)

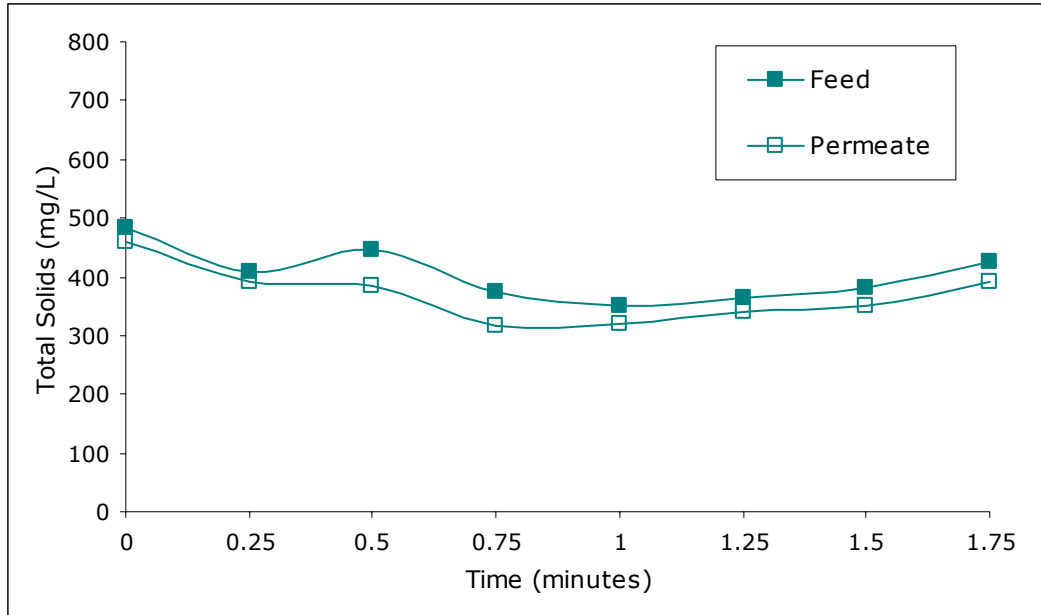


Figure 61. Feed and Permeate Total Solids Concentration for Solution 2 (Sludge)

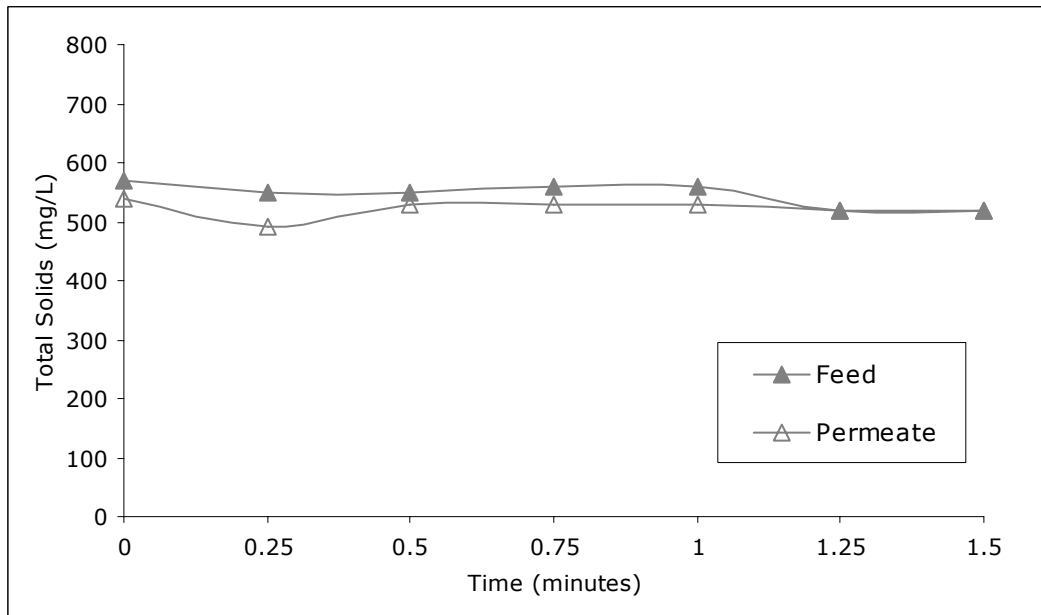


Figure 62. Feed and Permeate Total Solids Concentration for Solution 3 (Sludge)

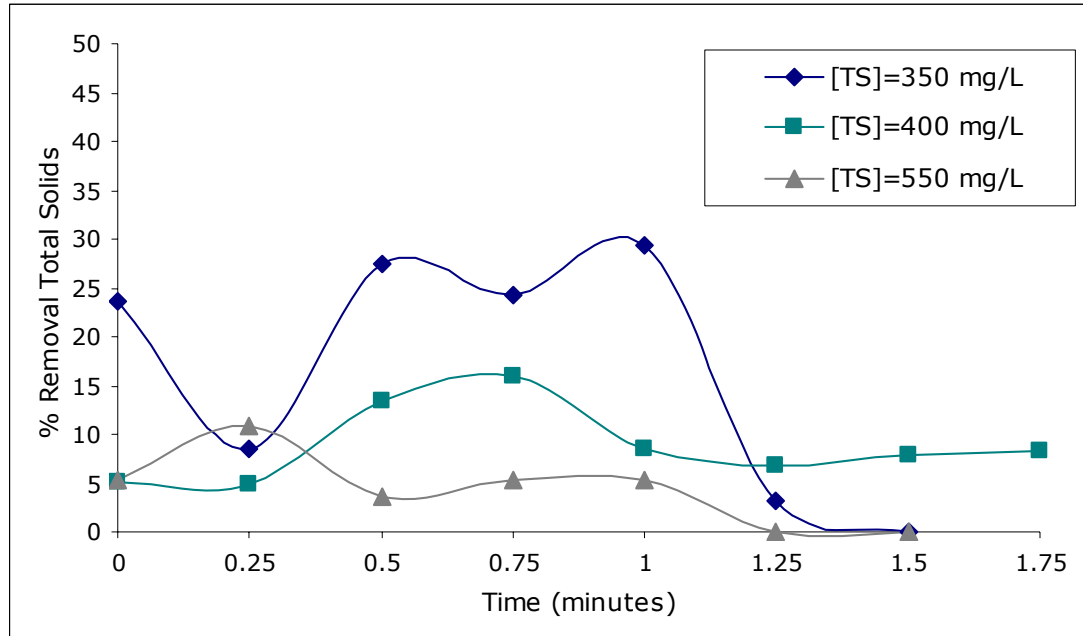


Figure 63. Percent Removal of Total Solids for Sludge Solutions 1, 2, and 3 (Sludge)

4.3 Flocculation-Enhanced Filtration

The focus of this phase was to study the results of adding chitin as a flocculant while still challenging the PRT with the same types of solutions that were used in the second phase (Section 4.2).

4.3.1 Chitin Feed Water

The purpose of adding chitin to the water contained in the reservoir was to understand the behavior of the PRT system with this flocculant. Jar testing was useful to ensure floc formation was occurring. However, the flocs formed did not have good settling characteristics so attempting to optimize the dosage was not possible with this procedure. Since the chitin has a somewhat variable particle size, it was also necessary to establish the behavior of different sizes and whether or not these particles were effectively removed. Although actual solids sampling was not conducted for this section, the flux characteristics were used to determine how the flakes could be behaving. For example, a reduction in flux with a certain pore size could

indicate that this size was effectively blocking the pores and not being able to get through the PRT membrane.

Chitosan was tested a few times in the flocculation-enhanced filtration phase but its characteristics as feed water were not explored. It is not expected that chitosan will have a greater effect on flux than chitin, since its physical appearance is powdery and not flaky. The main concern with chitin was that the shape and size of the flakes would reduce the permeate flux significantly.

Permeate Quantity Results and Discussion

Chitin solutions containing different concentrations were tested using the PRT cassette. The flux data indicated that the flux at equilibrium did not vary significantly from the initial flux (See Figure 64). This is a similar behavior to that seen for clean water trials, where the absence of particles translates into a fairly constant permeate yield. It can be inferred, then, that chitin particles alone are not able of forming a cake layer on the membrane surface. If this were the case, a flux decline during the first 0.5 hours of running the system would be evident, such as with bentonite and sludge solutions. Furthermore, the flux values that were obtained with different chitin concentrations are almost identical to those obtained with only clean water running through the system. This further reiterates that chitin particles alone do not deposit on the membrane surface. As expected from this graph, Figure 65 shows that the volume passed through the membrane during all trials was similar.

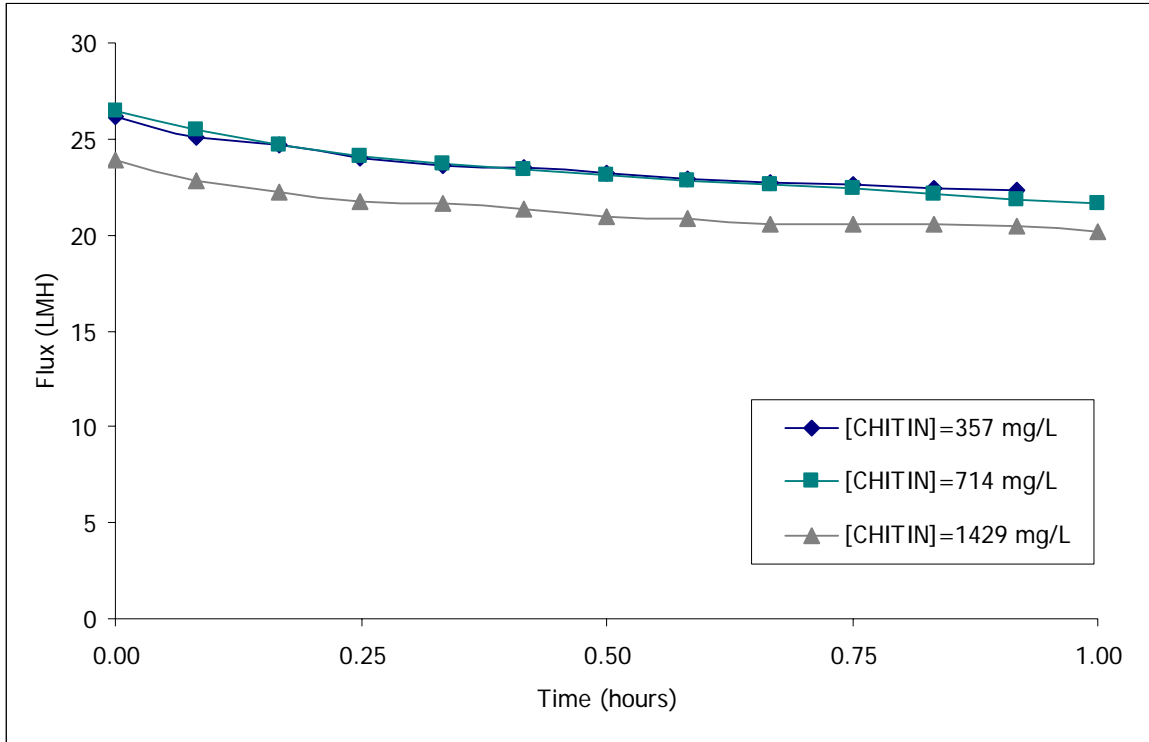


Figure 64. Flux vs. Time for Different Chitin Concentrations

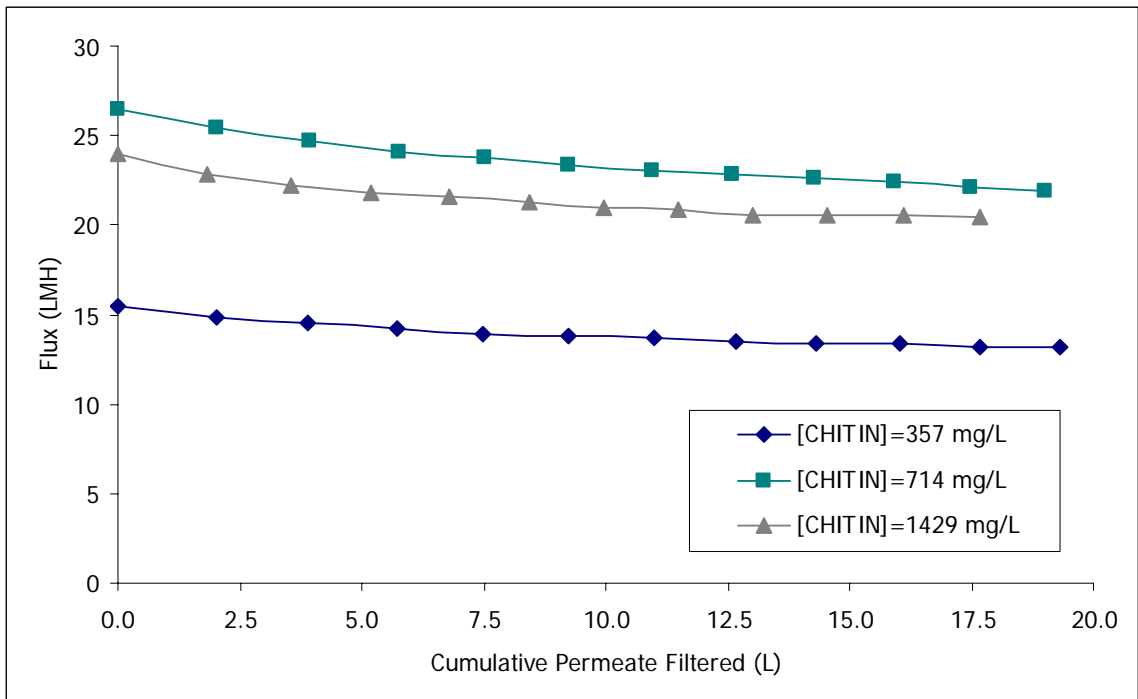


Figure 65. Flux vs. Cumulative Permeate Filtered for Different Chitin Concentrations

Further investigation of the behavior of the PRT system when exposed to chitin particles was performed given these results. It was important then to understand the effect of particle size on filtration characteristics since the distribution included various sizes. The three mesh sizes chosen were size 60 (opening 250 μm), size 80 (opening 180 μm), and size 200 (opening 75 μm). The chitin concentration was kept constant for all trials at a value of 266 mg/L. It was expected that the smaller chitin particles would clog the pores, leading to a rapid decline in flux and a lower equilibrium flux value. However, this was not the case for the trials performed. Instead, the larger chitin particles had the lowest flux while the smallest chitin particles had the highest flux (See Figure 66). The trend becomes even more evident when examining the flux versus cumulative permeate volume graph (See Figure 67).

