

EVALUATION OF SILVER NANOPARTICLES IMPREGNATED WOVEN FABRIC MICROFILTRATION MEMBRANES FOR POTABLE WATER TREATMENT

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DECLARATION

I hereby declare that this submission is my own work and to the best of my knowledge it neither contains material previously published or written by another person, nor material which to a major extent has been accepted for the award of any other degree at Durban University of Technology (DUT) or any other educational institution. I also declare that the intellectual content of this dissertation is the product of my own work. Any contribution made to the research by others especially in the use of equipment for sample analysis has been explicitly acknowledged in the dissertation.

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Achisa Mecha Cleophas

ABSTRACT

Lack of access to clean and safe potable water, especially for people living in rural areas of developing economies, is a matter of great concern in different parts of the world. Measures taken to address the challenges arising from this problem include the improvement of existing water purification methods and development of new appropriate technologies such as point of use (POU) water treatment technologies.

One such appropriate POU technology is the Remote Rural Water Treatment System (RRWTS) developed at Durban University of Technology (DUT) in South Africa. The RRWTS is based on polyester woven fabric microfiltration (WFMF) membranes and other locally sourced materials. The filtration unit consists of flat sheet modules assembled into a pack and permeate outlets connected to a manifold and then to a tap. The system is gravity driven and therefore eliminates the use of pumps and electricity. This system has shown potential for use in water treatment as it produces permeate with turbidity below 1 NTU, has a high permeate flow rate, and is easy to use and maintain. However, the major challenge facing its use is that permeate does not meet the set microbiological standards for drinking water (zero *E. coli* in 100 mL treated water). The RRWTS can ideally remove 95 to 99 per cent of the influent *E. coli*. This necessitates the use of a separate disinfection step, often using chlorine for complete removal of microbial contaminants.

The objectives of this study were: to investigate the incorporation of silver nanoparticles (AgNPs) into the WFMF membrane; to evaluate the disinfection efficacy of the AgNPs impregnated filter (coated filter); and to determine the long term performance of the coated filter in terms of disinfection and silver elution (90 days).

The study was conducted in four stages. Firstly, AgNPs were incorporated on the membrane using *in situ* chemical reduction of silver nitrate using sodium borohydride. Secondly, the filters were characterized using scanning electron microscopy (SEM) to determine the morphology, and the Sessile drop method for contact angle measurement was employed to determine the membrane hydrophilicity. In addition, X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy and UV- Visible Spectroscopy

were used to investigate the presence of AgNPs on the coated filter. Thereafter, the antibacterial efficacy of the filters was evaluated using a laboratory scale experimental rig and different microbial assays. Raw river water and deionized water spiked with *E.coli* (synthetic feed) were used as feed. Lastly, the effects of concentration of *E.coli* in the feed and silver elution on the disinfection performance of the coated filter over time were investigated. The performance criteria were based on permeate quality and they included: turbidity, concentration of *E.coli*, and silver concentration.

The characterization results depicted that AgNPs were successfully immobilized on the WFMF membranes by *in situ* chemical reduction. The incorporation of AgNPs was ascertained using UV-Vis Spectrophotometry, FT-IR and XRD. The Sessile drop test indicated that the membrane became more hydrophilic (77 per cent decrease in water contact angle) and the permeability increased significantly as a result of the coating ($p < 0.05$). The coated filters demonstrated excellent filtration performance producing permeate with turbidity less than 1 NTU for feed turbidities between 40 and 700 NTU. The disinfection efficacy was found to be excellent, producing permeate with zero *E.coli* concentration for feed concentrations between 10,000 CFU/ 100 mL and 85,000 CFU/100 mL. The *E.coli* removal efficiency was 100 per cent for a period of 63 days of continuous filtration. The ICP Atomic Emission Spectrometer (ICP-AES) results showed that the leaching of silver from the coated filters over time (90 days) was always below 0.1 mg/L which is the widely accepted guideline for potable water.

From the literature surveyed, this is the first study which investigated the use of AgNPs in WFMF membranes for potable water disinfection. The coated filters treated water to the set international standards for potable water in terms of physical and microbiological quality.

However, the study did not comprise investigation into the effect of different silver loadings on the filter performance. The study also employed *E.coli* as the indicator organism for faecal contamination. The results obtained can be used as a model for future work using other microorganisms and different silver loadings in order to compare the performance.

DEDICATION

This dissertation is dedicated to my parents and siblings whose continued support and encouragement have motivated me to aim for greater heights in academics and in life.

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NOMENCLATURE

Abbreviations

AgNO ₃	Silver nitrate
AgNPs	Silver nanoparticles
CFU	Colony forming units
DBPs	Disinfection by products
<i>E. coli</i>	<i>Escherichia coli</i>
FTIR	Fourier transform infrared
J	Permeate flux (L/m ² .h)
LMH	Units of flux (L/m ² .h)
NaBH ₄	Sodium borohydride
NTU	Nephelometric turbidity units
PFP	Potters for peace
POU	Point of use
ROS	Reactive oxygen species
RRWTS	Remote rural water treatment system
SEM	Scanning electron microscope
SPR	Surface plasmon resonance
TGA	Thermo gravimetric analysis
THM	Tri-halo methane
TMP	Trans-membrane pressure (kPa)
UV	Ultraviolet light
WFMF	Woven fabric microfiltration
WHO	World Health Organization
wt. %	Weight percentage
XRD	X-ray diffraction

Units

°C	Degree Celsius
cm	Centimetre
d	Day
g	Gram
h	Hour(s)
kV	Kilovolt
L	Litre
m	Metre
mg	Milligram
min	Minute(s)
mL	Millilitre
nm	Nanometre
µm	Micrometre
µS	Microsiemens
°C	Degree Celsius

1 INTRODUCTION

1.1 Background

1.1.1 Challenges of water provision in developing nations

Water is a basic need essential for the sustenance of all life forms. However, there is a great concern due to the lack of safe and clean drinking water, especially for people living in rural areas of developing nations. Statistics show that worldwide, over 780 million people live without access to safe drinking water and an estimated 2.5 billion lack basic sanitation (WHO/UNICEF 2012). Furthermore, annually, approximately 1.8 million people die due to diarrhoeal diseases; 90 per cent of these being children under the age of five years, mostly in developing countries found in sub-Saharan Africa and South-East Asia.

The water crisis is further compounded by the increasing demand for potable water due to population growth, and pollution of water sources making the water unsuitable for consumption without enhanced treatment (Savage and Diallo 2005). In spite of these challenges, it is known that improved water supply remarkably reduces diarrheal morbidity by 6 to 25 per cent while improved sanitation reduces it by 32 per cent (WHO/UNICEF 2006; Pradeep, T and Anshup 2009).

Water scarcity occurs when demand for water exceeds the supply. This issue is more prevalent in some regions of the world because water supplies are not evenly distributed in terms of time and geography. There are two types of water scarcity, physical and economic. Physical scarcity occurs when 75 per cent of the river flows are utilized for agriculture, industry and domestic purposes and the remaining 25 per cent are not sufficient to maintain the ecosystem. On the other hand, economic scarcity occurs when water sources are sufficient relative to water use, but access is constrained by lack of human capacity and financial capital. For example, in sub Saharan Africa, there is inadequate storage capacity to spread water availability over the year (Klop and Rodgers

2008). According to the International Water Management Institute (2008), different parts of the world are experiencing water scarcity (Figure 1-1).