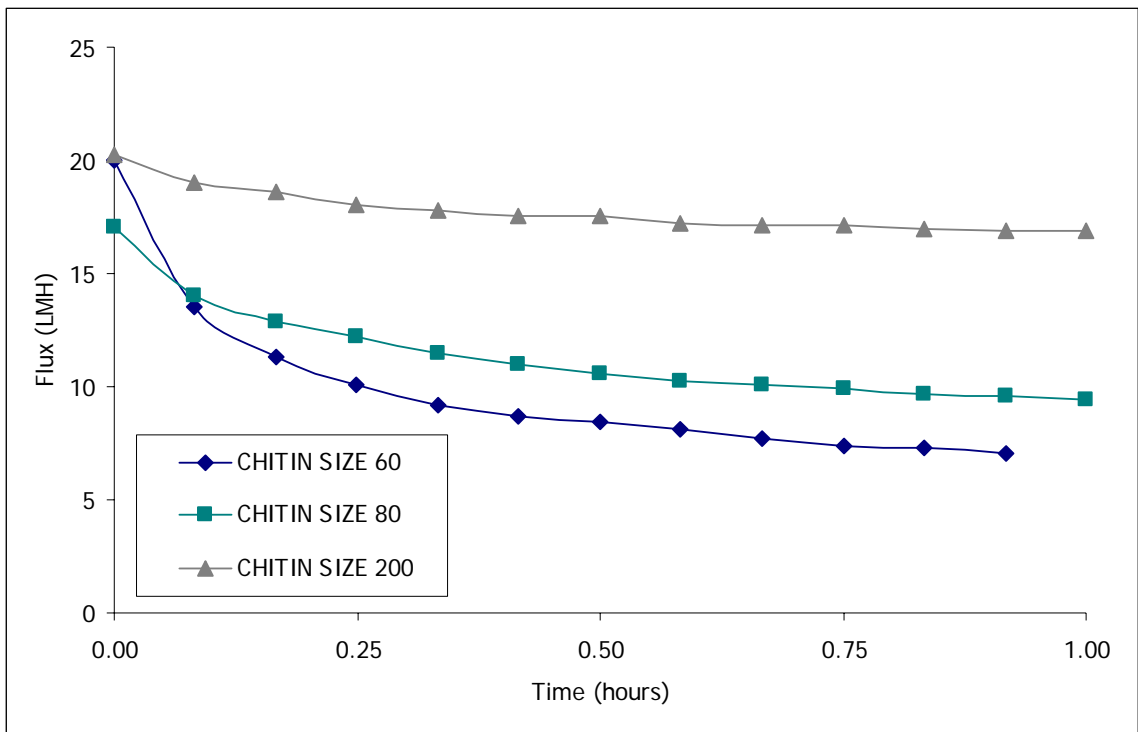


Figure 66. Flux vs. Time for Different Chitin Sizes

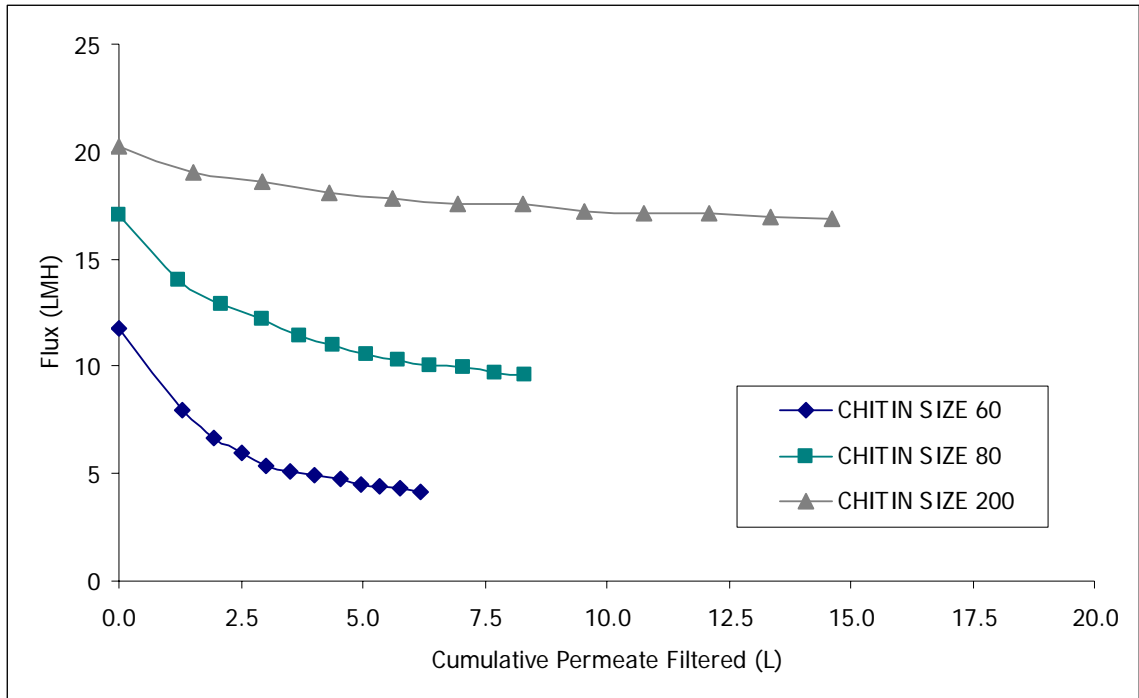


Figure 67. Flux vs. Cumulative Permeate Filtered for Different Chitin Sizes

This unexpected behavior can be explained if considering the PRT pore size and the chitin particle sizes. For example, a mesh size 200 corresponds to particle diameter between 75 μm and 150 μm . These flakes are much smaller than the pores that were observed through SEM imaging. Therefore, the chitin particles of size 200 are not being retained by the membrane. This is the reason why the flux is higher for this trial and there is more volume being able to flow across the membrane as compared to the other two chitin sizes. The size 60 and size 80 chitin are being effectively rejected by the membrane so that their stabilized flux is lower.

Figure 68 shows TMP as a function of time for the different chitin sizes. The profile of this graph corresponds to the presented data for flux. A lower TMP is obtained when using the smaller particles because these do not block the pores like the larger particles. Furthermore, resistance shows this same type of phenomenon since the values obtained are lower for the smallest chitin particle size (See Figure 69).

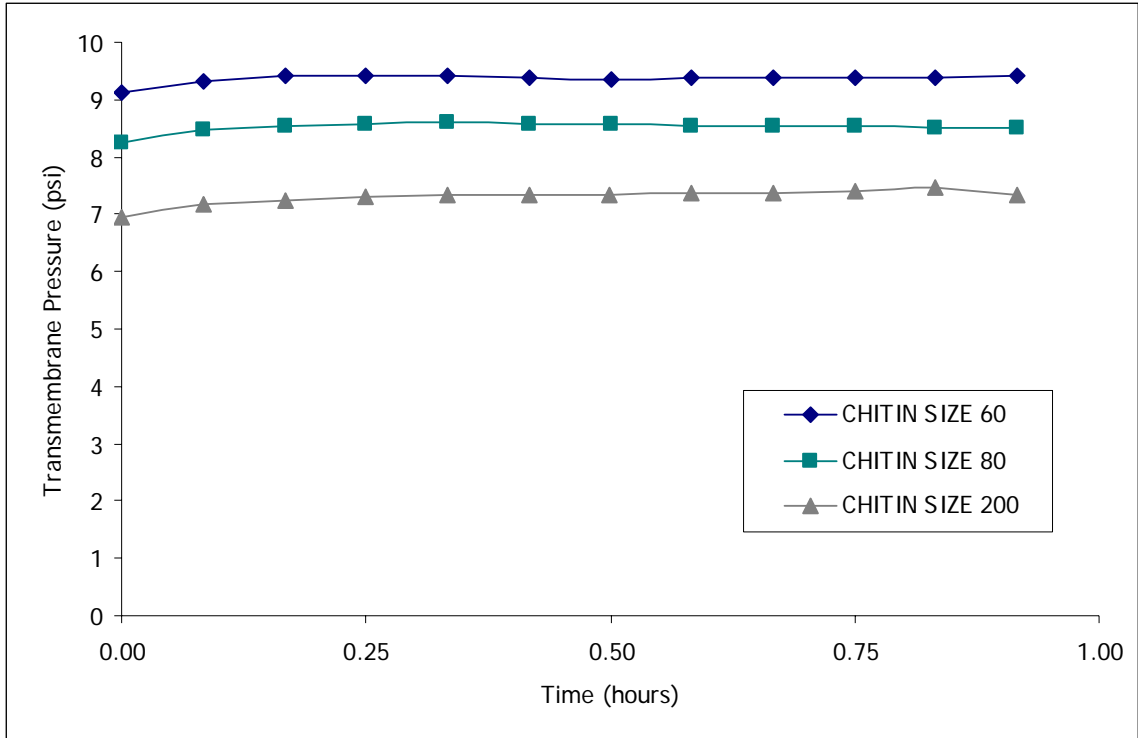


Figure 68. TMP vs. Time for Different Chitin Sizes

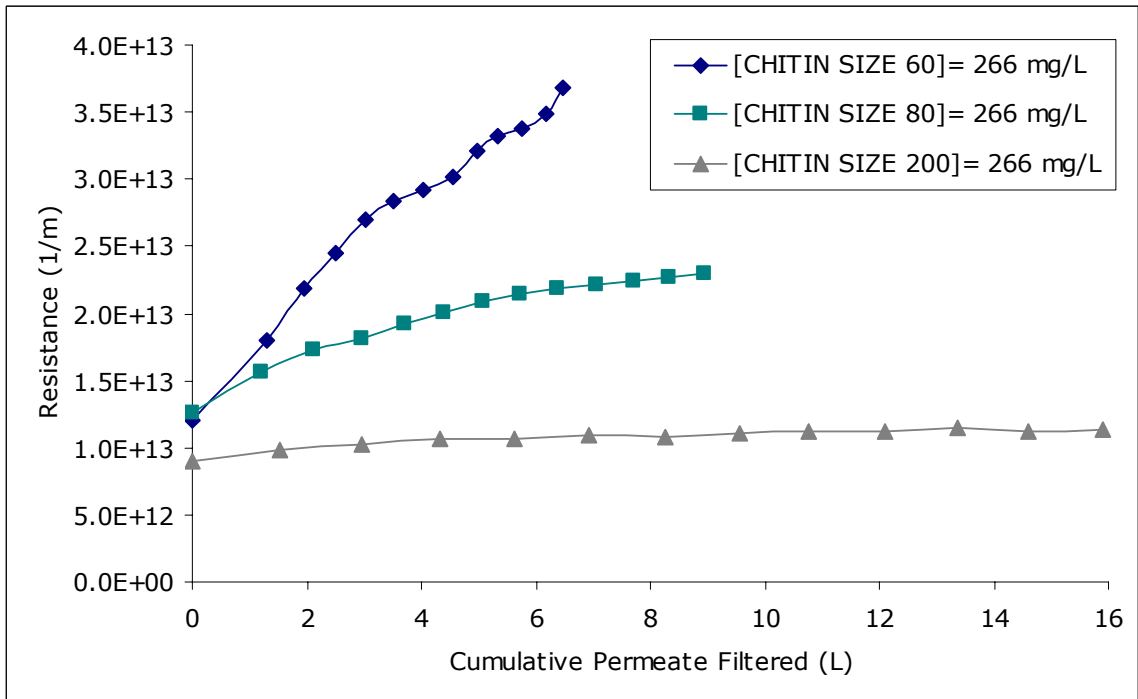


Figure 69. Resistance vs. Time for Different Chitin Sizes

Figure 70 reiterates that the smaller chitin particles are not able to effectively block the PRT pores and are rather able to flow through the membrane. The particles retained by size 60 and 80 sieves, on the other hand, show an increasing resistance profile as the cumulative permeate volume is also increased. This represents fouling in the membrane that occurs because the chitin flakes can block the membrane pores. The flat profile of the size 200 chitin (the smallest particle size) is similar to that of clean water, suggesting that the presence of these flakes does not foul the membrane.

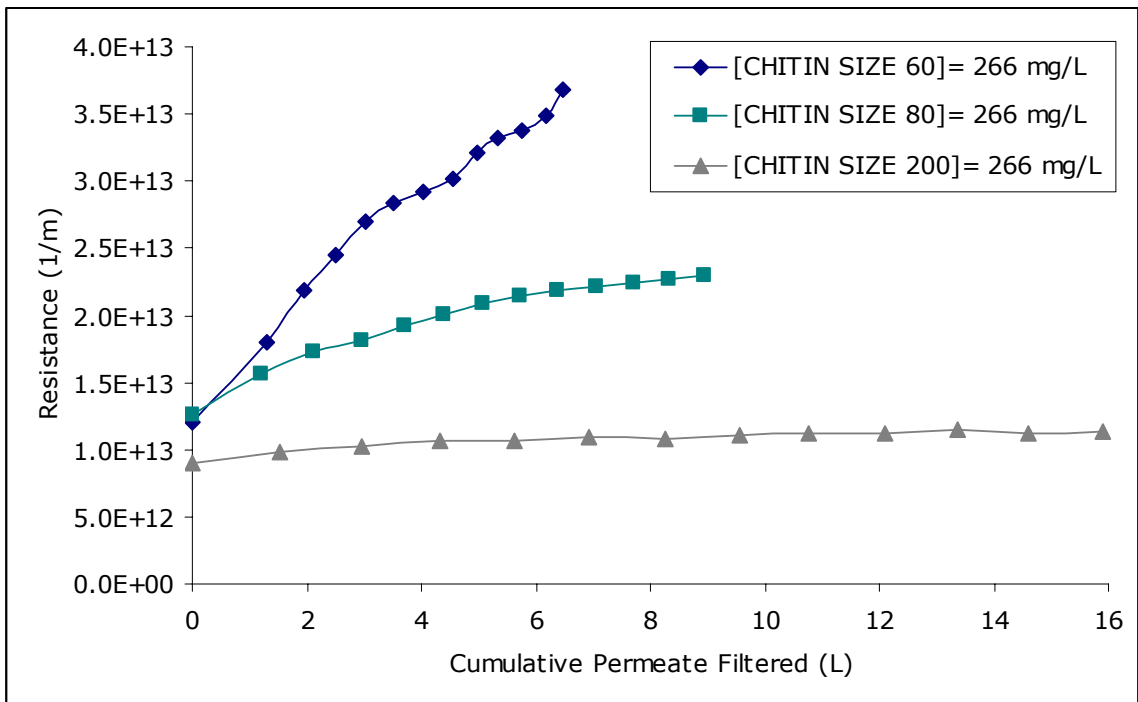


Figure 70. Resistance vs. Cumulative Permeate Filtered for Different Chitin Sizes

4.3.2 Bentonite and Chitin Feed Water

Various chitin amounts were added to various bentonite solutions. Although jar tests were performed to obtain an optimum flocculant concentration, the flocs formed did not have good settling characteristics. This made identifying the effectiveness of a specific dose difficult. Since jar

testing was not useful in determining optimum chitin concentrations, literature values were used (Divakaran and Pillai, 2002).

Mixing was allowed for 1 minute to allow for rapid mixing and then followed by 4 minutes at a low speed to allow for flocculation. The mixing was done for flocculant-containing solutions to promote the formation of flocs that could be easily rejected by the PRT cassette.

Permeate Quantity Results and Discussion

The addition of chitin affected the permeate flux (See Figure 71). This was the expected behavior since the chitin flakes are thought to block the pores and form a cake layer on the PRT's surface. Although this might be seen as a negative effect because less permeate can be obtained from the membrane, it can also be shown that the permeate will have a better quality (represented by a lower total solids concentration). Therefore, the use of the flocculant can be helpful overall for the process. As mentioned earlier, the relationship between rejection and flux is a trade off since it is difficult to obtain both at the same time.

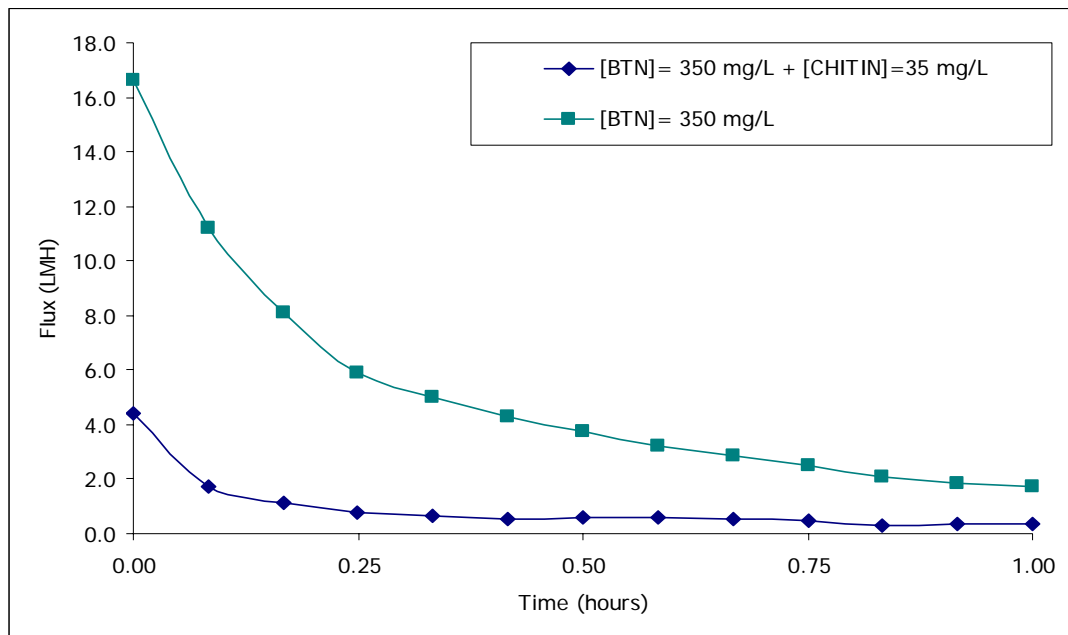


Figure 71. Effect of Chitin Addition on Bentonite Feed Water Flux

Permeate Quality Results and Discussion

A high bentonite concentration was chosen to establish whether or not chitin addition had a positive impact on the permeate water quality. The solution containing bentonite had a total solids concentration of 1,000 mg/L while the solution containing bentonite and chitin had a total solids concentration of 1,100 mg/L. The difference in the concentrations was the result of chitin addition. Table 6 summarizes the testing solutions used.

Table 6. Testing Solutions for Bentonite During Flocculation-Enhanced Filtration Phase

Solution	Bentonite Concent. (mg/L)	Chitin Concent. (mg/L)	Avg Total Solids (mg/L)
Bentonite	1,000	N/A	1,000
Bentonite and Chitin	1,030	70	1,100

Figure 72 shows that there was less than a 10% improvement in water quality (in terms of total solids) after filtration for the solution containing only bentonite. However, upon chitin addition, the permeate quality drastically improved. Furthermore, the feed solution containing both bentonite and chitin had a higher total solids concentration and consistently delivered permeate with a lower total solids concentration than the solution containing only bentonite. Percent removal of total solids also shows this effect (see Figure 73).

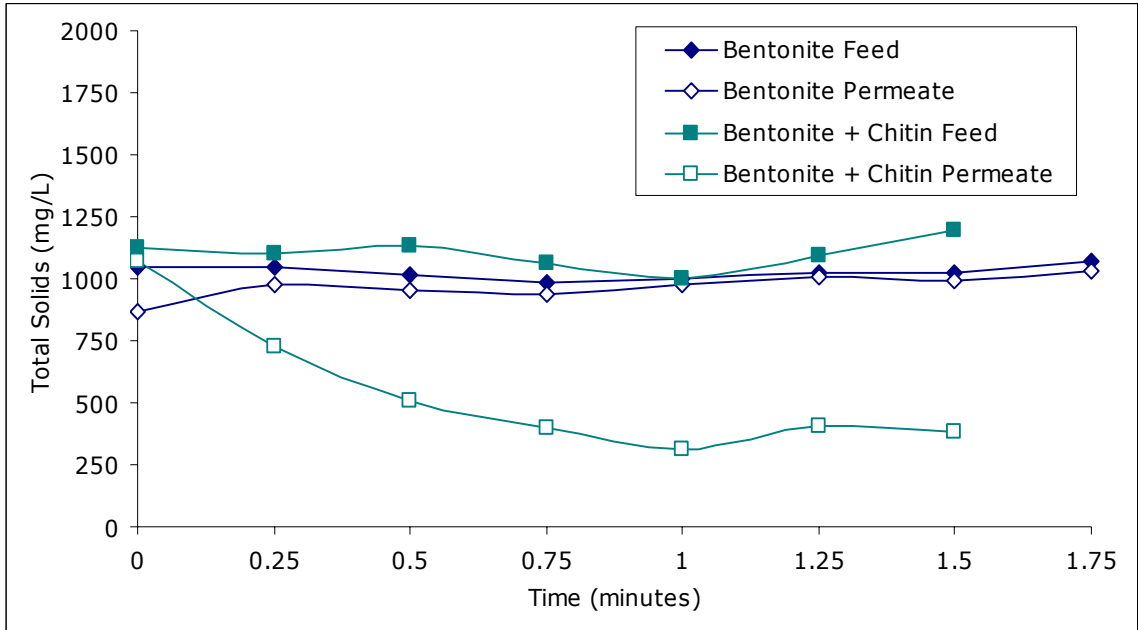


Figure 72. Effect of Chitin Addition on Total Solids Concentration in the Permeate

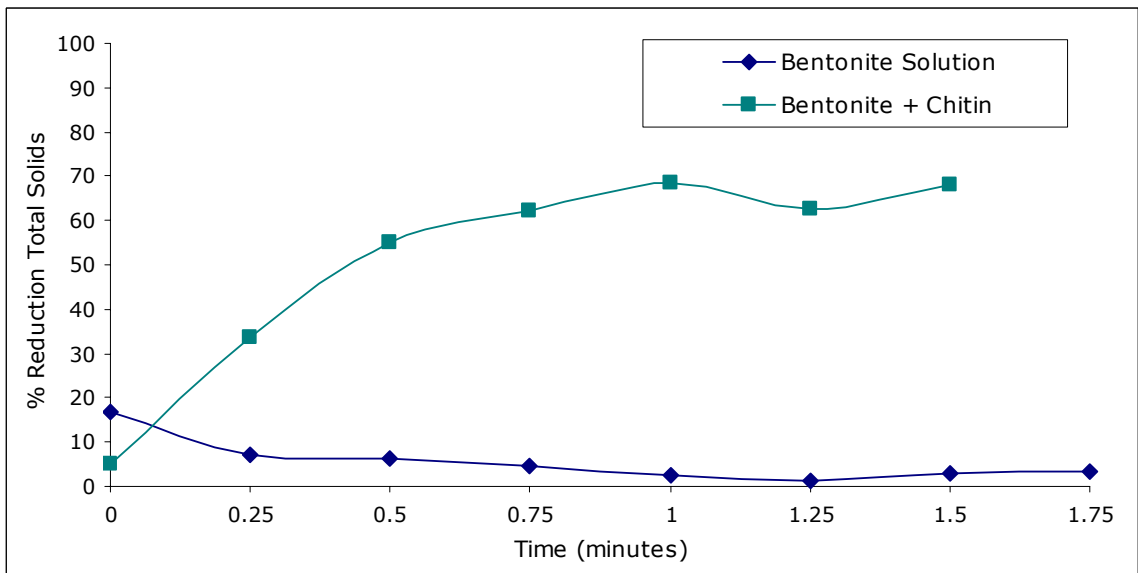


Figure 73. Effect of Chitin Addition on Percent Reduction of Total Solids

It is thought that the improvement of permeate water quality upon addition of chitin occurs through surface precipitation and charge attraction (McKay *et al.*, 1989; Evans *et al.*, 2002; Rae and Gibb, 2003). Jar testing did not reveal readily settling flocs although the formation of these was

observed. For the purposes of this the type of system being tested, it is the formation of actual flocs, and not their settleability properties, that will ultimately benefit the process.

4.3.3 Sludge and Chitin Feed Water

Chitin was added to various sludge solutions and allowed to mix slowly for several minutes. This was done to promote the formation of flocs that could be rejected by the PRT membrane.

Permeate Quantity Results and Discussion

As seen in Figure 74, the addition of chitin to sludge solutions helped attenuate the effect of doubling the sludge concentration. Therefore, although the total solids concentration was doubled, the flux through the PRT was not halved. In trials using sludge alone for the feed (see Section 4.2.2), the impact of total solids concentration was much greater as compared to solutions having chitin. Although the initial flux showed significant differences, the steady state flux that was reached after one hour of running the system was almost the same.

This same trend was observed for TMP (See Figure 75). However, it was unexpected that the solution with lower total solids concentration recorded higher TMP. However, the difference was less than 5%, which makes the two values virtually the same. This means that upon the addition of chitin, doubling the total solids concentration could have a negligible effect on TMP.

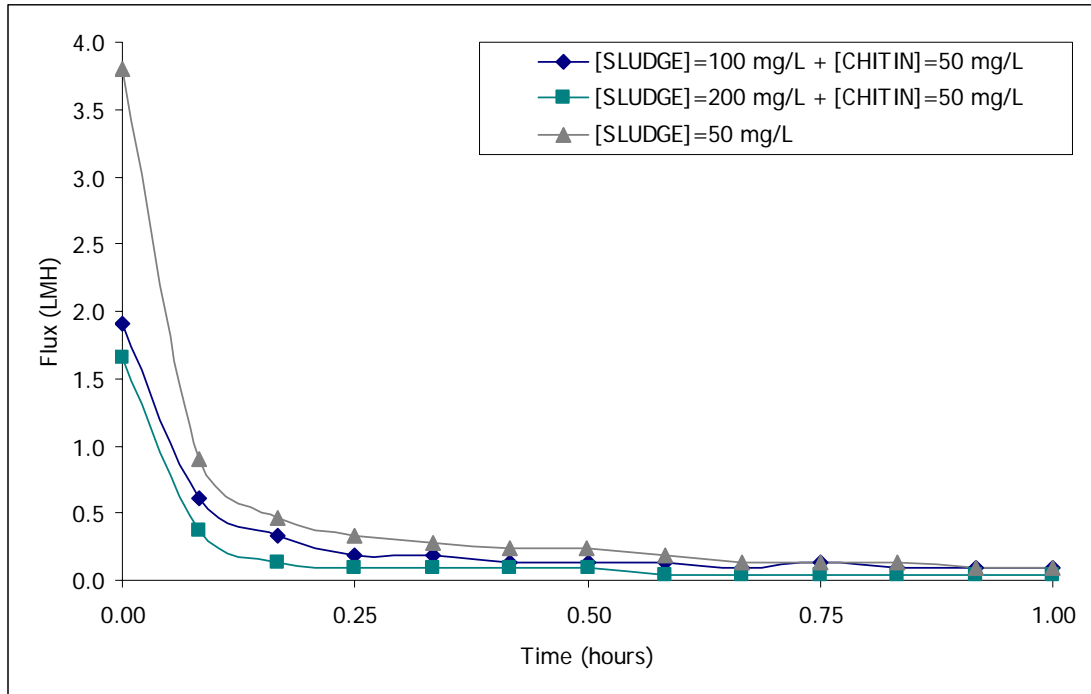


Figure 74. Flux vs. Time for Different Sludge Concentrations

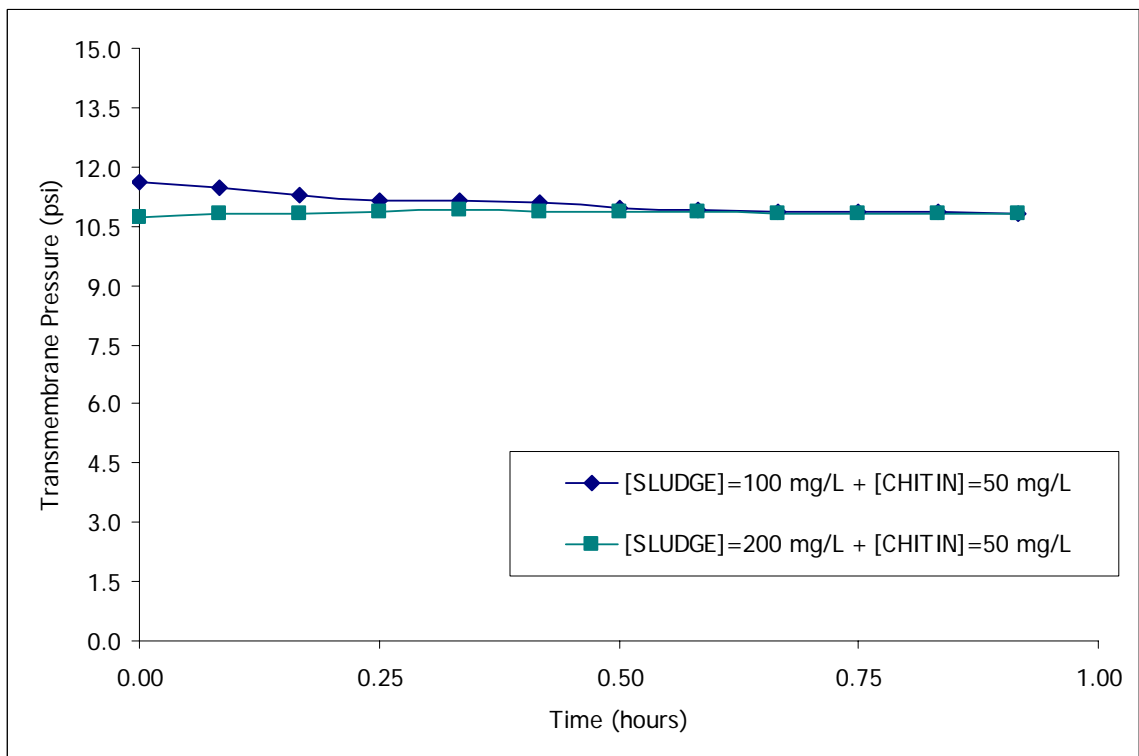


Figure 75. TMP vs. Time for Different Sludge Concentrations

Permeate Quality Results and Discussion

Different sludge solutions (See Table 7) were used to test the effect of chitin addition on permeate quality. In general, the addition of chitin reduced the total solids concentration in the permeate. However, for the three trials there was a significant improvement in the permeate which was followed by a period during which the quality worsened (See Figures 76, 77, and 78). This might suggest that there is a cake layer build-up that occurs and contributes to enhancing the rejection of the PRT. This translates into lower permeate total solids concentration. However, this cake layer seems to break through at some point during the run and that is why the permeate water quality decreases again.

Table 7. Testing Solutions for Sludge During Flocculation-Enhanced Filtration Phase

Solution	Anaerobic Sludge Added (ml)	Tap Water Added (L)	Chitin Concent. (mg/L)	Avg Total Solids (mg/L)
1	450	6.75 L	50	400
2	510	6.75 L	50	450
3	560	6.75 L	50	500

Overall, the best permeate water quality was observed for the middle concentration, which corresponds to 450 mg/L of total solids (see Figure 79). A picture of the feed water and permeate collected is shown in Figure 80 for side-by-side comparison. The improvement in terms of both particle removal and color is evident.

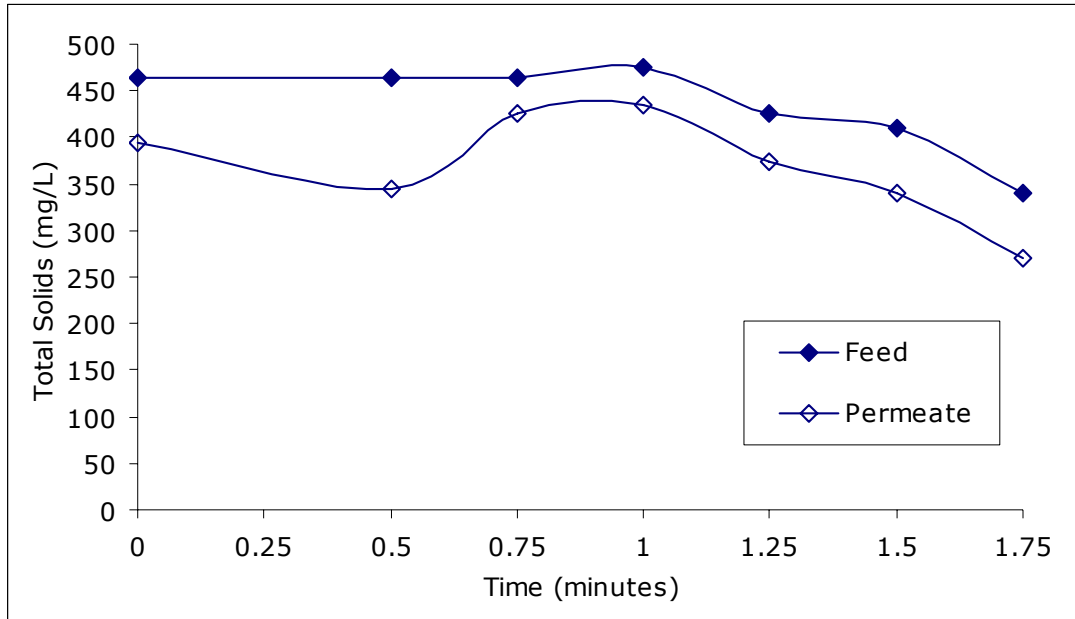


Figure 76. Feed and Permeate Total Solids Concentration for Solution 1 (Sludge and Chitin)

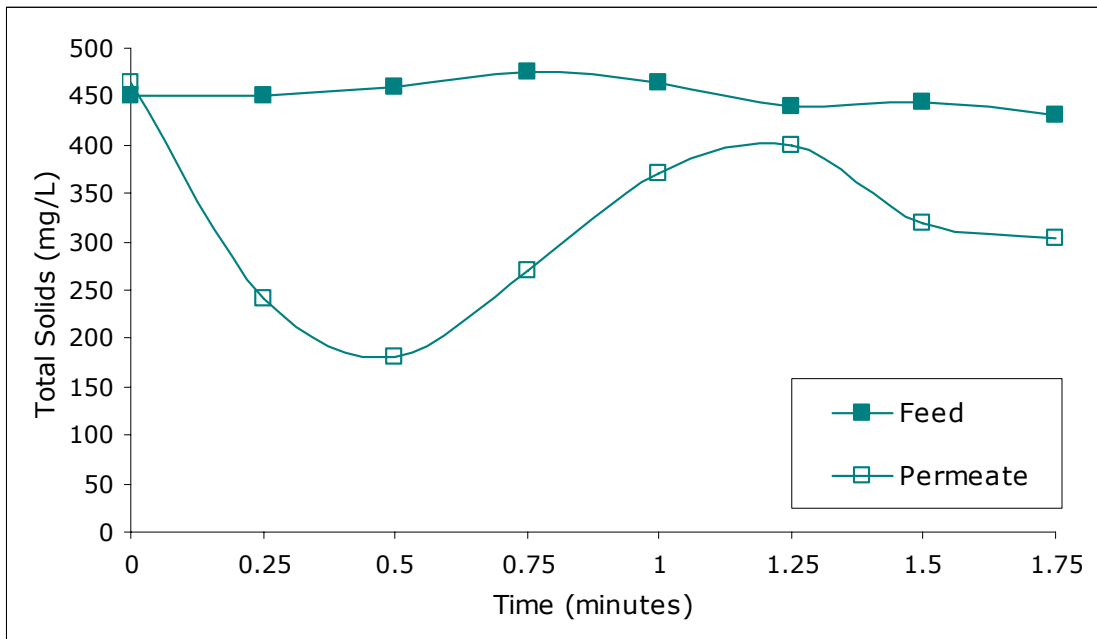


Figure 77. Feed and Permeate Total Solids Concentration for Solution 2 (Sludge and Chitin)

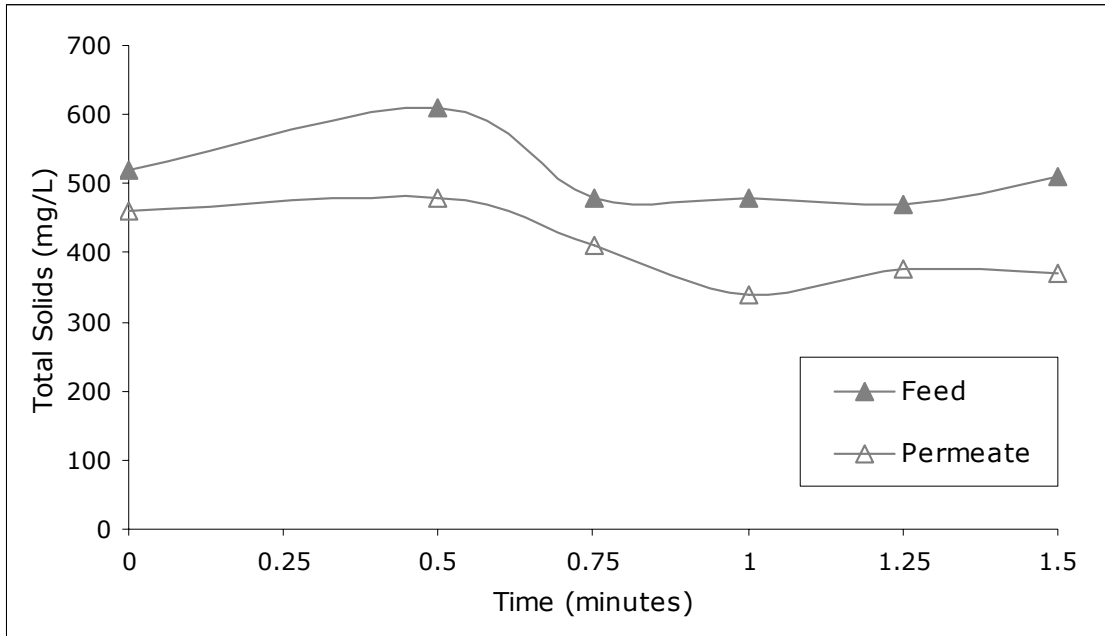


Figure 78. Feed and Permeate Total Solids Concentration for Solution 3 (Sludge and Chitin)