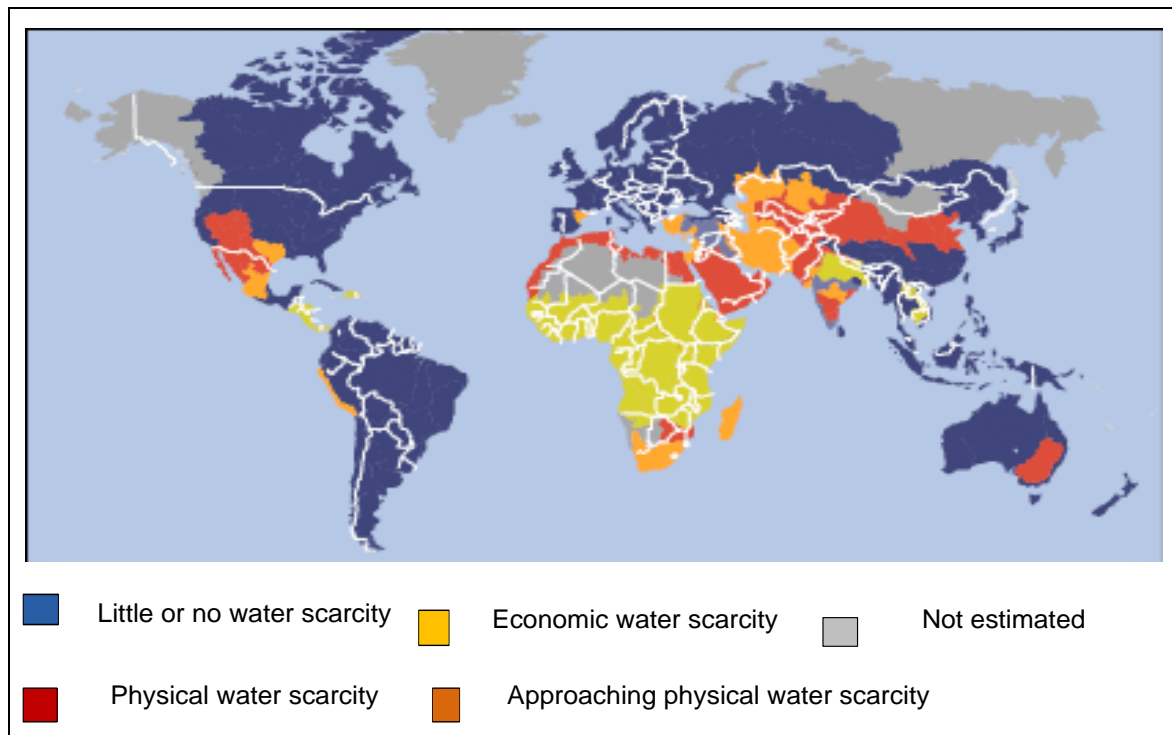


Figure 1- 1 : Water scarcity around the world

The low income nations mostly in sub-Saharan Africa and South-East Asia are especially vulnerable to water scarcity and are experiencing both physical and economic water scarcity. Furthermore, the water available is not of the right quality for direct human consumption without proper treatment.

1.1.2 Rural areas and water treatment systems

Rural areas in developing economies present unique challenges in terms of potable water provision. These include: rugged topographies; populations distributed over very wide areas; lack of skills for operation and maintenance of water treatment systems; poorly developed infrastructure; and the lack of finances (Pillay *et al.* 2009). People living in these areas have to fetch water that is normally untreated from local rivers or dams for use in cooking, washing and other domestic uses.

Thus, provision of safe water using conventional piped water systems to households may be a long way off for such people of the developing world. This means that many of the poorest people must continue collecting raw water and be responsible for treating and storing it at the household level (Sobsey 2002). This water is often prone to contamination resulting in outbreak of diseases. It is in response to the problems associated with the resulting waterborne diseases that new strategies for safe water provision in rural areas are being explored. These methods include treating drinking water at the household level and the devices that can be used are referred to as point-of-use (POU) technologies (Sobsey 2002; WHO 2011b).

The most commonly used small scale and POU water treatment methods include: boiling; UV disinfection; ozonation; chemical disinfection using chlorine and its derivatives; filtration using ceramic filters; and solar disinfection. However, these technologies have significant drawbacks. For instance, UV disinfection and ozonation require high costs for equipment and energy in order to implement. The use of chemical disinfectants such as chlorine, and iodine leads to the formation of disinfection by products (DBPs) which are carcinogenic and therefore harmful to consumers. The use of ceramic filters is hindered by low flow rates and the delicate nature of the filters makes them prone to breakages. In addition, boiling and solar disinfection are time consuming and can only treat small quantities of water at a time. These factors make the application of these systems in rural areas of developing economies difficult. A relatively new technology that can potentially overcome these challenges and which is gaining wide acceptance is the use of membranes for water treatment.

1.1.3 The use of membrane technology in water treatment

A membrane is an interphase separating two phases that restricts the transport of various species in a specific manner e.g. by size exclusion or based on diffusivity (Madaeni 1999; Persadh 2003). Membranes can be employed in water treatment in two ways. Firstly, they can be used as POU water treatment systems. Secondly, they can be a part of the water purification system before distribution to consumers (Madaeni 1999).

The raw water coming into the membrane module is referred to as the *feed* while the purified water that passes through the filtration surface is defined as *permeate*. The separation is achieved through the application of a driving force such as pressure, concentration gradient or electrical potential. Pressure driven membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The driving force for the separation process is the transmembrane pressure (TMP), between the feed and permeate sides.

MF and UF have potential advantages for application in potable water treatment in underdeveloped rural regions. These advantages include: the product quality does not depend on the skills of the operator or the mode of operation; and also they can be operated under low pressure thereby decreasing the energy costs.

Despite the success of membrane technology in large scale water treatment, the application of current commercial systems in rural areas faces significant drawbacks. These include: lack of robustness resulting from the delicate nature of the membranes, since most of them if left to dry or scratched can be easily damaged; and their costs are relatively high for people in rural areas. These factors, make current commercial membranes difficult to apply in small water treatment systems that would be sustainable in rural areas (Pillay *et al.* 2009). This necessitates the development of appropriate membrane technologies for such areas.

1.1.4 The Remote Rural Water Treatment System (RRWTS)

In a bid to address the challenges facing the use of current commercial membrane systems, researchers at Durban University of Technology (DUT) developed a simple, robust, inexpensive and easy to operate water treatment unit. This unit is called the Remote Rural Water Treatment System (RRWTS), for use in potable water production in remote rural areas. The core of the system is based on a flat sheet woven fabric microfiltration (WFMF) membrane. The membrane module consists of a rectangular polyvinyl chloride (PVC) frame containing a permeate outlet, two sheets of fabric glued to either side of the frame, and a mesh spacer between the sheets of fabric to facilitate

fluid flow to the permeate outlet (Pillay *et al.* 2009). The filtration unit consists of a number of modules assembled into a pack and permeate outlets connected to a manifold and then to a tap. The system is gravity driven and therefore eliminates the use of pumps and electricity. Figure 1.2 shows a cross section of the RRWTS.

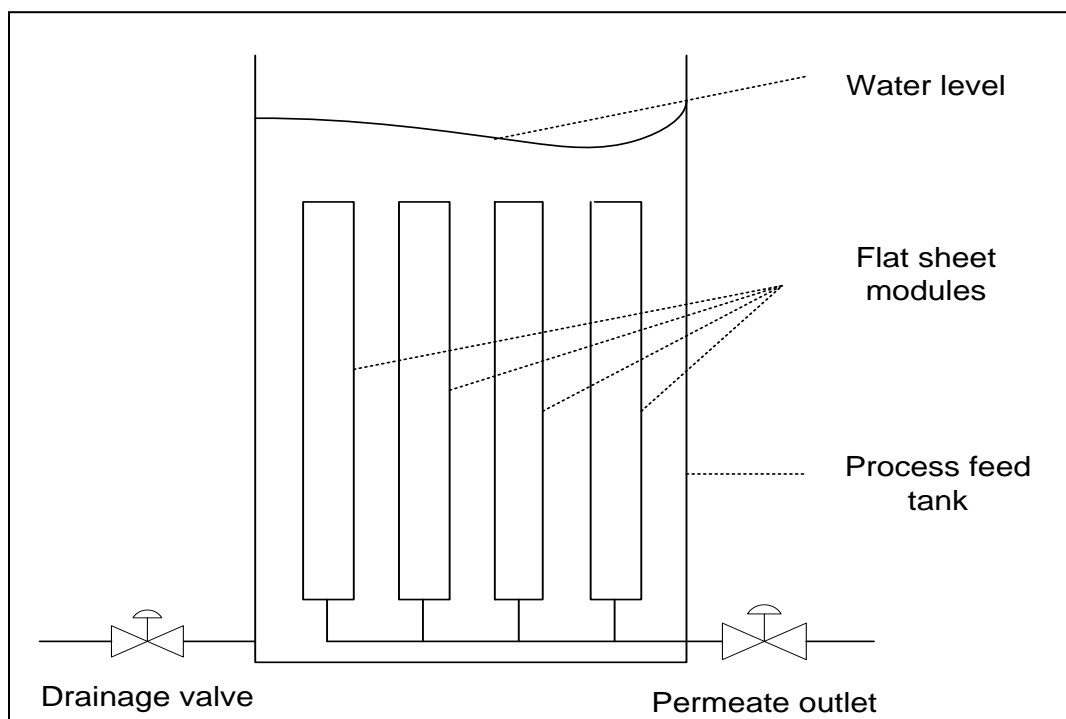


Figure 1- 2: Schematic representation of the cross section of the RRWTS

Previous studies by Pillay *et al* (2009) have shown that the RRWTS can reduce turbidity to less than 1 NTU irrespective of the feed turbidity. However, in terms of microbiological removal, it is not an absolute barrier to microorganisms and can achieve 95 to 99 per cent removal efficiency of *E.coli*, which does not meet the set international potable water standards. Potable water should have zero *E. coli* count per 100 mL of treated water (WHO 2011b). Therefore, to attain international standards, a disinfectant must be added such as chlorine. Indeed, membranes, along with post disinfection, can be effectively used for total removal of pathogens (Edzwald 2011).