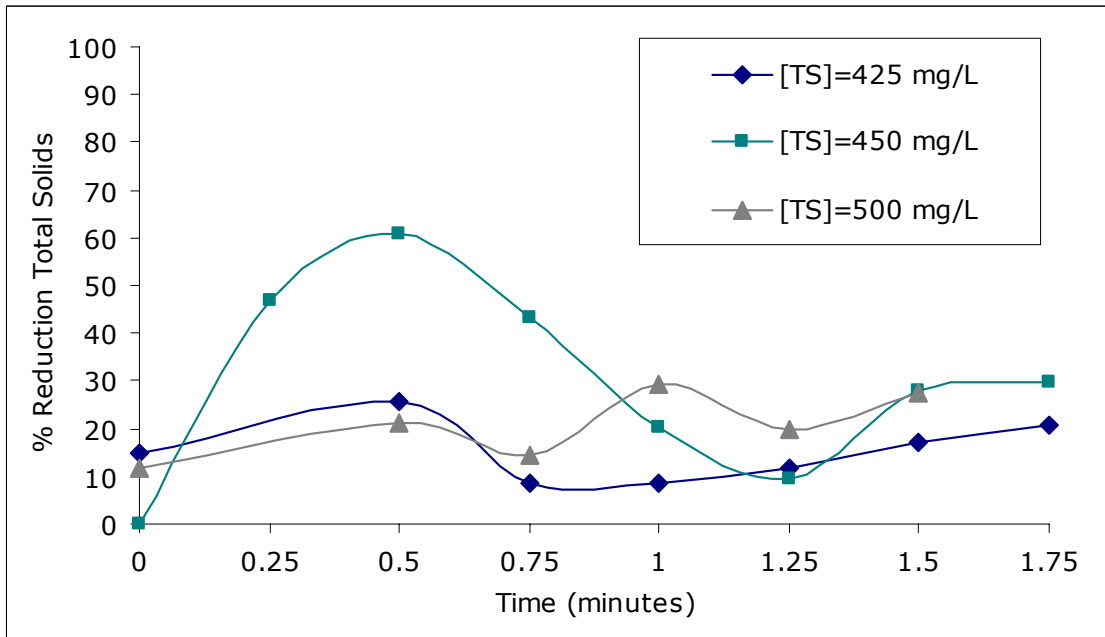


Figure 79. Percent Removal of Total Solids for Solutions 1, 2, and 3 (Sludge and Chitin)



Figure 80. Feed Water and Permeate Filtered (left to right)

A solution with a concentration similar to that which yielded the best quality permeate during chitin addition was compared to a solution without the flocculant. The solution with the sludge and chitin had an average total solids concentration of 450 mg/L in the feed. The solution that contained only sludge had an average total solids concentration of 400 mg/L in the feed. The difference was the amount of chitin added (50 mg/L).

Figure 81 shows that although the solution containing sludge and chitin had a higher total solids concentration in the feed, the permeate had a better quality during the first 45 minutes of the run. At this point, the breakthrough that is thought to account for the deterioration of the permeate quality occurred. However, the percent solids reduction was greater when using bentonite during the full run (See Figure 82).

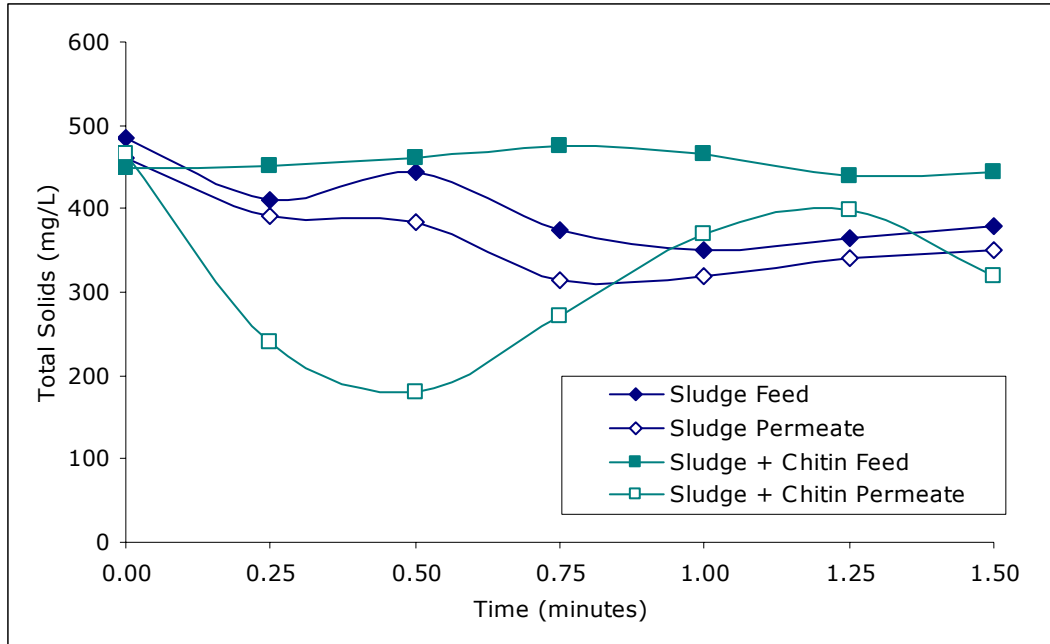


Figure 81. Effect of Chitin Addition on Total Solids Concentration in the Permeate

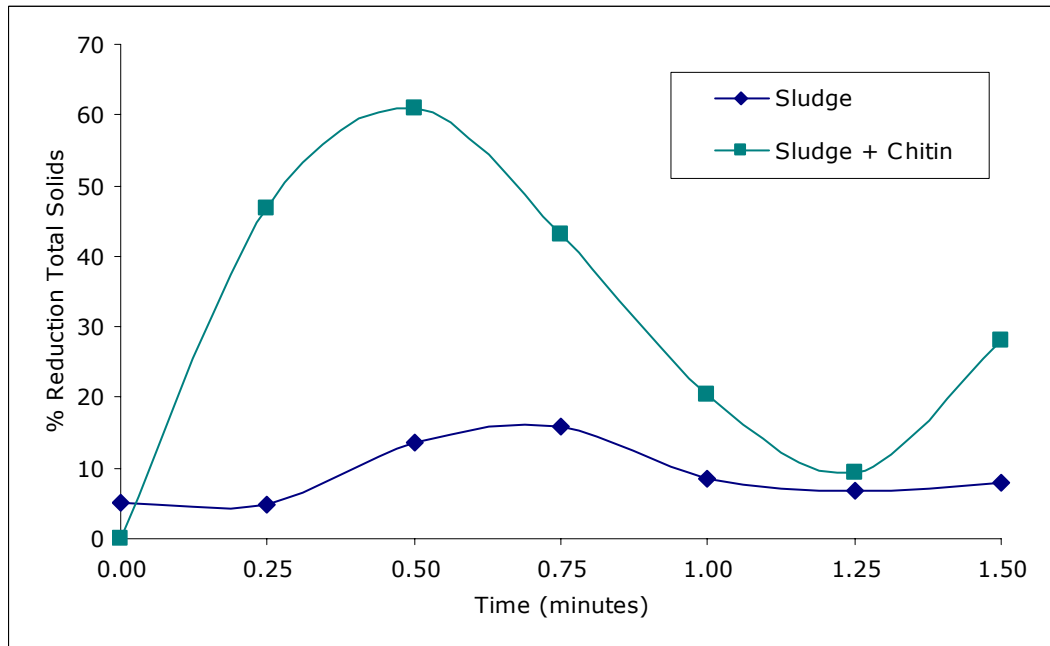


Figure 82. Effect of Chitin Addition on Percent Reduction in Total Solids

4.4 Life Cycle Analysis (LCA)

Life cycle analysis (LCA) is a tool used by industries and businesses to assess the effect their activities have on the environment. The approach takes into consideration all stages of production and includes gathering of raw materials, energy input, material transportation, ultimate product disposal, among others (See Figure 83).

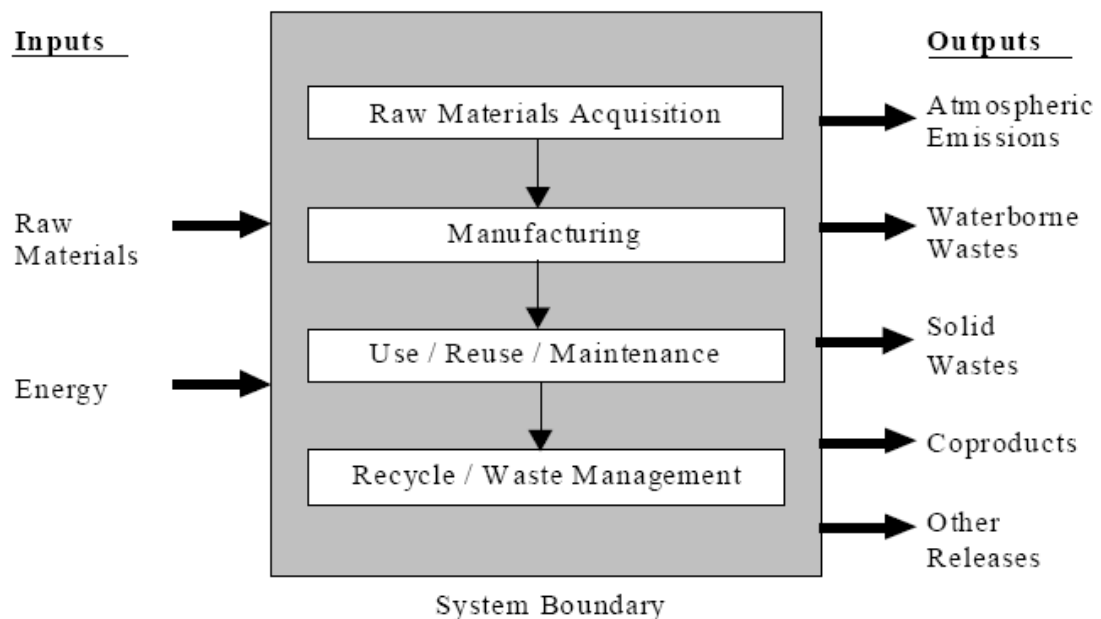


Figure 83. Life Cycle Stages (USEPA, 2006)

Life cycle analysis can be used to understand both the environmental and cost aspects of a manufacturing process to determine whether it can be sustainable. In an environmentally benign manufacturing process, the materials loop is closed by providing multiple life cycles (ITRI, 2001). This concept is illustrated in Figure 84, which shows a non-linear sustainable manufacturing model.

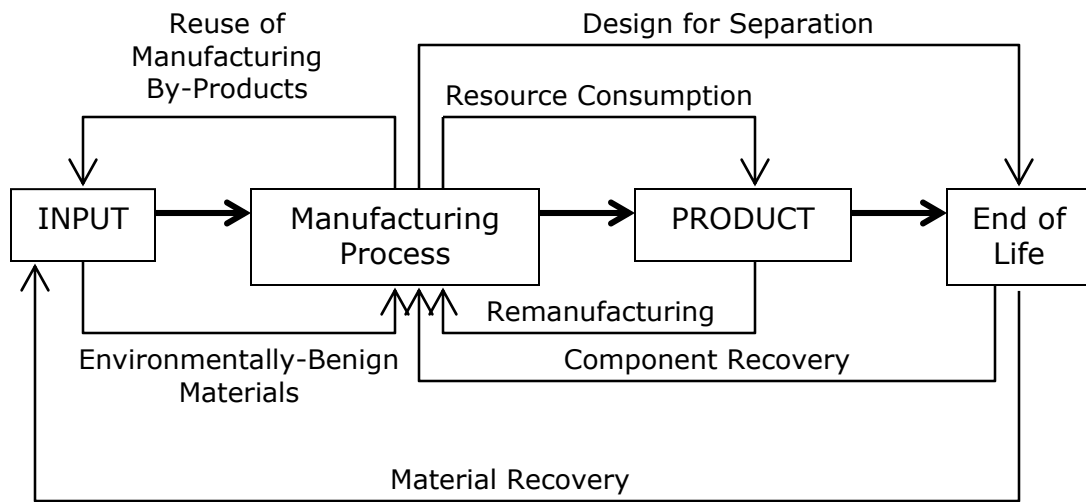


Figure 84. Sustainable-Nonlinear Model (ITRI, 2001)

In the case of scrap tires, the material is being kept viable through different life cycles. This means the vulcanized rubber is being used first in a tire, then in an extruded product (as PRT), and there is a potential for it to be used in rubber asphalt or other products down the line. However, there are energy requirements associated with each step. It is therefore necessary to establish if there is a significant advantage to recycling scrap tires as raw material for PRT. The objective, then, should be to have a more efficient and more environmentally-friendly process that utilizes less energy and resources. To determine if this is the case, the entire life cycle for the PRT needs to be considered. This includes not only its raw material (scrap tires), but also any other materials that are needed for the manufacturing process (like binders and lubricants). See Figure 85 for a simplified proposed model for the LCA of PRT.

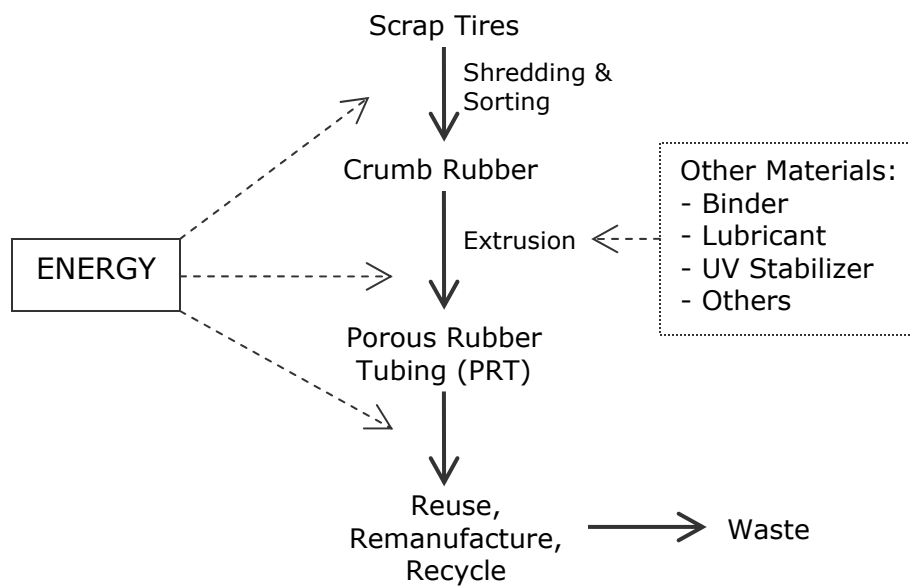


Figure 85. Proposed PRT Life Cycle Components

The energy component is important in the case of PRT. For example, to use scrap tires to manufacture PRT, they must first be shredded to make crumb rubber. In addition, manufacturing the other components of the PRT also requires energy. Although this process might appear to be energy-intensive, the recycling component provides another use for a material that would otherwise be discarded. This means that instead of using new raw materials to manufacture a membrane, this process makes use of a waste material. However, in order to provide more advantages that motivate the industry to shift towards using scrap tires for PRT for water filtration, it is important to enhance the steps that are currently lacking. In this manner, the use of natural lubricants and binders might provide an additional environmental and financial advantage.

4.5 Summary of Results

The following tables (Tables 8 and 9) summarize the results that were obtained in terms of operational parameters and feed and permeate total solids concentration.

For clean water, an increase in pump setting was reflected in an increase in both permeate flux and TMP. These tests were run to obtain a sense of the permeability of the PRT as a membrane. Furthermore, there was variability in terms of the material itself, although the same manufacturer was used throughout the study. Once challenged with two types of feed water, one containing bentonite and one containing sludge, the flux decreased. This behavior was mostly evident for sludge feed water. In the case of bentonite, the decrease in flux was less which could indicate that the clay particles were not being retained by the membrane. These results can also be seen in the solids tests that were run. The PRT was also tested using chitin to establish if these particles were able to be rejected by the membrane. An almost negligible decrease in flux as compared to clean water was observed for the smallest particles (size 200). This indicated that these particles were able to get through the material, although solids testing was not done. The other two sizes (size 60 and 80) showed a decrease in flux accompanied by an increase in TMP. These results indicated that the particles were probably being rejected by the PRT. No solids data is available for these trials either.

Total solids testing was done in order to determine whether or not PRT was able to reject particles on its own. The results showed that although there is a decrease in total solids concentration, the improvement was slight and highly variable. Therefore, the PRT was not able to consistently deliver permeate of a certain quality. For this reason, a third phase of study was explored in which chitin was used as a flocculant in conjunction with the filtration step.

After chitin addition, the results were promising; especially in the case of bentonite feed water. The addition of the flocculant allowed for up to 62% total solids reduction with a standard deviation of less than 24%. Although these results are far from optimum, they are encouraging. In order to implement this type of system, modifications must be made so that it is capable of consistently delivering adequate permeate.

Table 8. Summary of Operational Parameters

Experiment Description	Initial Flux LMH	Steady	Initial Resistance 1/m	Final Resistance 1/m
		State Flux LMH		
Clean Water Pump Setting 2 (133 mL/min)	8.27	7.47	1.71E+13	2.13E+13
Clean Water Pump Setting 3 (283 mL/min)	15.71	12.41	1.13E+13	1.71E+13
Clean Water Pump Setting 4 (432 mL/min)	26.95	19.89	6.08E+12	1.19E+13
Bentonite 357 mg/L	29.65	3.36	8.94E+12	9.09E+13
Bentonite 714 mg/L	26.01	2.38	1.14E+13	1.37E+14
Bentonite 1429 mg/L	14.88	1.98	2.34E+13	1.73E+14
Sludge 350 mg/L	8.34	0.37	4.10E+13	9.79E+14
Sludge 400 mg/L	5.76	0.23	6.46E+13	1.56E+15
Sludge 550 mg/L	3.81	0.09	1.05E+14	4.12E+15
Chitin 357 mg/L	26.16	22.15	3.93E+12	6.51E+12
Chitin 714 mg/L	26.46	21.60	6.61E+12	8.63E+12
Chitin 1429 mg/L	23.94	20.16	6.03E+12	7.87E+12
Chitin Size 60 266 mg/L	19.98	6.70	1.20E+13	3.68E+13
Chitin Size 80 266 mg/L	17.04	9.43	1.26E+13	2.30E+13
Chitin Size 200 266 mg/L	20.25	20.16	9.00E+12	1.14E+13
Bentonite 350 mg/L + Chitin 35 mg/L	4.44	0.37	6.47E+13	7.48E+14
Sludge 100 mg/L + Chitin 50 mg/L	1.91	0.09	1.64E+14	3.13E+15
Sludge 200 mg/L + Chitin 50 mg/L	1.65	0.05	1.75E+14	6.26E+15

Table 9. Summary of Total Solids Results

Experiment Description	Avg Feed TS mg/L	Stand Dev mg/L	Avg	Stand Dev mg/L	Avg % TS Reduction	Stand Dev
			Permeate TS mg/L			
Bentonite 350 mg/L	735	22.0	694	18.9	5.5	3.8
Bentonite 700 mg/L	1027	27.6	969	50.4	5.6	4.9
Bentonite 1400 mg/L	1639	170.2	1504	65.5	7.5	8.7
Bentonite 700 mg/L + Chitin 70 mg/L	1101	60.8	545	267.8	62.3	23.5
Sludge 15 mg/L	547	19.8	523	16.0	4.4	3.7
Sludge 25 mg/L	354	42.0	291	18.6	16.6	12.3
Sludge 50 mg/L	404	45.6	369	47.7	8.9	3.9
Sludge 25 mg/L + Chitin 50 mg/L	435	48.4	369	56.9	15.3	6.4
Sludge 50 mg/L + Chitin 50 mg/L	452	14.4	318	91.4	29.8	20.1
Sludge 100 mg/L + Chitin 50 mg/L	512	51.9	406	54.7	20.7	6.9

4.6 Feasibility Assessment of PRT as *ECOL-Mem*

Porous Rubber Tubing (PRT) was tested as a possible material to be used in a membrane filtration system to be used in developing countries. The system is termed *ECOL-Mem* and each letter of the acronym *ECOL* stands for a characteristic the material must possess.

The letter "E" stands for environmentally-friendly. Since the PRT is manufactured from a waste product such as scrap tires, it aids in using a material for multiple purposes. This increases its life cycle and allows the industry to close the materials' loop. Although the manufacturing process of PRT requires the addition of other materials (like binders and UV stabilizers), the crumb rubber is being obtained from waste tires that have been previously used. As compared to traditional membrane materials, the PRT system creates a new market for scrap tire-derived products while reducing the amount of "virgin" materials required. Also, the system that has been devised for this study utilizes low pressure, which translates into a low energy demand.

The letter "C" stands for capacity-building. According to the patents of the product, the extrusion process is simple enough that it can be done with standard extrusion equipment (Mason, 1985). However, since the PRT has not been optimized for this type of application, further research is needed to establish alternate ways of manufacturing it and simplifying the process so that it can be done on-site. The durability and toughness of the PRT makes it resistant to mishandling and both chemical and mechanical cleaning, which allows its use by people with limited training or expertise. Therefore, the system can be used in a point-of-use mode that helps build the capacity of the population in developing countries.

The letter "O" stands for obtainable. Scrap tires are a world-wide problem and, consequently, are available virtually everywhere. This means that the main material's source for PRT is widely accessible. Further research could expand the limited list of binders that can be used, which could decrease the cost and make the manufacturing process simpler.

The letter “L” stands for low-cost. The PRT can be more cost-effective than traditional membrane materials. Aside from having a lower initial capital cost, it is also more durable. This means that it had a longer life and does not need to be replaced as often as more traditional membranes. The current off-the-shelf cost is US\$18 per foot square (US\$194 per meter square). Although this cost might seem steep, widespread manufacturing can help drive the price down. This is the case with many products, including membranes. Furthermore, there is a possibility for further cost reductions if the composition of the PRT is altered so that it contains either a lower binder fraction or a binder that is less expensive. Low energy operation and easy maintenance also contribute to lowering the costs. In the laboratory setting in which PRT was evaluated, the peristaltic pump used operated at a setting of 4 (with 10 being the maximum). This corresponded to around 0.38 kW/hour of energy consumption. However, the possibility of coupling hydrostatic pressure and a hand pump with the PRT system could eliminate the need for electricity. Figure 86 shows the TMP that can be generated with a varying hydrostatic pressure head and applied vacuum. For example, a TMP of 13 psi (which was the highest calculated value for a feed solution containing 700 mg/L of bentonite) can be obtained through a water column with a depth of 9 meters. If, on the other hand, the hydrostatic pressure is combined with a device (like a hand pump) that can generate a vacuum equal to 4 psi, the depth of the water column is reduced to 6.5 m. Another advantage to using a filtration system is that it reduces the amount of chemical addition required to water treatment. This reduces not only capital cost but also maintenance cost due to disposal of the sludge that is generated.

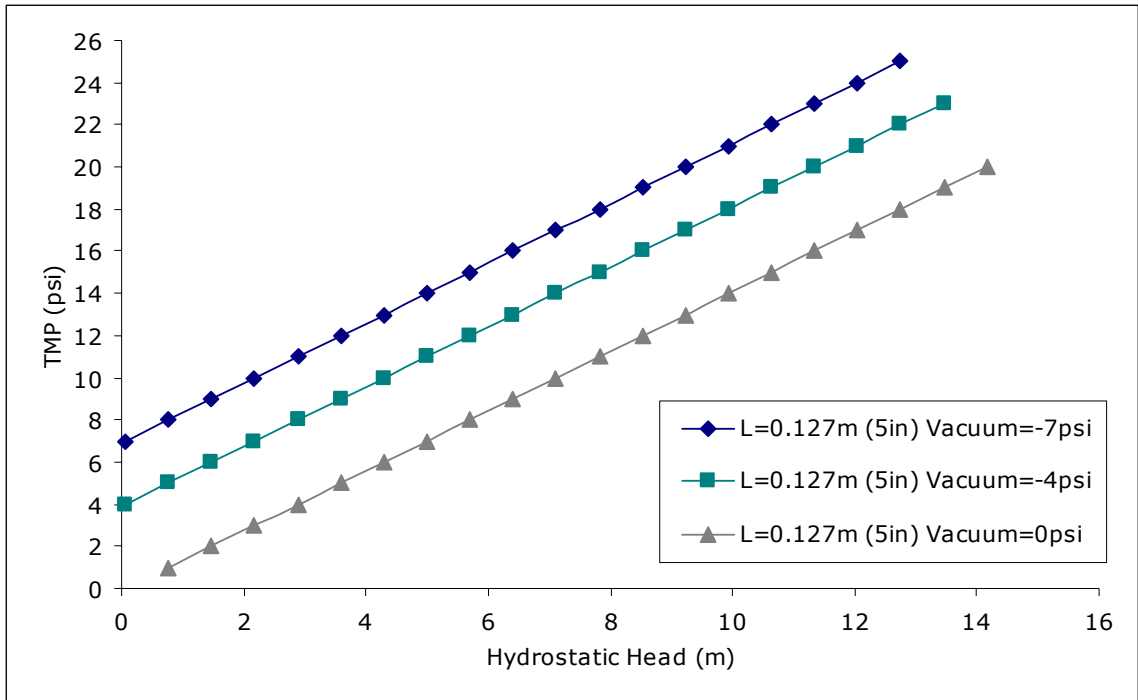


Figure 86. TMP vs. Hydrostatic Head Under Varying Conditions

Although the results that were obtained for the permeate water quality need to be improved, they are promising. It is important to keep in mind that the product that was tested is intended for a different application so there are still opportunities to optimize the manufacturing process. Therefore, it is safe to conclude that PRT is a promising material for use as *ECOL-Mem*.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Porous rubber tubing (PRT) commercially available as a soaker hose for drip irrigation was evaluated as a possible membrane filtration material for a system termed *ECOL-Mem*. This type of system is aimed at providing an alternative solution to the problem of access to safe drinking water and basic sanitation in developing countries.

The study was divided into three phases: intrinsic properties, filtration properties, and a flocculation-enhanced filtration coupling. During the first phase, the system was run with clean water in order to establish characteristics such as resistance and permeability. Also, the variability of the commercially available material from lot to lot was investigated.

During the second phase of the study, different feed solutions were used as feed water in the filtration system. These were meant to simulate turbid river water by using bentonite and impaired source water by using diluted sludge. Filtration characteristics were obtained from this phase which included operational parameters like permeate flux and TMP as well as performance results like removal of total solids. The total solids test was chosen as a preliminary indication of water quality since particulate matter in the water can help harbor pathogens from disinfection steps (Gadgil *et al.*, 1997; Oates *et al.*, 2003). It was determined that the PRT as it is currently available was not able to provide a significant improvement in the permeate water quality.

These results lead to the third phase of study during which a flocculation-enhanced filtration system was explored. The flocculant used was

chitin, which is a biopolymer that is obtained from waste shellfish (Gupta and Kumar, 2000). Upon chitin addition, significant improvements were recorded in the permeate water quality. For example, a feed solution containing 1,000 mg/L of bentonite and 100 mg/L of chitin was filtered and yielded a permeate containing up to 62% less total solids. Although the sludge feed water did not yield such improved results, the water quality was increased after the addition of the flocculant.

Porous rubber tubing is a feasible candidate for *ECOL-Mem* because it is ecologically-friendly, capacity-building, obtainable, and low-cost. The results that were obtained from this preliminary evaluation show that the commercially available product needs further refinement before it is capable of consistently providing good quality permeate under the conditions tested. However, if the system is coupled with chitin addition for flocculation, it can reduce the total solids concentration by up to 65%. Although the PRT used for this study was not intended for a water filtration application, it is possible to adapt it for this purpose. The results shown by this study indicate that this is a promising technology that could be further refined to increase rejection in order to consistently deliver permeate of a high quality. This can help solve the problem of access to safe drinking water and sanitation in developing countries while also addressing waste management.

5.4 Recommendations for Future Research

This study was aimed at determining whether or not commercially available PRT was a good candidate for use in a membrane-based filtration system. However, the material is not currently being manufactured for this type of application. Therefore, it is possible that the rejection can be increased by altering the manufacturing process. Rejection can also be increased by investigating the mechanisms through which chitin is able to flocculate the feed water. This effort should aim to optimize the flocculation-enhanced filtration system.

Once the rejection capabilities of the material have been enhanced, it is necessary to better test for the water quality of the permeate. In addition, more testing should be done on the possibility of substance leaching since this is a waste-derived material.

A complete life cycle analysis should be performed in order to determine how advantageous the use of PRT as a membrane material can be. Furthermore, its use in conjunction with a flocculant, such as chitin, should also be addressed in a life cycle analysis to identify all advantages the system can provide. It is also important to determine whether or not this type of technology can be applied in developing countries by incorporating field testing.

In addition to PRT as a suitable candidate for the role of *ECOL-Mem*, other materials should be explored in the path to address the issues of lack of access to safe drinking water and sanitation in developing areas.

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APPENDICES

Appendix A: Instrument and Device Calibrations

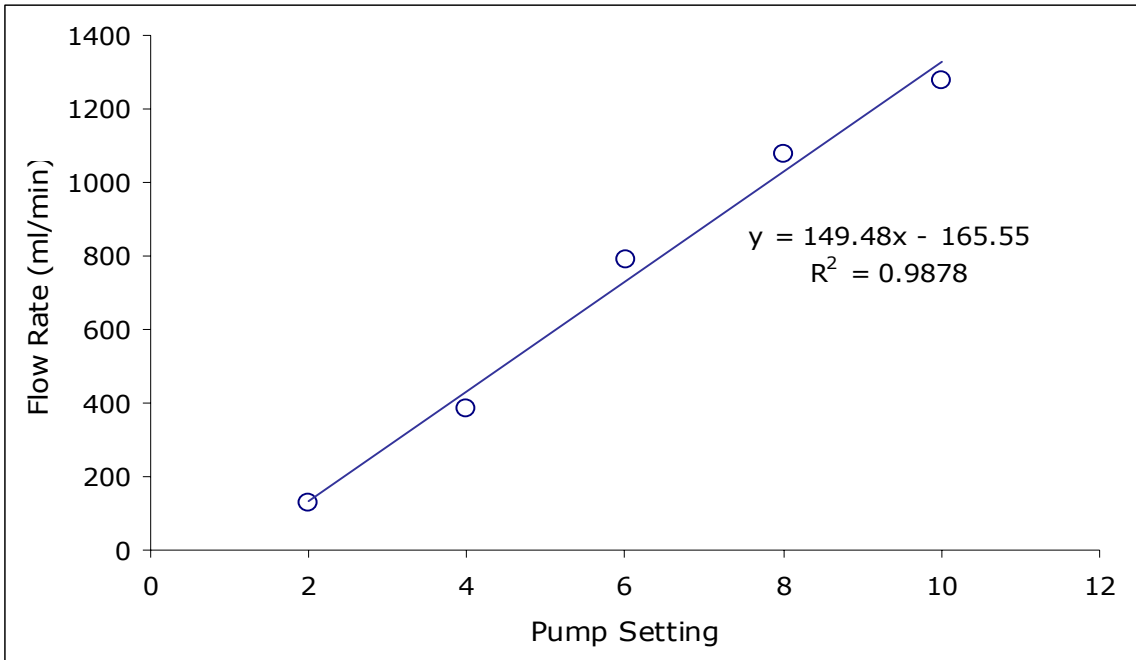


Figure 87. Pump S1 Calibration Curve

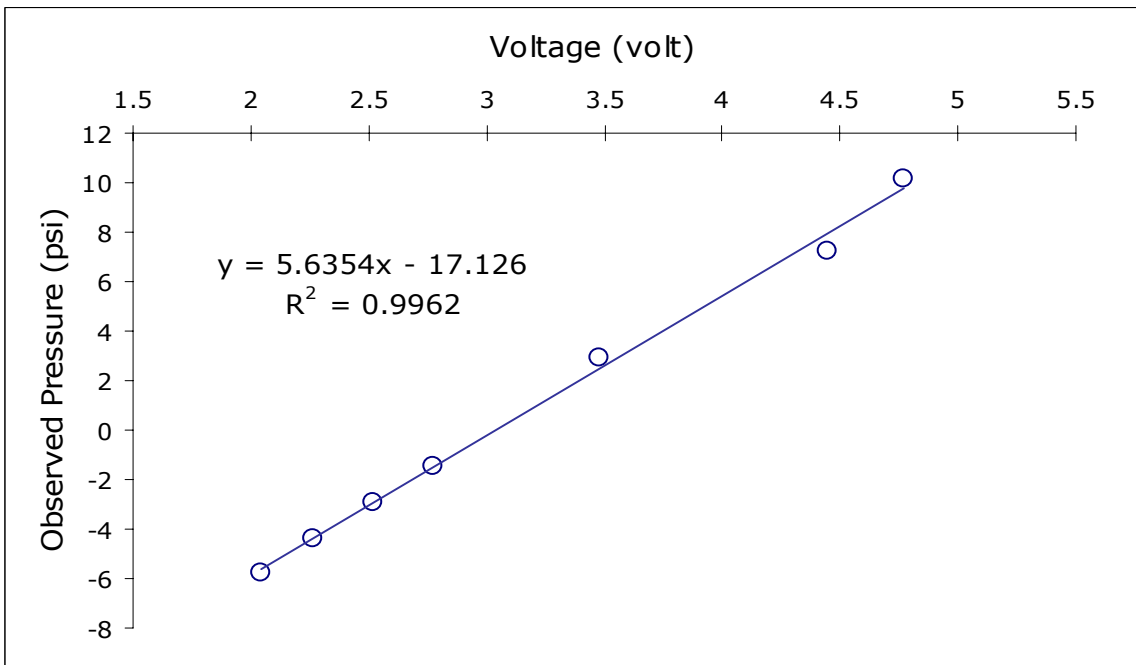


Figure 88. Pressure Transducer S1 Calibration Curve

Appendix A: (Continued)