However, the main challenge of post disinfection when left to the user is the possibility of human error in disinfectant dosing. This can result in overdosing, underdosing or even forgetfulness to add the disinfectant. These can have adverse effects on the consumers

such as: formation of DBPs that are carcinogenic due to overdosing; and the risk of contracting disease resulting from underdosing or not adding disinfectant at all. This has prompted investigations into the incorporation of antimicrobial materials in membranes in order to improve their disinfection efficacy and prevent the human error resulting from chemical dosing by consumers. In this regard, the use of nanotechnology based materials has come to the limelight.

1.1.5 Silver nanoparticles (AgNPs) as a potential disinfection technology

The use of nanotechnology for water disinfection has gained prominence in recent times. For instance, the formation of DBPs by conventional disinfectants such as chlorine and ozone has motivated researchers to explore the antimicrobial activity of nanomaterials, such as silver, titanium dioxide and copper. These antimicrobial nanomaterials, unlike conventional chemical disinfectants, are not strong oxidants and are not likely to produce harmful DBPs. Their incorporation into treatment processes, has the potential to replace or enhance conventional disinfection methods (Li, Q *et al.* 2008).

Silver is a widely studied oligodynamic material due to its antimicrobial effectiveness on a range of microorganisms, low toxicity to human beings, and ease of incorporation on various substrates for disinfection applications. The main known negative health effect from silver is *argyria*, a condition in which the skin and hair are discoloured resulting from silver overload in the tissues (WHO 2011b). AgNPs are nanoscale clusters of metallic silver atoms, engineered for antimicrobial and sterile applications (Jones and Hoek 2010). AgNPs when incorporated into a membrane, release silver ions. These ions, although at concentrations too low to adversely affect human health, are harmful to bacteria that would otherwise colonize the membrane surface. Incorporation of antimicrobial AgNPs makes the membranes reactive instead of a simple physical barrier, thereby performing multiple functions in one unit (Li, Q *et al.* 2008).

It has been stated that functional nanomaterials having antimicrobial properties, can be used to build high performance, low cost, easy to use and maintain small scale POU systems for use in areas not connected to a central water supply or even for use during emergencies such as floods (Li, Q *et al.* 2008; Tansel 2008; Hotze and Lowry 2011). AgNPs are common nanomaterials whose use in water disinfection has been widely

investigated (Pradeep, T. and Jain 2005; Oyanedel-Craver and Smith 2008; Dankovich and Gray 2011). The key advantages of using AgNPs for water treatment are that they do not produce any taste, odour, colour in the treated water or form DBPs (Solsona and Méndez 2003). AgNPs have been previously successfully incorporated in polyurethane foams (Pradeep, T. and Jain 2005), ceramic filters (Oyanedel-Craver and Smith 2008), carbon (Yoon *et al.* 2008) and polymeric nanofibres (Barakat *et al.* 2010) and depicted good disinfection ability using a variety of microorganisms.

However, AgNPs have not been incorporated to the polyester based WFME for water disinfection purposes. Therefore, this study endeavoured to investigate the performance of the WFME incorporated with AgNPs as a POU technology for water treatment. The use of nanoparticles in this study was motivated by the facts that compared to bulk silver, they are low cost with a controllable release rate of silver ions (Lv *et al.* 2009). The immobilization of AgNPs on the WFME membrane ensures that the release of silver ions can be optimized, so that the filter will have great potential for use in water disinfection (Yang, F *et al.* 2009). The RRWTS incorporating AgNPs uses a synergistic mechanism in order to achieve the reduction of microbial contamination in water. The first mechanism is filtration; the filter will ideally separate any particle or organism that is larger than the pore size of the filter. The second mechanism is the inactivation of microorganisms by the AgNPs attached to the filter.

1.1.6 Purpose of the study

This study investigates the incorporation of AgNPs in the RRWTS to enhance its disinfection efficacy. This will ensure that filtration and disinfection are achieved in one step instead of the usual two steps. It is envisioned that this system will be advantageous in terms of ease of operation, low cost (equipment, operation and maintenance), overall simplicity and excellent disinfection capability.

1.2 Objectives of this dissertation

The overall aim of this study was to investigate the incorporation of AgNPs in the WFMF membrane in order to enhance its disinfection efficacy as a POU potable water filter. The specific objectives were:

1. To investigate the incorporation of AgNPs on the WFMF membrane and the characteristics of the coated membrane.
2. To investigate the filtration and disinfection efficacy of the coated filter using river water and synthetic feed.
3. To investigate the performance of the coated membrane filter over time in terms of disinfection efficacy and silver elution.

1.3 Approach

The study was conducted in three main stages. Firstly, the incorporation of AgNPs on the WFMF membrane was investigated by employing the *in situ* chemical reduction of silver nitrate (AgNO_3) using sodium borohydride (NaBH_4) to produce and attach AgNPs on the WFMF membrane. The coated membrane was characterized using different microscopy, analytical and spectroscopy techniques (SEM, XRD, FTIR, and Sessile drop contact angle measurement, UV-Vis Spectroscopy, ICP-AES, and TGA). The filters were assembled and integrity testing done using air pressure technique. The filters were used to filter water with different turbidities in order to investigate the filtration performance.

Secondly, the disinfection efficacy of the coated filter was investigated for short term trials. Disk diffusion test and glass bottle test were done using membrane disks in contact with media containing *E.coli*. The flow test was conducted by filtration of water containing different *E.coli* concentrations. The *E.coli* concentrations in the feed and permeate were determined.

Lastly, the long term disinfection performance of the coated filter was studied. In addition, investigation of silver elution from the coated filters with time and the effect of the elution on the disinfection efficacy were also investigated. These investigations were conducted over a period of 90 days.

1.4 Dissertation organization

This dissertation contains six chapters organized as follows:

Chapter 1 provides the general background to the problem being researched and presents the basis for this study. The objectives and purpose of the study are also given.

Chapter 2 provides background information from existing literature on the treatment of potable water and specifically on disinfection. It presents the use of POU water treatment technologies, the use of current commercial membranes and their limitations and introduces the RRWTS as a viable interim solution for potable water treatment in rural areas. It highlights the use of AgNPs incorporated on the WFMF membranes for water disinfection.

Chapter 3 presents the investigation of the incorporation of AgNPs on the WFMF membrane and the characterization of the membranes. It also presents the filtration performance test.

Chapter 4 presents the investigation of the disinfection performance of the coated filter for short term trials. It provides information on the antimicrobial assays employed to investigate the disinfection efficacy of the coated filter.

Chapter 5 presents the investigation of the long term disinfection performance of the coated filter. It examines the effect of time on the leaching of silver from the coated filter and the relationship between the leaching and disinfection efficacy.

Chapter 6 provides the overall summary of the dissertation. It summarizes the main findings, and identifies the limitations of the study. Lastly, it provides recommendations for future work.

2 LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of the literature relevant to this study. The information is presented in six sections. Firstly, the disinfection of water is evaluated with regard to provision of clean and safe drinking water in rural areas. Secondly, the drinking water quality guidelines recommended by the WHO are presented. Thereafter, an overview of UF and MF processes is presented since these processes are readily applicable in rural areas. Furthermore, challenges facing the use of current membrane systems in rural areas are discussed. The RRWTS is then presented as a viable alternative POU water system in these areas. Lastly, the incorporation of AgNPs in water filters to enhance the disinfection efficacy is presented.

At the end of this chapter, a summary of the literature reviewed is provided and the gaps in knowledge which are the basis of this study are clearly identified. In addition to the literature survey presented in this chapter, more literature concerning the specific objectives of each of the subsequent chapters (3, 4 and 5) is also presented in the said chapters.

2.2 Disinfection of water

2.2.1 The need for disinfection

Disinfection is the removal of pathogenic microorganisms, and is typically the last purification process for drinking water treatment. Pathogens are any type of microorganism capable of causing disease (Kawamura 2000). Disinfection can be achieved by adding a given concentration of chemical agents such as chlorine to the water and allowing contact between the water and the disinfectant for a pre-determined

period of time. Physical methods of disinfection of water such as irradiation with UV-light and boiling can also be used (Schutte, F 2006).

The presence of pathogens such as bacteria, viruses and protozoa, necessitates the disinfection of water in order to prevent the transmission of waterborne diseases through the contaminated water (Tansel 2008). Disinfection satisfies the core objective of water supply systems, which is, to provide consumers with drinking water that is sufficiently free of microbial pathogens in order to prevent the occurrence waterborne diseases (Edzwald 2011). The addition of a disinfectant to water should satisfy two requirements. Firstly, it should provide primary disinfection, which is the inactivation of pathogens at the water treatment plant. Secondly, it should ensure secondary disinfection by providing a protective disinfectant residual throughout the distribution system. This ensures protection against further intrusion by pathogens resulting from recontamination by biofilm growth or leakages in the distribution system (Edzwald 2011).

Water intended for human consumption should be safe, palatable and aesthetically pleasing in order to prevent consumers from contracting waterborne diseases such as cholera, typhoid fever and dysentery (WHO/UNICEF 2006; Cabral 2010). These diseases are predominantly due to faecal contamination of water sources and thus are related to sanitation conditions. Provision of safe drinking water and observance of proper sanitation can significantly improve the health of consumers and eliminate waterborne diseases which are a major risk in developing countries (Momba *et al.* 2008).

2.2.2 Contaminants in water

Fresh water is mainly available as surface water and collected rainwater which are commonly used as sources for drinking water in developing countries. The majority of this water is, however, contaminated with pathogenic microorganisms and a range of suspended and dissolved matter. Release of used and untreated water into rivers is common in developing countries where up to 90 per cent of water goes untreated after use, thereby degrading the quality of surface waters (Hotze and Lowry 2011). All water contains natural contaminants, particularly inorganic contaminants that arise from the geological strata through which the water flows and anthropogenic pollution by both

microorganisms and chemicals (Fawell and Nieuwenhuijsen 2003). Contaminants in water can be categorized as being physical, chemical and microbiological in nature. There are guidelines for a number of contaminants present in drinking water (WHO 2011b). These guidelines are presented later in section 2.3, Table 2-2.

2.2.2.1 Physical contaminants

a. Suspended solids

The presence of suspended solid matter in water determines the turbidity of the water. High turbidity can reduce the efficiency of disinfection by increasing the disinfectant demand. The disinfectant demand is the capacity to react with and consume the disinfectant. A higher demand due to the suspended matter and organics in water necessitates a greater disinfectant dose in order to achieve adequate biocidal treatment. It is recommended that the turbidity of water should be less than 1 NTU before disinfection (WHO 2011b).

b. Colouring agents

The presence of colour in water is normally associated with the presence of humic and fulvic acids or as a result of high metal content (iron, manganese and copper). Colour can be removed through oxidation or coagulation. Water meant for drinking should be clear and free from colour in order to be appealing to consumers (Spellman and Drinan 2000). Consumers are likely to doubt the quality of water despite being well treated if it has some colour.

c. Taste and odour

These are normally associated with the presence of dissolved volatile organics. Knowledge about the nature of the odorous compound is essential in the identification of the source and consequent selection of an appropriate treatment process (Walt *et al.* 2009). Taste tends to reflect inorganic constituents, while odour mainly reflects organic constituents. Taste is often influenced by temperature and pH (Edzwald 2011).

2.2.2.2 Chemical contaminants

Sources of chemical contaminants in water include: industrial effluent; run off from farms using fertilizers; and leachate from rocks. The most important chemical contaminants from a health perspective include arsenic, fluoride, and nitrates from agricultural activities.

2.2.2.3 Microbiological contaminants

The contamination of drinking water by pathogens causing waterborne diseases is the most important aspect of drinking water quality. This is mainly due to contamination of water by faecal matter containing pathogenic organisms. The microbiological quality of water is determined by the type and numbers of microorganisms present in the water. Most of these microorganisms are harmless but if the water is polluted, pathogens which cause diseases may be present. Pathogens in water can be classified as bacteria, viruses and protozoa. Table 2-1 shows the common pathogens found in drinking water sources. The waterborne transmission of the pathogens listed has been confirmed by epidemiological studies and case histories (WHO 2011b).

Table 2- 1: Pathogens transmitted through drinking water (WHO 2011b)

Bacteria	Viruses	Protozoa
<i>Burkholderia pseudomallei</i>	Adenoviruses	<i>Acanthamoeba</i> spp.
<i>Campylobacter jejuni</i> , <i>C. coli</i>	Astroviruses	<i>Cryptosporidium hominis</i> / <i>Parvum</i>
<i>Escherichia coli</i> - Pathogenic	Enteroviruses	<i>Cyclospora cayetanensis</i>
<i>E. coli</i> - Enterohaemorrhagic	Hepatitis A virus	<i>Entamoeba histolytica</i>
<i>Francisella tularensis</i>	Hepatitis E virus	<i>Giardia intestinalis</i>
<i>Legionella</i> spp.	Noroviruses	<i>Naegleria fowleri</i>
Mycobacteria (nontuberculous)	Rotaviruses	
<i>Salmonella</i> Typhi	Sapoviruses	
<i>Shigella</i> spp.		
<i>Vibrio cholerae</i>		

Microbial water quality is normally verified based on the analysis of faecal indicator microorganisms, with the organism of choice being *E. coli* or, thermo tolerant coli forms (WHO 2011b).

2.2.3 Disinfection techniques for water

According to Schutte (2006), microorganisms can be removed, inhibited or killed by a range of methods or a combination of them:

- Physical destruction processes involve heating and UV-light irradiation. Heating water by boiling or by solar energy is possible in small scale especially in situations where there is no other form of disinfection available.
- Physical separation processes include gravity separation and filtration. The former includes coagulation, flocculation, sedimentation and floatation while the latter involves using membranes, ceramic filters, slow sand filters, etc. It is of great importance that these processes are optimized as protozoan cysts are largely resistant to chemical agents and their removal is primarily dependent on efficient coagulation–flocculation, sedimentation and filtration.
- Chemical destruction and prevention of multiplication involves the use of chemical agents and is the most popular means of potable water disinfection. The most commonly used chemicals include chlorine gas, chlorine dioxide, sodium hypochlorite, monochloramine, bromine, iodine, ozone, hydrogen peroxide, silver and copper.
- Biological destruction occurs in a slow sand filter operating under gravity. The natural bacteria and protozoa within the top layer of the filter (*Schmutzdecke*) actively treat the water. The *Schmutzdecke* is a biofilm which forms at the sand-supernatant boundary consisting of bacteria and other organic compounds. This layer interacts with the water as it passes through leading to separation of particles smaller than the inter-granular space between the sand and other biodegradable contaminants (Ray and Jain 2011).

2.2.4 Mechanisms of disinfection

There are three general mechanisms of pathogen inactivation using chemical disinfectants:

- Deactivation through the destruction of the cell wall, or impairment of the functions of the semi-permeable membranes. The cell membrane consists of basic compounds such as phospholipids and lipo polysaccharides, and is stabilized by magnesium and calcium cations. Thus, if ionized, disinfecting molecules are absorbed or repelled by electrical charges leading to the dissolving of non-polar molecules into the lipid phase, and transport of other molecules through the membrane and disturbance of the membrane structure (Maris 1995).
- Interference with energy-yielding metabolism processes of the microorganism. This renders the enzymes non-functional.
- Interference with biosynthesis and growth by preventing the synthesis of normal proteins, nucleic acids, coenzymes, or the cell wall.

Figure 2-1 shows the potential targets for disinfectants on Gram-negative and Gram-positive bacteria.

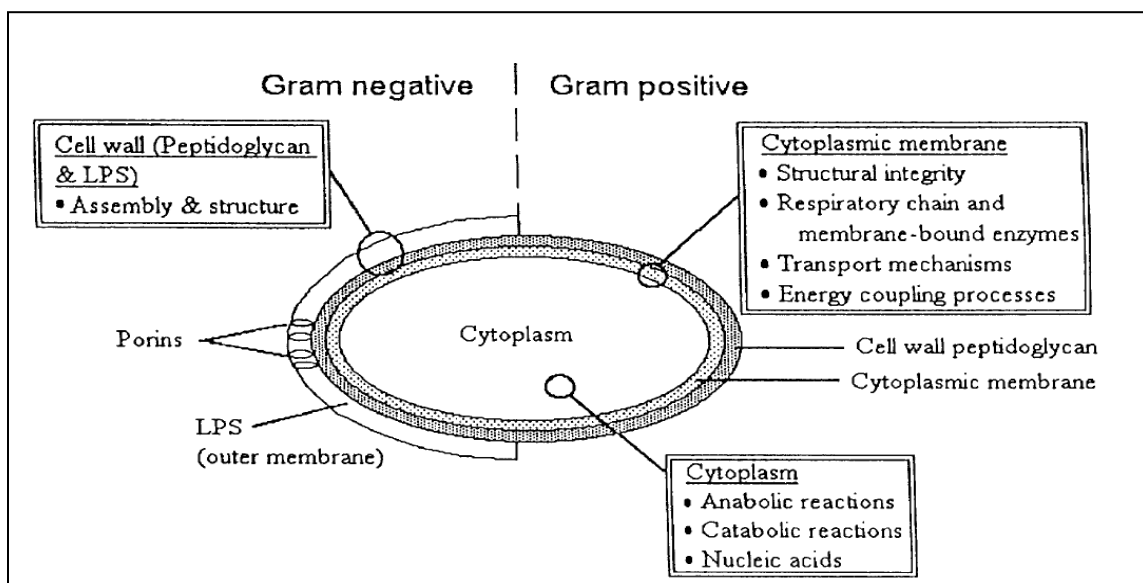


Figure 2- 1: Potential targets for biocides on Gram negative and Gram positive bacteria (Denyer and Stewart 1998)

It has been stated that for the case of nanoparticles, their major antimicrobial mechanisms include: direct interaction with the microbial cells; disruption of the cell envelope; and penetration leading to oxidation of cell components. Furthermore, the production of secondary products such as reactive oxygen species (ROS) or dissolved heavy metal ions cause significant damage to microorganisms (Li, Q *et al.* 2008). The antibacterial action of silver ions released from AgNPs is shown in Figure 2-2.