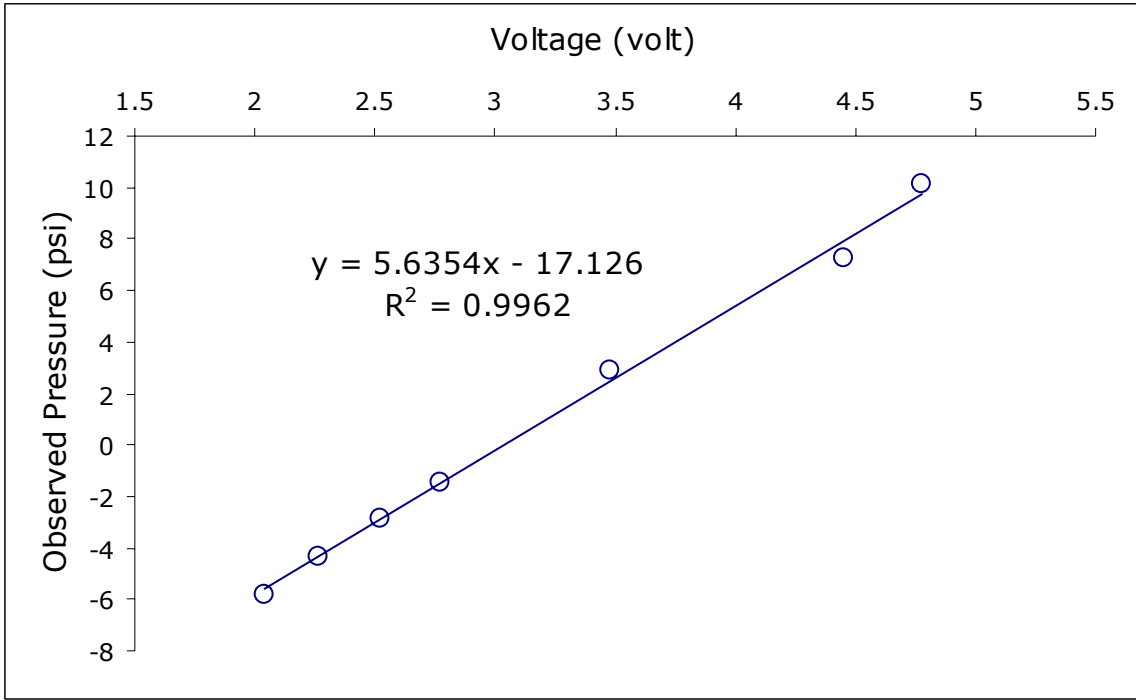


Figure 89. Pressure Transducer S2 Calibration Curve

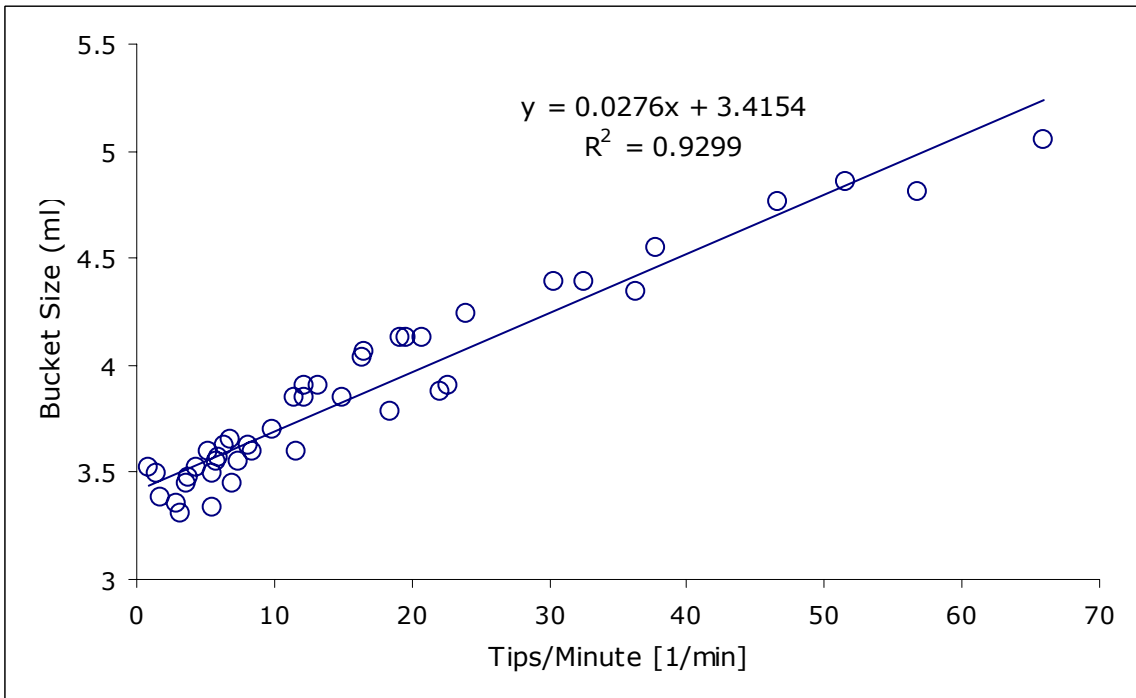


Figure 90. Rain Meter B Calibration Curve

Appendix A: (Continued)

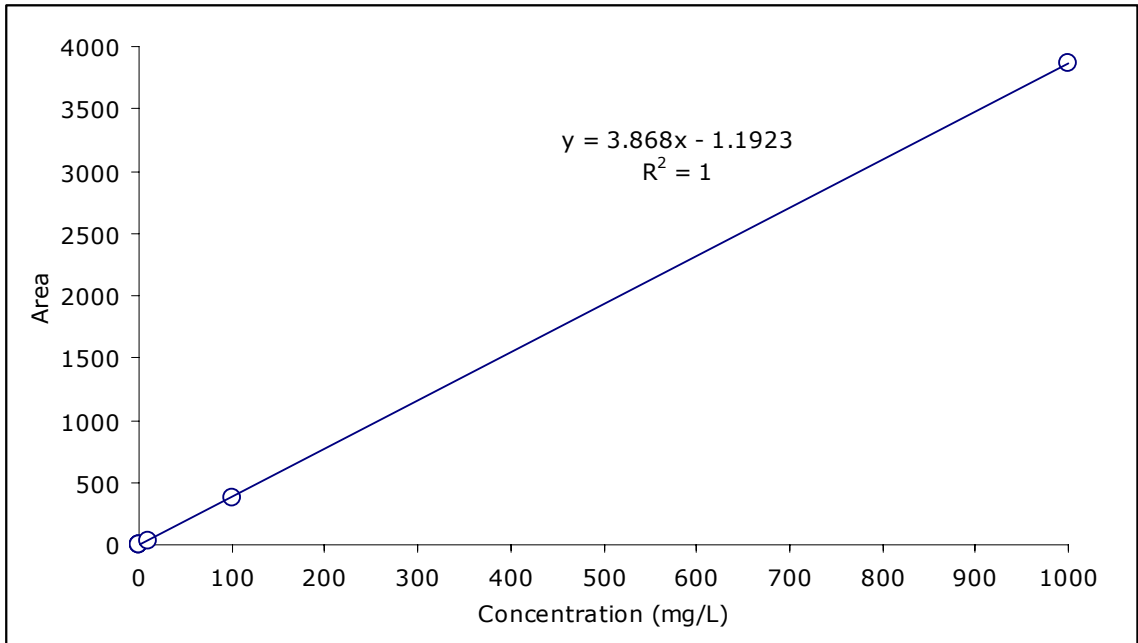


Figure 91. TOC Analyzer Calibration Curve

Appendix B: Other Reactor Configurations Evaluated

Several changes were made in the system setup as the study progressed. These include modifications for mixing, feed reservoir shape, and cassette configuration.

The first cassette configuration was termed loop reactor. It consisted of semi-circular segments of PRT where the ends were connected to a manifold which had valves that could be open or shut to activate or deactivate certain segments. The cassette was immersed in a rectangular glass reservoir (See Figure 92). Since mixing was not possible because the container was too narrow, the permeate recycle tubing was introduced in the bottom of the reservoir to prevent solids from settling. However, proper mixing was not possible by just using the permeate recycle tubing so other options had to be considered.

Mixing of the feed solution needed to be effective at maintaining homogeneity but also needed to be gentle so that the particles did not disintegrate. Therefore, an air pump, such as those used in home aquariums, was tested. Although the mixing was improved, there were still solids being deposited at the bottom of the reservoir. This was especially noticeable at the far ends of the glass container.

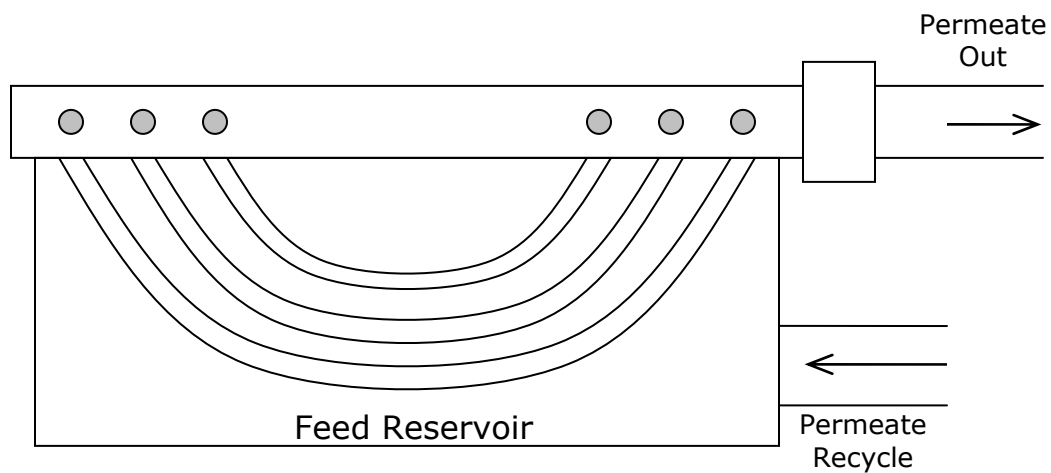


Figure 92. Loop PRT Reactor Configuration

Appendix B: (Continued)

The feed reservoir was then changed to a shape that would decrease the dead volume at the corners. The shape of the PRT cassette was also modified. In the new configuration, segments of PRT were placed vertically and joined at the ends by t-shaped fittings. In trying to employ a system that could be readily available, an aquarium that included an air pump was tested. This new feed reservoir had a pentagonal shape, so the PRT cassette followed that shape. However, the reservoir was not made of glass, which posed a potential for leaching due to chemical reaction of the aquarium walls and the cleaning solution used.

Therefore, the system was modified once again. This time, a glass container was used as a reservoir and was filled with 6.75 L of feed water. This specific volume provided the same pressure head as the previous
Appendix B: Other Reactor Configurations Evaluated (Continued)

systems considered. The PRT cassette configuration was kept the same, except 4 additional segments were attached. This increased the total filtration area. Since reports had been done in terms of flow rate per unit of area (flux), the modification did not invalidate previously collected data.

Appendix C: Scanning Electron Microscopy Images

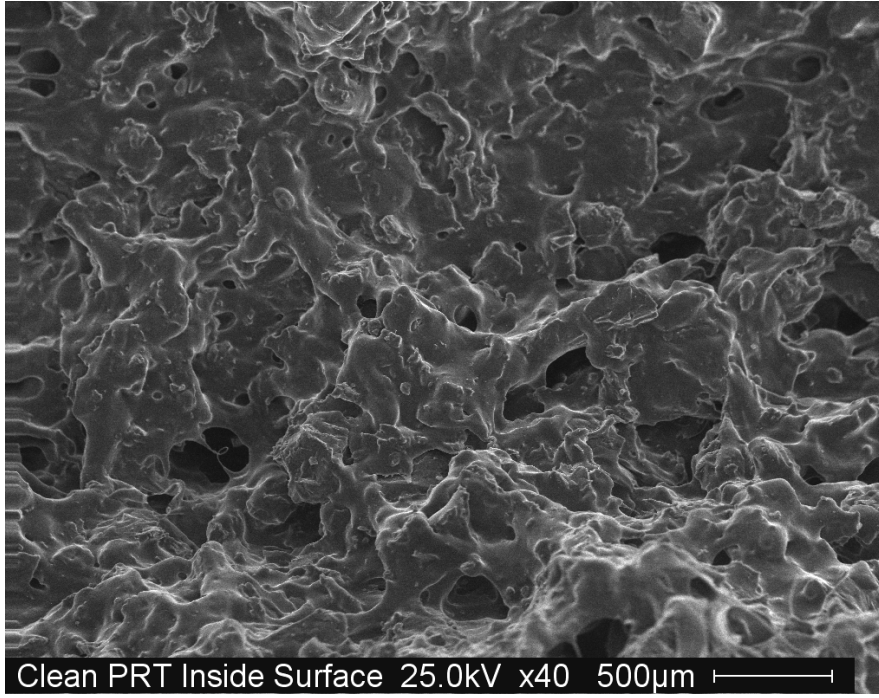


Figure 93. SEM Image of 1/4" Diameter PRT Inside Surface (Clean, T1)

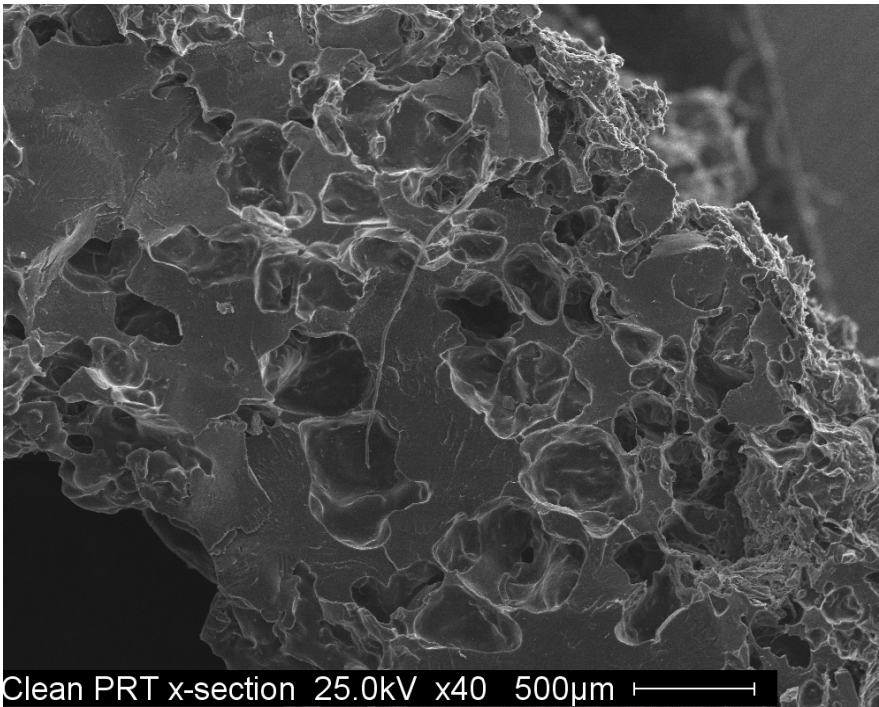


Figure 94. SEM Image of 1/4" Diameter PRT Cross Section (Clean, T1)

Appendix C: (Continued)

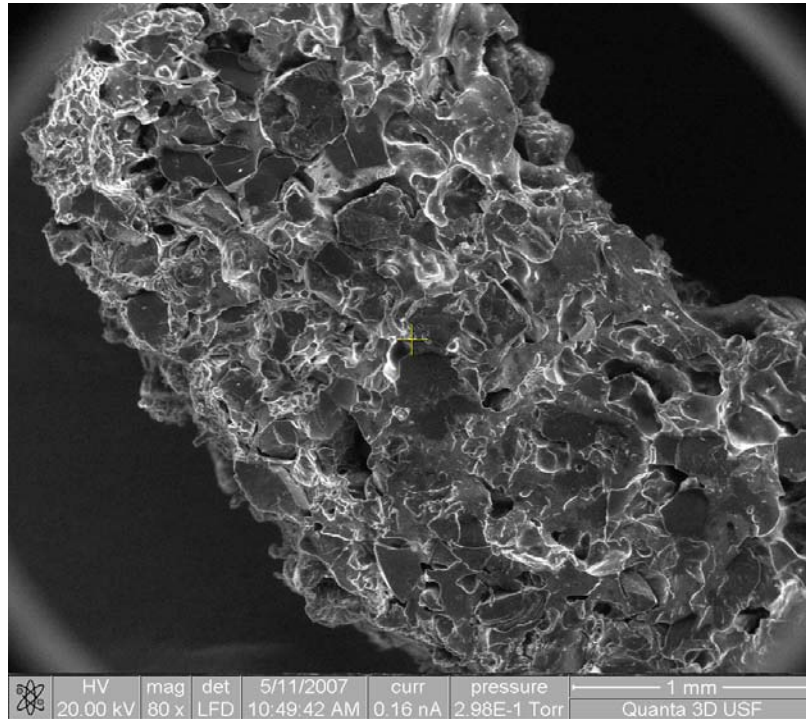


Figure 95. Environmental SEM Image of 1/4" Diameter PRT Cross Section (Clean, T1)

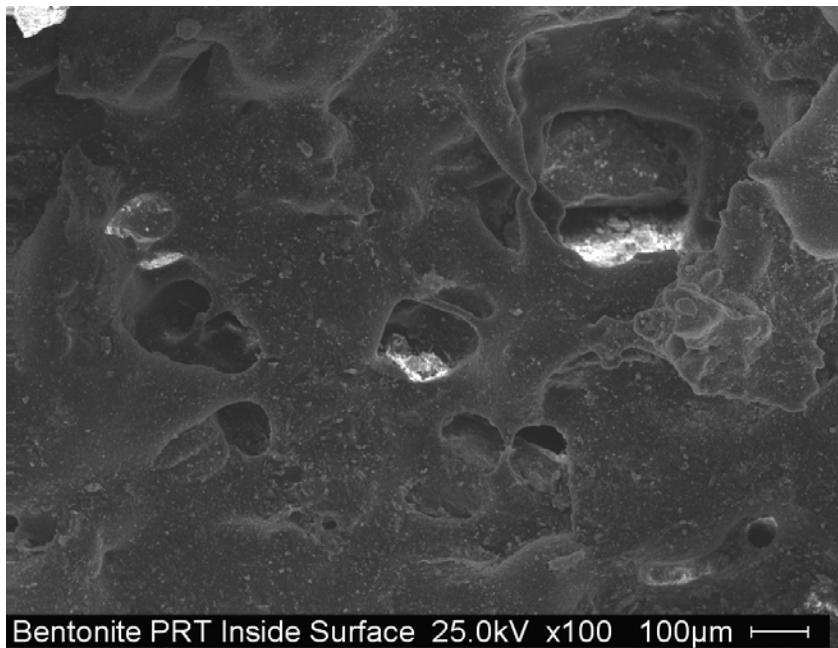


Figure 96. SEM Image of 1/4" Diameter PRT Inside Surface (Bentonite, T1)

Appendix C: (Continued)

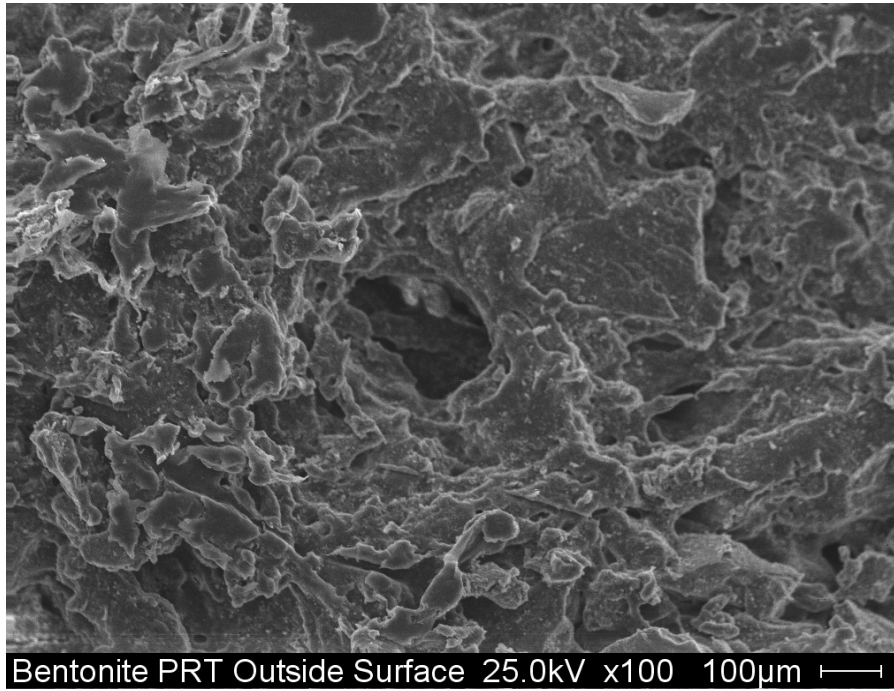


Figure 97. SEM Image of 1/4" Diameter PRT Outside Surface (Bentonite, T1)

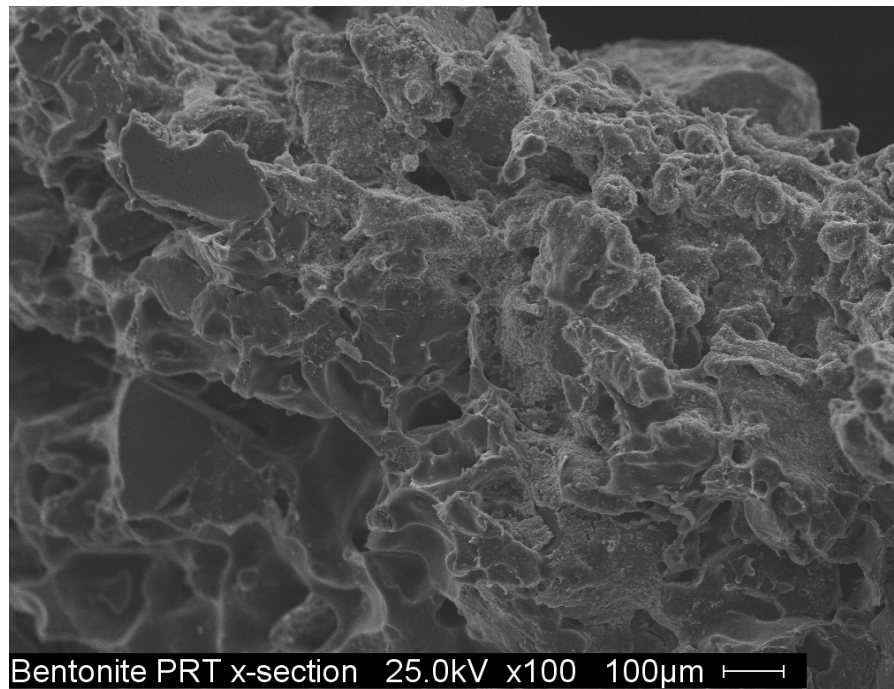


Figure 98. SEM Image of 1/4" Diameter PRT Cross Section (Bentonite, T1)

Appendix C: (Continued)

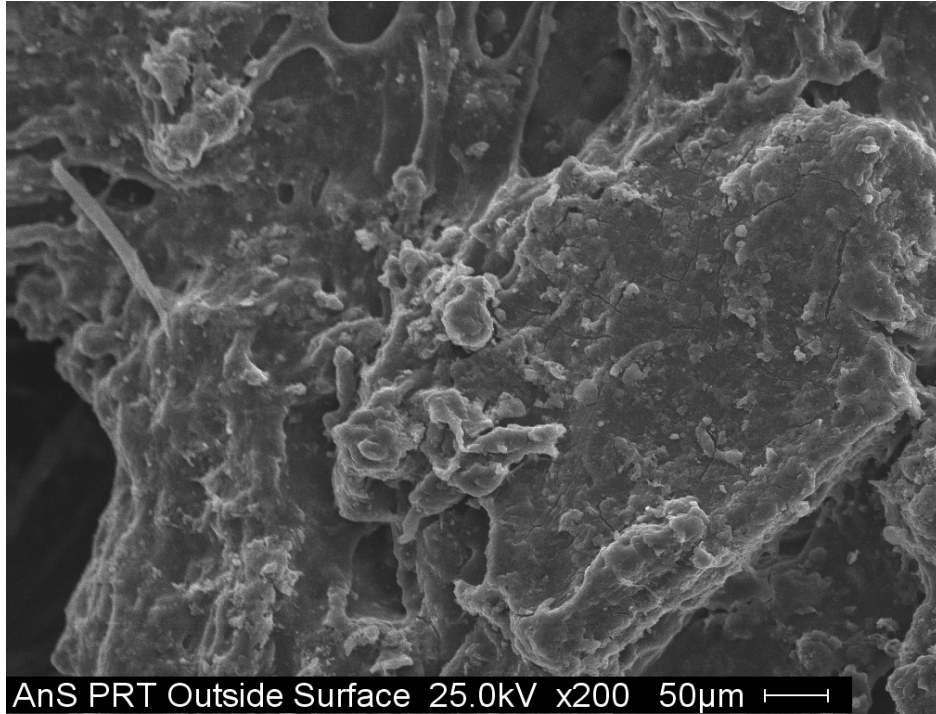


Figure 99. SEM Image of 1/4" Diameter PRT Outside Surface (Sludge, T1)

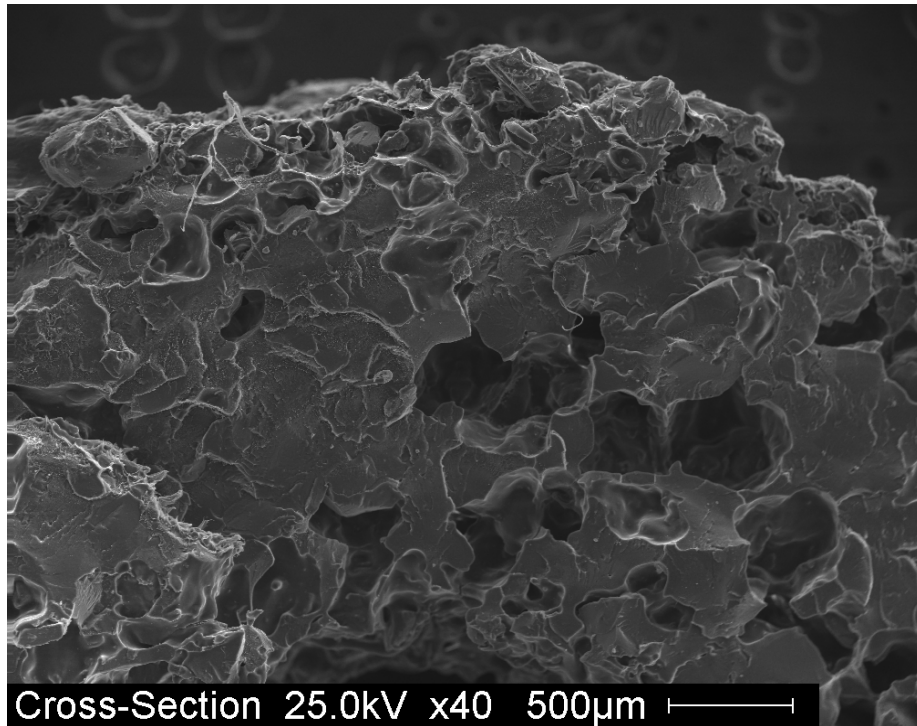


Figure 100. SEM Image of 1/2" Diameter PRT Cross Section (Clean)

Appendix C: (Continued)

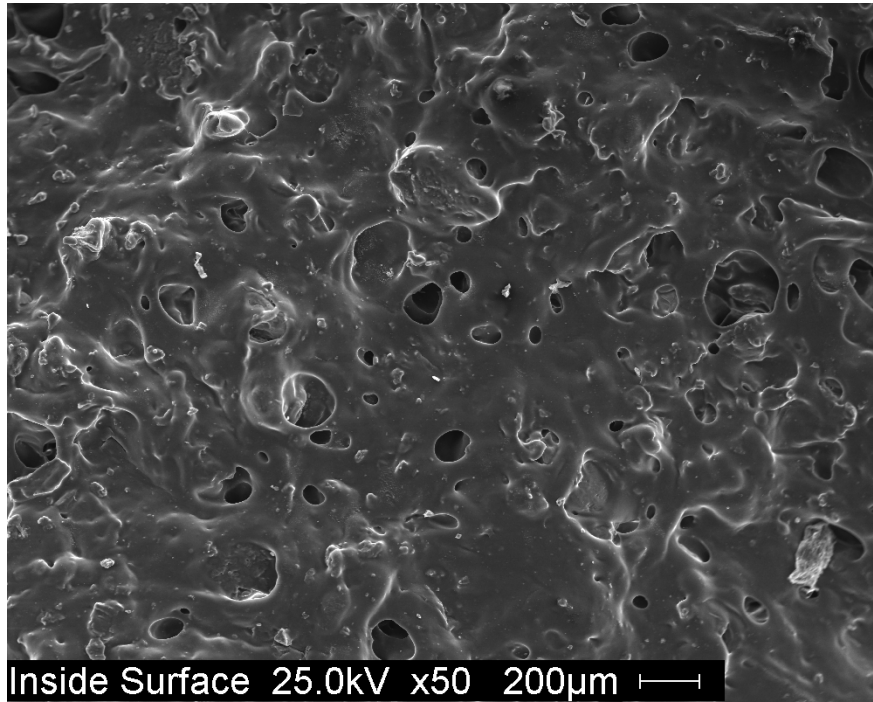


Figure 101. SEM Image of 1/4" Diameter PRT Inside Surface (T3)

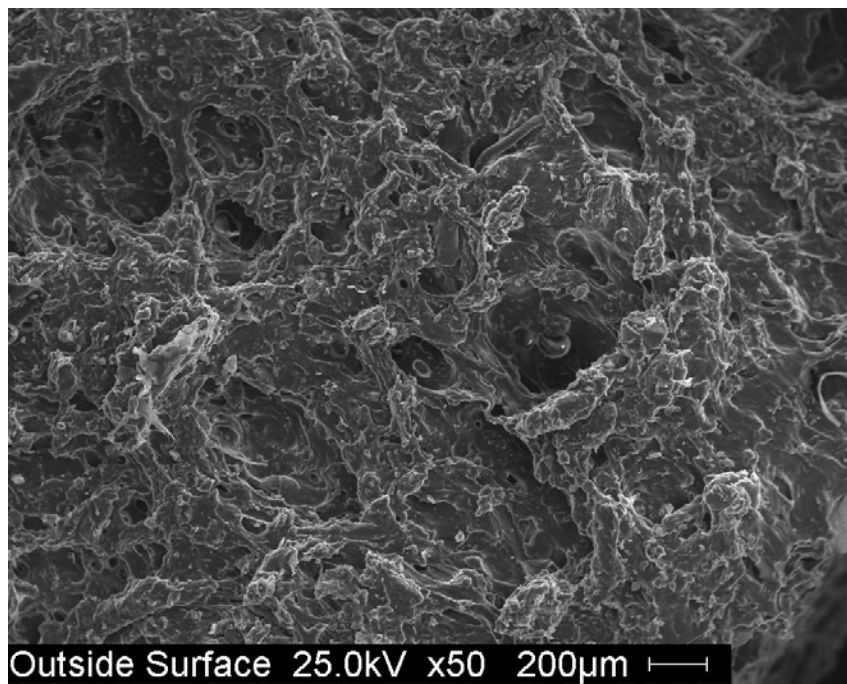


Figure 102. SEM Image of 1/4" Diameter PRT Outside Surface (T3)

Appendix C: (Continued)

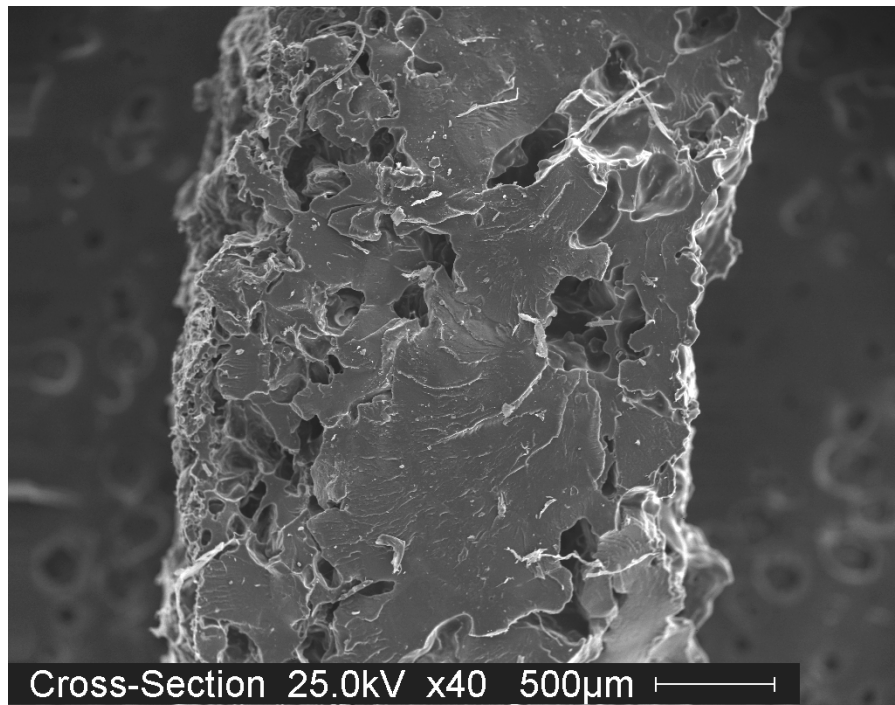


Figure 103. SEM Image of 1/4" Diameter PRT Cross Section (T3)

Appendix D: System Pictures



Figure 104. 1/2" Diameter PRT Close-up

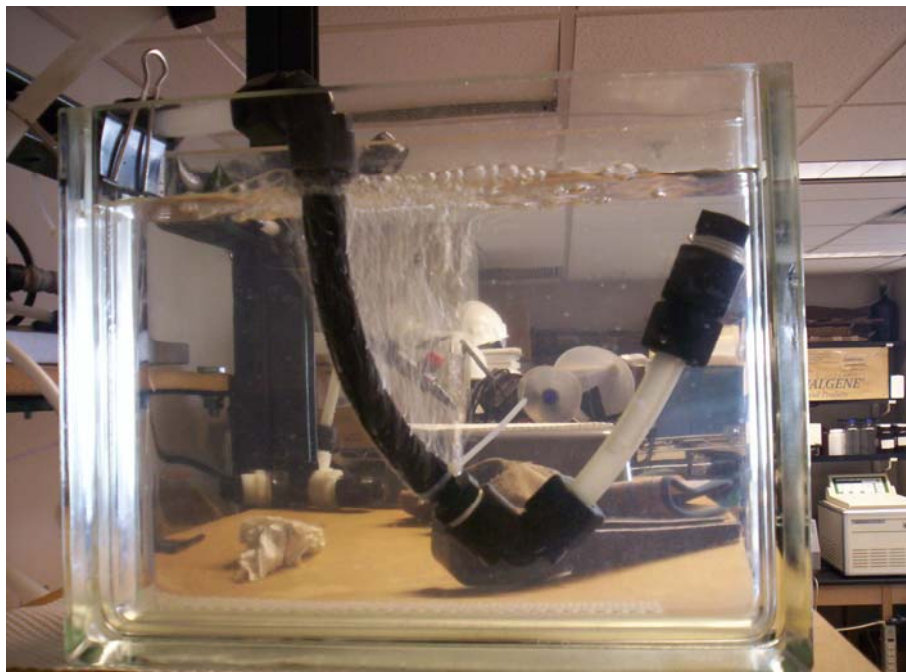


Figure 105. 1/2" Diameter PRT Backwashing with Air

Appendix D: (Continued)