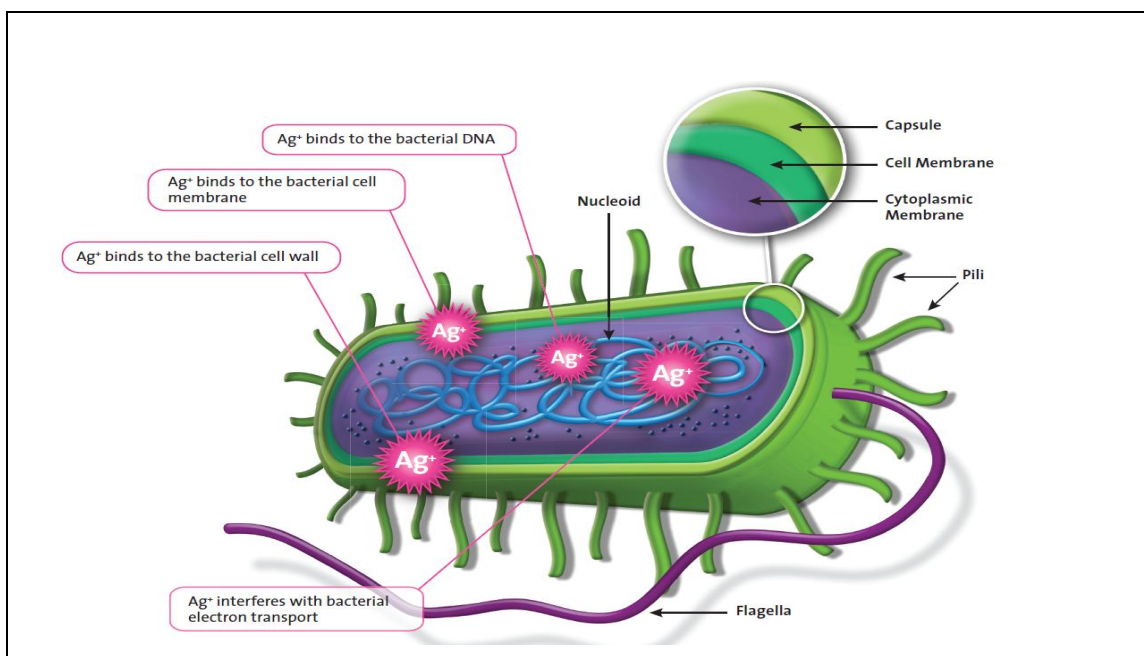


Figure 2- 2: Bacterial target sites for silver cations (Lindsay 2011)

The use of membrane technology, especially MF and UF is another method of disinfecting water. This is accomplished by filtering water using membranes with a pore size less than the size of the microorganisms. MF membranes generally have pore sizes in the range 0.1 μm to 5.0 μm . Hence by selection of a membrane close to but less than the minimum size of the microorganism of concern, good disinfection can theoretically be achieved. A major drawback resulting from this method is that MF membranes tend to result in some breakthrough of bacteria after a period of time. However, this can be prevented by regular cleaning of the filters. The removal of the much smaller viruses seems to be possible with these membranes as well since most viruses are attached to larger bacteria or other particles. UF membranes with pore sizes less than 0.1 μm can also be used (Solsona and Pearson 1995).

2.2.5 Factors affecting disinfection processes

The factors determining the amount of disinfectant used to achieve the required disinfection include (Schutte, F 2006; Binnie and Kimber 2009):

- The target organism - *E.coli* is considered more resistant than most pathogenic bacteria and some viruses and this is one of the reasons why it is used as an indicator organism.
- Chemical properties of the water that is disinfected and the disinfectant.
- Disinfectant demand of the water.
- pH of the water.
- Temperature of the water at the point of disinfectant and throughout distribution system. Increases in temperature lead to increased rates of chemical disinfection.
- Concentration of disinfectant and contact time required for full disinfection.
- Retention time in the distribution system and disinfectant decay during distribution and storage.
- The presence of suspended matter in the water that may shield the organisms from the disinfectant.

2.2.6 Current large scale water disinfection practices

Most of the large scale water supply systems especially municipal supplies rely on the conventional water treatment method in order to meet the set standards of potable water treatment. Conventional treatment of water for potable use involves a multi barrier approach using a number of treatment steps aimed at achieving the following objectives: removal of suspended and colloidal matter to an acceptable level by means of coagulation-flocculation, sedimentation and sand filtration; disinfection to produce water that is free from microbial pollution; and chemical stabilization of the water to prevent corrosion of pipelines, or the formation of chemical scale in distribution network.

The conventional water treatment process train is illustrated in Figure 2-3.

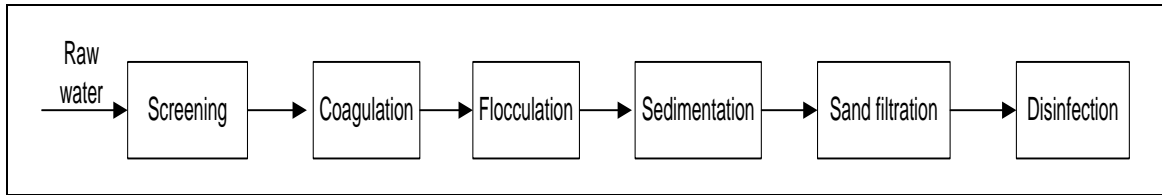


Figure 2- 3: Schematic representation of the conventional water treatment process

High turbidity levels can reduce the efficiency of disinfection by creating a disinfectant demand and lead to the formation of by products. The particles may also provide absorption sites for toxic substances in the water, protect pathogens and indicator organisms from disinfection by adsorbing them, and interfere with the microbiological assays (Edzwald 2011). It is recommended that water to be disinfected should have a turbidity of less than 1 NTU (WHO 2011b).

The selection of the appropriate combination of processes to treat water from a particular source depends on factors such as the turbidity of the water, the nature of the suspended material, and the chemical properties of the water among others. Generally, the conventional water treatment process includes the following steps:

- Screening is used to separate large solid particles such as stones and debris from water.
- Coagulation is aimed at destabilizing the colloidal particles and is achieved through the addition of chemicals (coagulants) to the water. The most common coagulants are aluminium sulphate, ferric chloride, hydrated lime, and polyelectrolytes.
- Flocculation process follows coagulation and its aim is to cause the individual destabilized colloidal particles to collide with one another and with the precipitate formed by the coagulant in order to form aggregates that could easily be removed by means of sedimentation or flotation. To achieve this, the water containing the coagulant is stirred at a slow rate, causing the individual particles to agglomerate.
- Sedimentation process whereby the aggregates that have been formed during coagulation and flocculation are allowed to settle from the water is then done.

The flocs collect as sludge at the bottom of the sedimentation tank from where they can be removed. The clean water overflows from the sedimentation tank to collection troughs.

- Sand filtration in which the water is allowed to filter through a layer of sand in a specially constructed container, to remove the small remaining floc particles and allow clean water to permeate from the bottom of the sand bed.
- Disinfection is performed by adding a disinfectant to the water in order to inactivate pathogens present in the water before it is distributed to the consumers.

The disinfectants normally used for conventional water treatment include:

1. Chlorine

Chlorine is the most commonly used disinfectant for drinking water. Filtration prior to disinfection is necessary to reduce pathogen levels, making disinfection more reliable by removing turbidity to less than 1 NTU prior to disinfection. A residual of 0.2 mg/L is also required in the distribution system. The benefits of maintaining a residual include: suppressing microbiological deterioration; providing a simple means for monitoring to check that disinfection has been carried out; and providing very limited protection against recontamination (Jackson *et al.* 1999). The disadvantage of chlorination is the formation of DBPs such as tri halo methanes (THMs) which are carcinogenic.