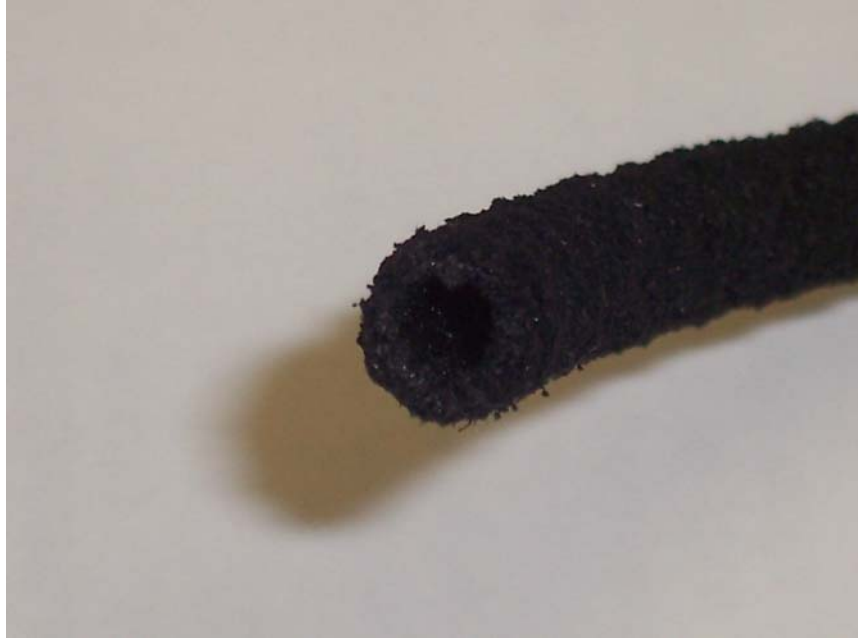


Figure 106. 1/4" Diameter PRT Close-up



Figure 107. 1/4" Diameter PRT Backwashing with Air

Appendix D: (Continued)



Figure 108. Commercial PRT Brand Used

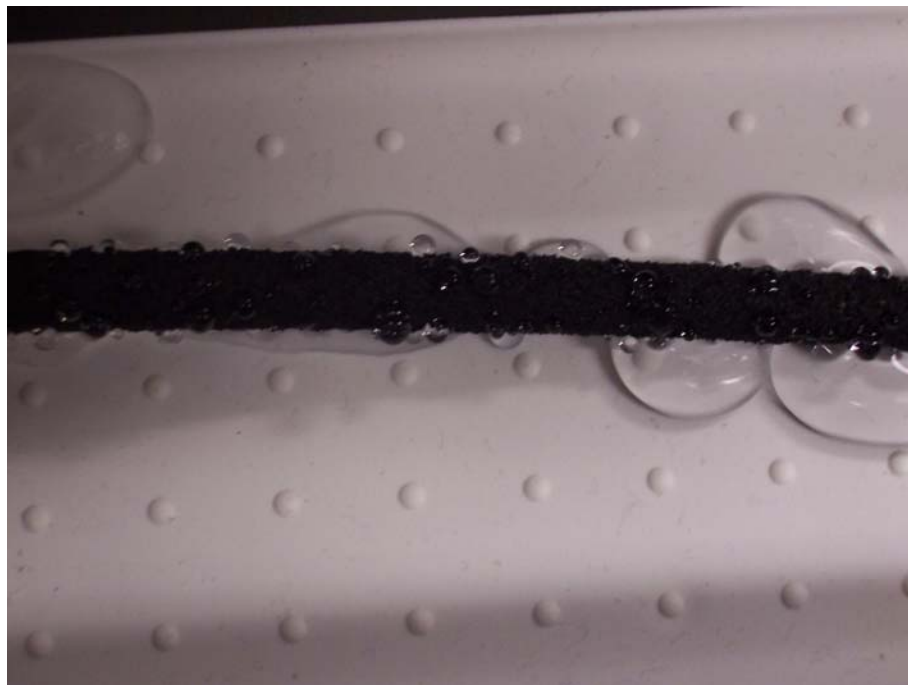


Figure 109. Water Seeping Through PRT

Appendix D: (Continued)

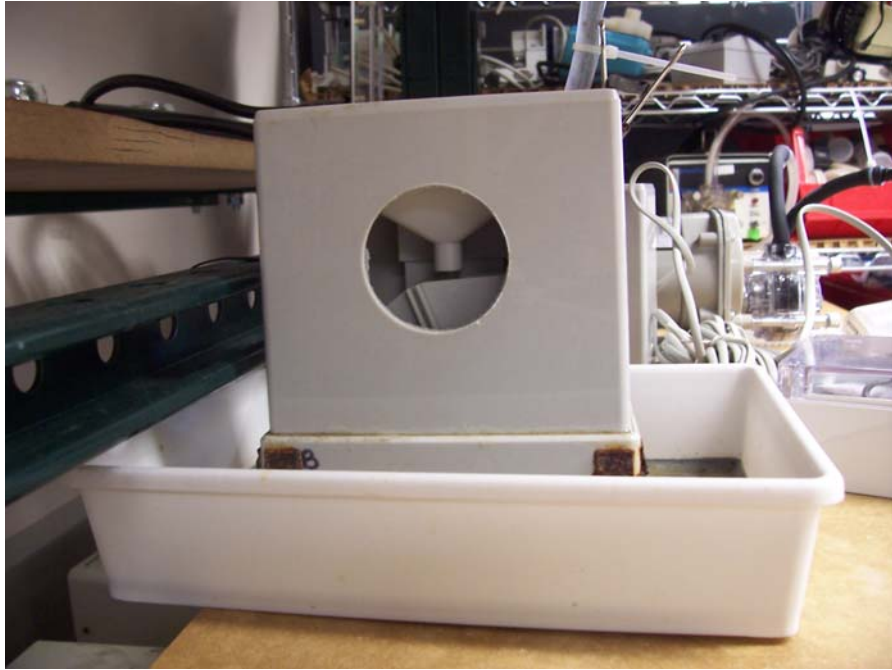


Figure 110. Wire Rain Meter



Figure 111. Data Logging Device

Appendix D: (Continued)



Figure 112. Jar Testing Apparatus

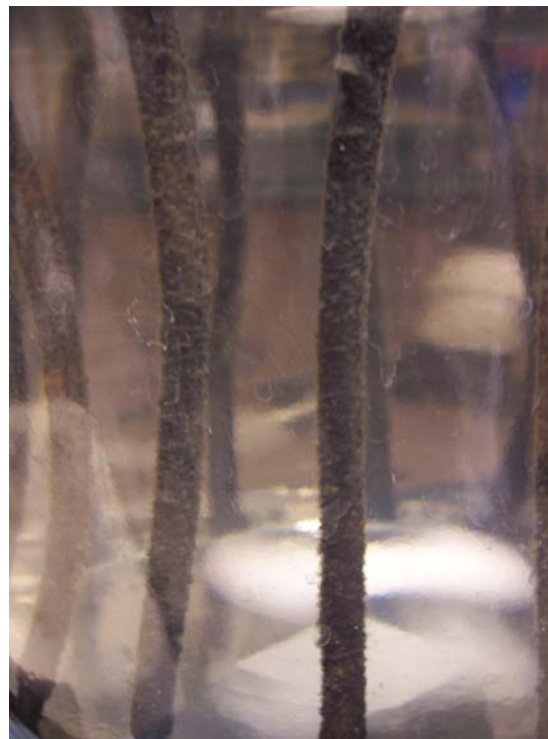


Figure 113. Cake Layer Build-up on PRT (Sludge)

Appendix E: Other Types of Feed Water Tested

In an attempt to fully characterize the behavior of the PRT membrane when challenged with different types of feed water, solutions containing sand and grinded cat food were evaluated as well. The data contained in this appendix corresponds to those trials, which were done earlier in the study and discarded for different reasons.

The purpose of testing sand with the system was to simulate surface water (e.g., rivers and lakes). However, only one trial was done because the sand particles proved to have a high density, making them difficult to keep in suspension. Furthermore, the possibility of the particles being able to flow through the membrane was a concern for the integrity of the pump and the tubing. The sand was sieved prior to being tested. The specific particle size used for the test was between 250 μm and 355 μm (Size 60). The following graph shows the relationship between flux and TMP and time.

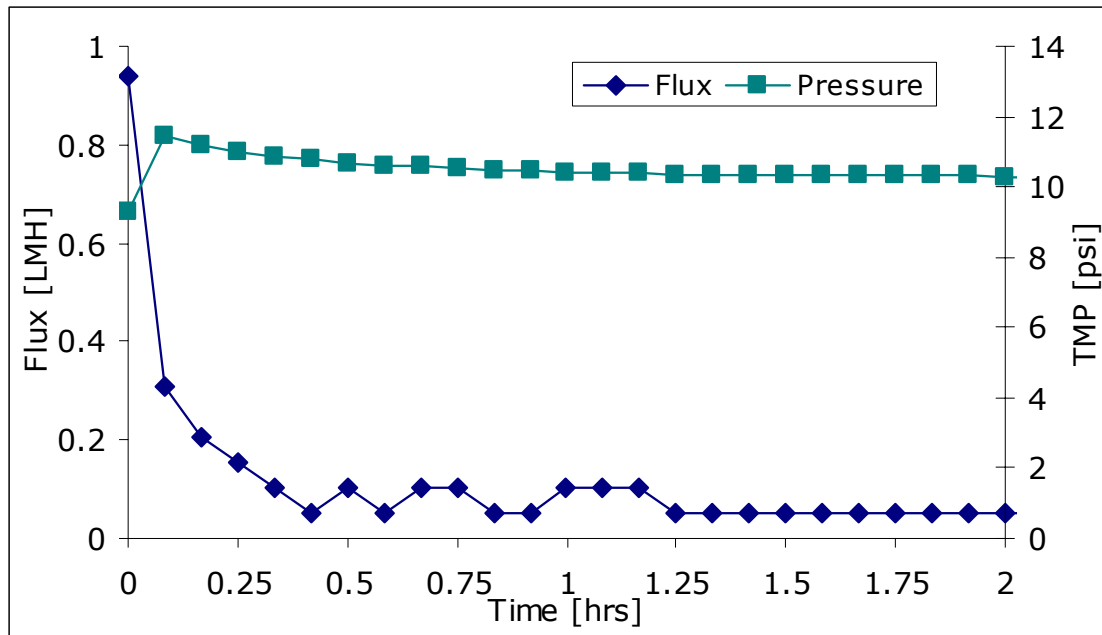


Figure 114. Flux and TMP vs. Time for Sieved Sand at a Concentration of 2,857 mg/L

Appendix E: (Continued)

The previous graph shows a trend towards an almost negligible flux from the beginning. However, the concentration used for this test was significantly higher than those used for tests presented in Chapter 4.

Tests were also run using grinded cat food as simulated feed water. The advantage of using this type of feed is that the particle size can be properly controlled by sieving the grinded cat food prior to testing. However, the high content of fat, protein, and carbohydrates fouled the membrane rapidly and made chemical cleaning cumbersome. Therefore, this data was not presented in Chapter 4. Figure 115 shows a plot of both flux (represented by the filled-in symbols) and TMP (represented by the clear symbols) versus time. The tests in this case were run for 15 hours each.

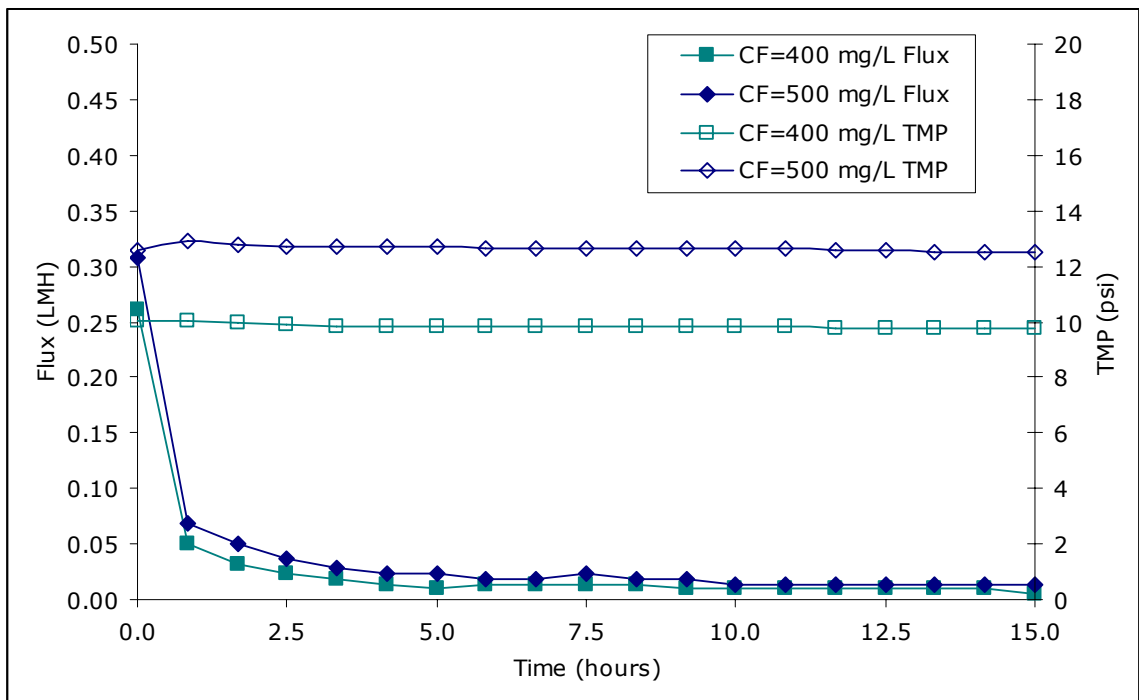


Figure 115. Flux and TMP vs. Time for Grinded Cat Food at a Concentration of 400 mg/L and 500 mg/L

Appendix E: (Continued)

The previous graph shows that there was a slightly higher flux when the grinded cat food was at a concentration of 500 mg/L versus 400 mg/L. The 500 mg/L trial was done prior to the 400 mg/L trial. It is possible that the cleaning of the membrane was not effective and there was residual pore blockage transferred from one test to the next. Therefore, the data obtained from tests using cat food were not used to draw any conclusions in this study because it was difficult to establish whether or not the PRT membrane had the same initial conditions for each trial. When using diluted sludge as feed water, these problems were not observed.

Appendix F: Total Carbon Test Results

This set of experiments explored the possibility of substances leaching from the PRT, since the material is derived from a waste product. This was done by using total carbon concentration as an indicator. However, further research on specific compounds is recommended to fully assess any health concerns.

A set of experiments was devised to assess the leaching of substances from the PRT while submerged in water. The experiment consisted of soaking a segment of PRT in water for several days (See Figure 116).



Figure 116. PRT Leaching Experiment

Samples were taken after 1, 2, 3, 4, and 45 days to obtain total carbon (TC) and run using a total organic carbon analyzer. Once a sample was collected, the water was discarded and replaced with fresh water. This was done to ensure that the total carbon concentration was not remaining constant due to saturation. The average results are found in Table 10, where all concentrations are given in mg/L of carbon.

Appendix F: (Continued)

Table 10. Average Total Carbon Concentration

Days	Blank RO Water	Blank NF Water	Blank Tap Water	Tap Water 1	Tap Water 2	NF Water 3	NF Water 4	RO Water 3	RO Water 4
1	N/A	1.652	29.46	28.95	27.99	1.921	1.986	N/A	N/A
2	N/A	1.449	27.59	28.02	28.12	1.552	1.495	N/A	N/A
3	0.255	N/A	28.66	28.9	28.67	N/A	N/A	0.543	0.388
4	0.269	N/A	26.81	29.46	27.96	N/A	N/A	0.370	0.303
45	0.279	N/A	26.79	31.55	31.01	N/A	N/A	1.357	1.41

During the first two days of the experiment, nanofiltration and tap water were used to soak the PRT. After the third day, the samples were soaked using reverse osmosis water since it is more aggressive. The differences in TC are evident with tap water containing the highest TC.

The RO water, which was the most aggressive, yielded significantly higher TC concentrations when in contact with the PRT as compared to the blank. The percent difference between the blank and the sample with the PRT was more than 390% after 44 days of not changing the water (See Table 11). The results for the tap water were significantly less severe. In this case, the percent difference between the sample with the PRT and the blank remained under 17% even after 44 days of soaking. Not enough data was collected for the case of nanofiltration water, but it can be assumed that the results will be at an intermediate point between the results for tap water and RO water.

Table 11. Average Increase in Total Carbon Concentration

Time Elapsed (days)	RO Water Percent Difference	NF Water Percent Difference	Tap Water Percent Difference
1	N/A	18.3	-3.4
2	N/A	5.1	1.7
3	82.2	N/A	0.4
4	25.3	N/A	7.1
45	395.3	N/A	16.8