2. Chloramines

Chloramination has the advantages of producing very small amounts of THMs, levels that are not significantly harmful to human health; in addition, chloramine residual lasts longer than free chlorine. However, chloramines are less effective than chlorination as bactericides and viricides (Kawamura 2000).

3. Chlorine dioxide

It has been used as a primary disinfectant in large scale systems in Europe mainly for taste and odour control, oxidation of iron and manganese and control of THMs. It has

high oxidation power and is a better bactericidal agent than hypochlorous acid in water. However, it has higher operational costs than chlorine (Kawamura 2000).

4. Ozone

It is the most powerful oxidant and disinfectant and has been widely used in Europe. In practice, it is normally used together with a disinfectant such as chlorine in order to provide a residual. Its advantages include strong disinfecting power, better flocculation and filter performance, reduction in the formation of THMs precursors before final chlorination. The disadvantages include: high capital cost; lack of a disinfectant residual; and the need to be produced on site because it cannot be stored (Kawamura 2000).

5. UV light

UV disinfection of drinking water is well established especially in developed countries and is often used as a substitute for chlorination. The system consists of a quartz-sleeved UV lamp in contact with the water. The water flows along the annular space between the quartz sleeve and the outer wall of the chamber (Jackson *et al.* 1999). The disinfectant dose delivered by a UV system is expressed as UV radiation energy density. UV-light can provide as effective a barrier to micro-organisms (bacteria and viruses) just like chlorine, and is often considered to be more effective against viruses. Its advantages include: it does not add chemicals that can cause secondary taste and odour problems; there is no risk of overdosing; no DBPs are formed; and it requires short contact times of three to five seconds leading to a compact installation.

The limitations of UV disinfection include: suspended matter may absorb UV radiation or shield microbes from UV radiation and result in less UV light reaching the target and hence reduced microbial disinfection; no disinfectant residual; UV light can also result in skin and eye damage to operators of the equipment. In addition, the ability of bacteria and other cellular microbes to repair UV-induced damage and restore infectivity, is disadvantageous (Sobsey 2002).

2.2.7 Current disinfection practises for rural areas

Rural areas of developing nations are mostly affected by faecal contamination resulting from poor sanitation facilities. The inhabitants of these areas obtain water from rivers and dams and often use it without any treatment. In most developing economies, water treatment and distribution infrastructure is well developed in urban areas unlike in rural areas (Momba *et al.* 2008).

The installation of conventional water treatment plants in these areas is hampered by a number of challenges. For instance, rugged topography and vast tracts of land with long distances between homesteads; these often requiring long piping systems for water distribution which is not economically feasible. Lack of proper infrastructure in rural areas often characterized by poor transport systems with some interior places being inaccessible. Furthermore, lack of finances due to low economic activity and general lack of stable sources of income for the people in these areas are key challenges; in addition, the governments of these mostly undeveloped countries, lack finances to implement conventional treatment in such areas. Lastly, the remoteness of rural areas presents a significant challenge. Rural communities are mostly situated away from the major centres. This often limits access to management and supervision facilities for water-supply infrastructure and services. For these areas, implementation of centralized systems is generally expensive and unsustainable (Peter-Varbanets *et al.* 2009).

The lack of quality potable water is a major hindrance to health and economic development especially in most developing countries. Consequently, this has made the provision of potable water as a priority in the affected countries (Pillay *et al.* 2009). The use of interim solutions such as POU water treatment systems is a potential option.

POU systems comprise a range of water treatment systems that can be used by households or communities in order to reduce contaminants in collected water at the point of consumption. POU water treatment systems have been proposed as an effective and practical interim solution for provision of safe potable water, especially, for consumers in small or rural communities and relying on surface water (Sobsey 2002). These systems have gained wide acceptance as being practical solutions to problems of

degradation of drinking water sources in rural areas of developing economies, where collecting water outside the home and storing it for household use is the norm.

POU systems can also potentially reduce the challenges of conventional water treatment and distribution, such as: the loss of water resulting from leakages in pipes; deterioration of water quality associated with aging water distribution networks leading to recontamination during distribution; and also in the reduction of the costs associated with piping systems. These technologies, therefore, have the potential to fill the service gap where conventional treatment and distribution systems are not possible or feasible. This is envisioned to potentially result in substantial improvement in health in developing countries (WHO 2011b). POU treatment is also suited to catastrophic situations that necessitate emergency supplies of potable water. For instance, breakdowns in water supply systems caused by natural disasters, war and human conflict, often results in people being confined in temporary settlements such as refugee camps or shelters where these systems can be used.

The following is a review of the commonly used POU water disinfection systems:

a) Chemical disinfection

Chemical disinfection of household drinking-water in developing countries is done mainly using free chlorine, in liquid form such as 1 per cent hypochlorous acid. This form of free chlorine is convenient and easy to dose. The dosing should be done properly in order to ensure enough chlorine residual during storage and use. It is recommended that a free chlorine residual of 0.2 mg/L in stored household water treated by chlorination is suitable (WHO 2011b). Chlorination may also be done using calcium hypochlorite which is a white, dry solid containing approximately 65 per cent chlorine, and is commercially available in granular and tablet forms. The use of chlorine tablets is illustrated in Figure 2.4.

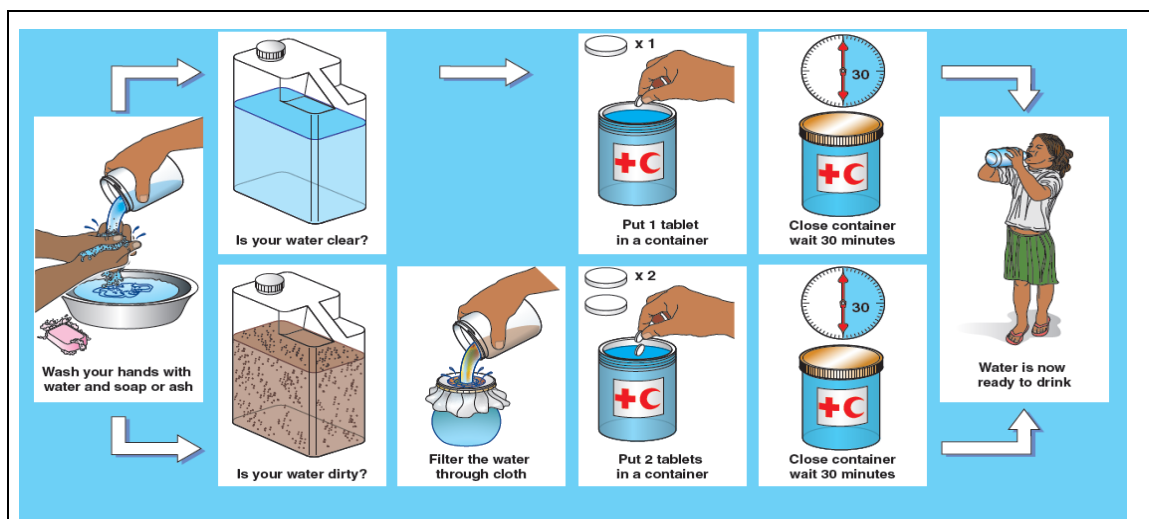


Figure 2- 4: Procedure for water treatment using chlorine tablets (Kayaga and Reed 2011)

Other chlorine based commercial disinfectants include WaterGuard and PuR (Figure 2- 5). WaterGuard is a dilute 1 per cent sodium hypochlorite solution in a 150 mL bottle. It is best suited for clear water. It is administered by mixing 4 mL to 20 L of raw water. The water is stirred and left to disinfect for about 30 minutes. The process of using PuR involves placing the contents of one sachet of PuR powder in 10 L of water and stirring vigorously for five minutes. The water is left to flocculate and the flocs to settle and then filtered over a clean cotton cloth. The filtrate is left to disinfect for 30 minutes, after which it is ready to drink. In Kenya, water with turbidities as high as 1850 NTU have been successfully reduced to 3.2 NTU with a single treatment (Alekal 2005).



Figure 2- 5: Photographs of WaterGuard and PuR packaging

The challenges in the use of chlorine and its derivatives include: the formation of DBPs; the dangers of users overdosing or underdosing; and the fact that it may not be readily available in the rural areas.

b) Solar disinfection

Solar water disinfection is a low cost method that is relatively easy to understand, and is environmentally friendly since it uses sunlight only. It utilizes the UV radiation in sunlight as well as the heat from sunlight energy to inactivate microbes (WHO 2011a). A particularly popular form of modern solar water disinfection is called Solar Disinfection (SODIS). In SODIS, clear, transparent 1 or 2 L poly ethylene plastic bottles are filled with water of low turbidity and set in the sun to heat throughout the day (Figure 2-6). The bottles are exposed to the sunlight for 3-6 hours on a sunny day or 48 hours on a cloudy day, generally in countries situated in the tropics, where sunlight is strong and plentiful.

The limitations of this method are: long waiting time for disinfection; small quantity of water disinfected at a time; dependence on the availability of sunlight which may vary depending on the season hence only suitable in the tropics where sunlight is abundant. Moreover, it does not remove turbidity and requires time for the treated water to cool down before consumption.

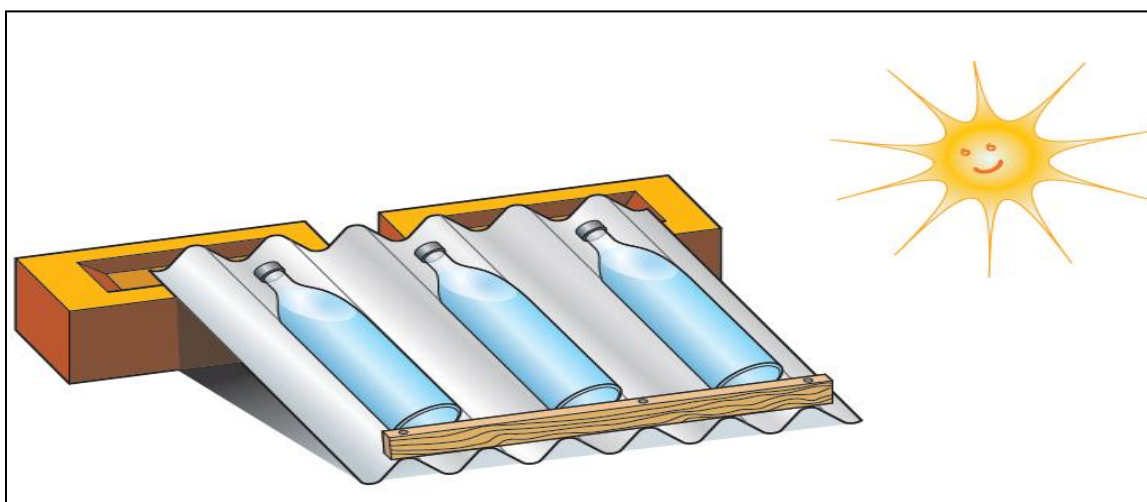


Figure 2- 6: An illustration of solar disinfection (Kayaga and Reed 2011)

c) Filtration

Filtration may be considered as a method of disinfection but its mechanism is based on the fact that bacteria are removed rather than inactivated. Filtration is the mostly used process for the removal of particulate matter and turbidity, by water flowing through a porous media. The effectiveness of filtration in reducing microbes varies widely, depending on the type of microbe and its size. In addition, other factors include the type and characteristics of the filtration medium or system.

Ceramic filters are commonly used for POU water treatment. The filters are made of clay and are normally pot shaped. The ceramic filter element is manufactured with local materials and skills with a mixture of clay, sawdust, and water and is pressed into a pot shape with press moulds. Once the filter element has its shape, it is fired in a kiln and the sawdust is combusted to leave porous material. The filtration process involves pouring the raw water in the filtering element and collecting treated water from the plastic faucet (Figure 2-7).

Ceramic filters coated with silver such as the one that has been commercialized by Potters for Peace (PFP), a non-governmental organization, have been used for disinfection of water. The filter element, in this case, is coated with a mixture of colloidal silver, for disinfection purposes (Halem 2006). Their use for the removal of faecal coli forms, and protozoan oocysts has been found to be significant.

However, their main limitations are: they tend to be relatively costly if all materials are not locally available; variability in quality control of locally produced filters; they tend to easily break; cleaning of the filter by scrubbing removes the nano silver coating hence reducing the antimicrobial capacity; and have low permeate flow rates of 1- 3 L/h for non-turbid waters (Bang *et al.* 2011).

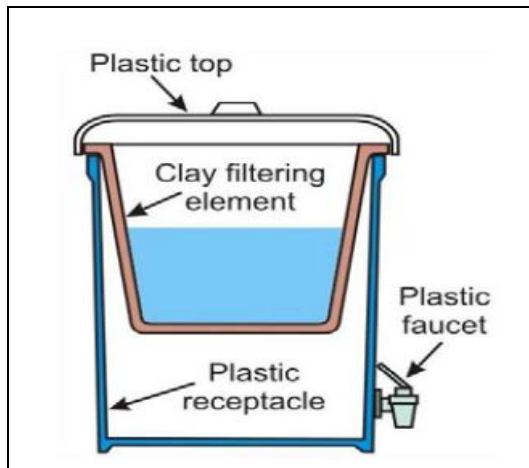


Figure 2- 7: Schematic representation of a ceramic pot filter (Halem 2006)

d) Ozonation

Ozone is commonly used in developed countries and it is a strong oxidant capable of rapidly and extensively inactivating a variety of waterborne pathogens, including chlorine-resistant *Cryptosporidium parvum* oocysts (Sobsey 2002). Ozone is a gas and is unstable in water, therefore, unable to provide a stable disinfectant residual. Its use as a POU water treatment system is relatively expensive and difficult to maintain because ozone leaks can be hazardous. Moreover, it requires electricity and therefore not amenable for use in rural areas which lack this facility.

e) Boiling

Boiling is an established method for killing pathogens in water. The water is heated and allowed to boil for one full minute or more. The water is thereafter allowed to cool, and then transferred to a clean covered container (Sobsey 2002). However, boiling is not a very economical way to disinfect water in developing countries because free or low cost firewood usually required as fuel for boiling may not be sufficiently available nearby, and it takes time both to acquire the firewood and to boil the water. Moreover, it does not remove turbidity, requires time to cool the water before consumption which can lead to recontamination, may alter the taste of the water, and that hot water can cause serious accidents in the home.

f) Membrane based systems

There are a few membrane systems, which are applicable as POU systems in rural areas. These are presented in section 2.4 of this chapter.

Overall, the major concern regarding the use of POU technologies is the problem of monitoring treatment performance so that it is comparable to central treatment and is of the required standards. However, this can be accomplished with regular tests of treated water by trained people in the community or the service providers in order to determine whether it meets the set standards (Goodrich *et al.* 2003).

2.3 Drinking water quality guidelines

Drinking water safety is judged based on national standards or international guidelines. The most widely used are the WHO Guidelines for Drinking Water Quality (Fawell and Nieuwenhuijsen 2003). They provide guidelines on microbiological, chemical, aesthetic and physical aspects. The following is a comparison of South Africa's SANS 241 standards (Standard 2011) and WHO guidelines (WHO 2011b) for drinking water.

Table 2- 2: Drinking water quality guidelines and standards (Standard 2011; WHO 2011b)

Parameter	Units	WHO Guideline	SANS 241-1 Standard
Physical quality requirements			
Colour	mg/L Pt	< 15	< 15
Dissolved solids	mg/L	< 1000	< 1200
Odour	TON	< 5	<5
pH value @ 25 ⁰ C	pH units	6.5-8.5	5.0-9.7
Taste	FTN	< 5	< 5
Turbidity	NTU	< 1	< 1
Chemical quality requirements – macro determinand			
Ammonia as N	mg/L	< 1.5	< 1.0
Calcium as Ca	mg/L	< 200	< 150
Chloride as Cl ⁻	mg/L	< 250	< 300
Fluoride as F ⁻	mg/L	< 1.5	< 1.5
Nitrate as N	mg/L	< 11	< 11
Silver as Ag	mg/L	< 0.1	Not specified
Sodium as Na	mg/L	< 50	< 200
Sulfate as SO ₄ ²⁻	mg/L	< 250	< 250
Zinc as Zn	mg/L	< 3	< 5
Chemical quality requirements – micro determinand			
Aluminium as Al	µg/L	< 200	< 300
Antimony as Sb	µg/L	< 20	< 20
Arsenic as As	µg/L	< 10	< 10
Cadmium as Cd	µg/L	< 3	< 3
Total Chromium as Cr	µg/L	< 50	< 50
Copper as Cu	µg/L	< 2000	< 2000
Cyanide (recoverable) as CN	µg/L	< 500	< 70
Iron as Fe	µg/L	< 2000	< 300
Lead as Pb	µg/L	< 10	<10
Manganese as Mn	µg/L	< 400	< 100
Mercury as Hg	µg/L	< 6	< 6
Nickel as Ni	µg/L	< 70	< 70
Selenium as Se	µg/L	< 40	< 10
Chemical requirements — organic determinand			
Total trihalomethanes	µg/L	< 100	< 300
Phenols	µg/L	<9	< 10
Microbiological Safety Requirements			
<i>E. coli</i>	count/ 100 mL	0	0
Thermo tolerant (faecal) coli form bacteria	count/ 100 mL	0	0

The focus of the present study was on treatment of water from sources available in rural areas. For such areas, the major contaminant in the water sources is faecal matter resulting from poor sanitation facilities leading to wash out of faecal matter to rivers. Since the rural areas normally do not have high industrial activities, the chemical contamination is expected to be relatively low.

Therefore the parameters of interest in this study were as follows:

- Turbidity of the water

Production of permeate with a turbidity of less than 1 NTU was the desired target.

- *E.coli* concentration

Production of permeate with zero *E.coli* concentration was the desired target. Practically, it is tedious to determine the presence of all the different pathogenic organisms in water. Therefore, certain organisms such as *E.coli*, are used to give an indication of the possible presence of pathogens (Schutte, F 2006). These organisms are referred to as indicator organisms. The use of indicator organisms is based on the premise that enteric bacterial pathogens will have similar survival characteristics as the indicator organisms. As a consequence, standards of water quality are expressed in terms of these indicator organisms (Jackson *et al.* 1999). As noted earlier, potable water should be free of *E.coli*, i.e., zero *E.coli* per 100 mL of treated water (WHO 2011b).

- Silver concentration

This parameter was of interest because the filters employed were coated with AgNPs and hence had a potential of leaching silver into permeate. Silver is considered a safe metal and is present in drinking water sources at levels of 0.005 mg/L which is considered low. However, where silver is used to maintain the bacteriological quality of drinking water, it is recommended that up to 0.1 mg/L is acceptable without risk to human health (WHO 2011b). The desired target was a silver concentration of less than 0.1 mg/L in treated water.

2.4 Overview of MF and UF processes

2.4.1 Introduction to membrane processes

Membranes are used in the filtration of water such that water molecules are allowed to pass through but other matter is excluded based on size (Ray and Jain 2011). Membranes produce a consistent permeate quality regardless of feed water conditions because they act as an absolute barrier to particles larger than the membrane's pore size (Azrague and Osterhus 2008). Membrane processes are classified based on the driving force for the separation. Pressure driven processes include MF, UF, NF and RO. Diffusion based process include, dialysis, and membrane absorption. Membrane distillation is a heat based process while electro dialysis is an electric based process.

Pressure-driven membrane processes are the most commonly used in water treatment. The hierarchy of pressure-driven membrane processes is illustrated in Figure 2-8 and the pore sizes and operating pressures of the membranes are shown in Table 2-3.

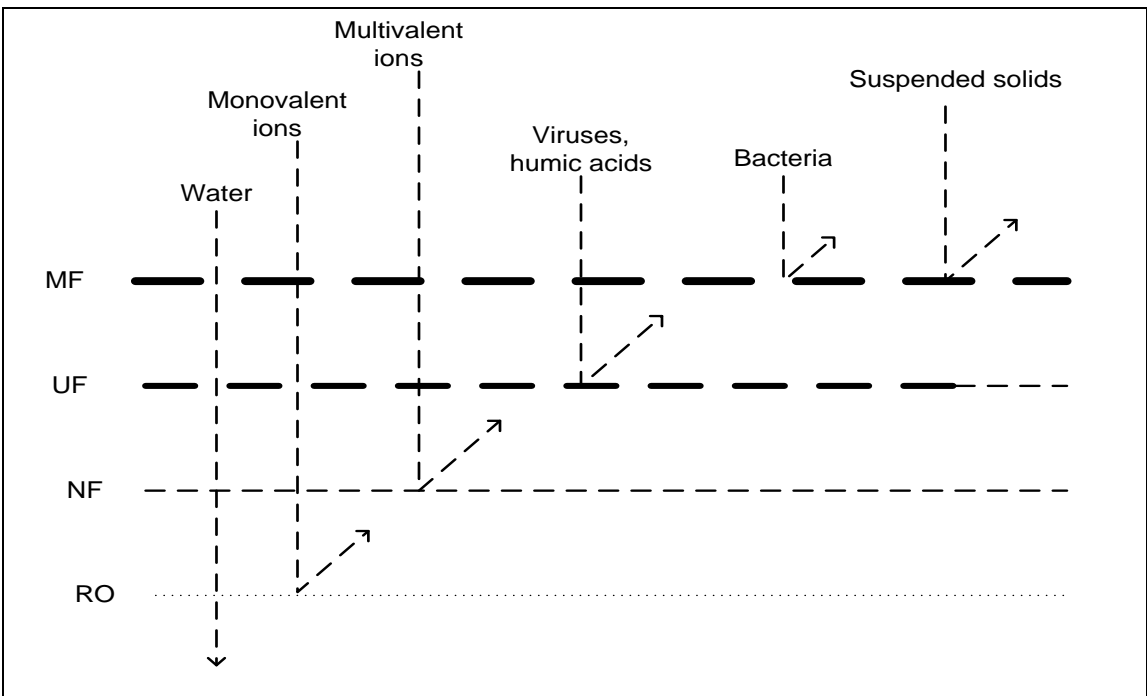


Figure 2- 8: Hierarchy of pressure driven membrane processes

Table 2- 3: Classification of pressure driven membrane processes

Process	MF	UF	NF	RO
Pressure (Bar)	0.5-2	0.5-2	5-12	8-70
Pore size (µm)	0.05-1.0	0.005-0.5	0.0005-0.01	0.0001-0.001

The study reported here aimed at developing a membrane based system that can be applied in rural areas of developing nations. The system should be able to operate without the use of electricity or pumps. The pressure driven membrane processes that meet these criteria are MF and UF. These processes are considered as being appropriate in reducing the colloidal and microbial burden of source waters (Basri *et al.* 2010) and will be discussed further.

2.4.2 Mechanisms of separation in MF and UF processes

The main removal mechanism in MF and UF processes is size exclusion. Therefore, these processes can theoretically achieve perfect exclusion of particles regardless of operational parameters such as influent concentration, pressure or the skills of the operator. The separation is based on the membrane pore size and the quality of product is determined by the membrane (Crittenden *et al.* 2005). The major mechanisms of separation in MF and UF include:

1. Straining

This is also called sieving, and it occurs when particles are physically retained because they are larger than the pores (Figure 2-9). However, this does not mean that there is 100 per cent retention of particles larger than the membrane pore size. The interconnecting voids in membrane filters have a distribution of sizes, including some larger and others smaller than the retention rating. Therefore, particles smaller than the retention rating may be trapped in smaller passageways and larger particles may pass through the membrane in other areas (Crittenden *et al.* 2005).

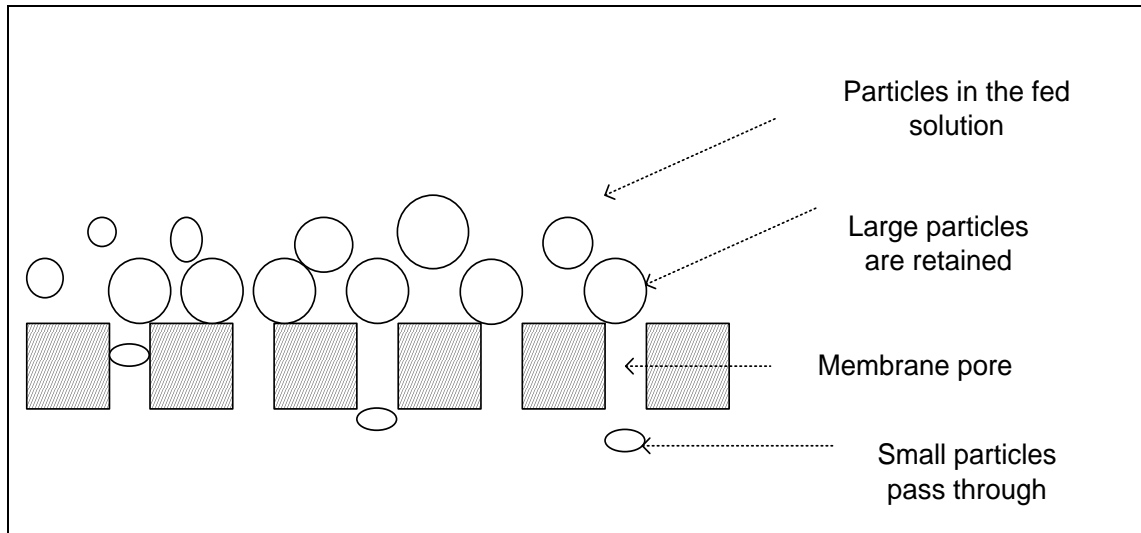


Figure 2- 9: Schematic representation of separation of particles by straining in MF and UF processes

2. Cake filtration

This is a process whereby particles that are small enough to pass through the membranes are retained by a cake of larger material that collects at the membrane surface during filtration (Figure 2-10). This cake acts as a pre-coat filtration medium, often called a dynamic membrane since its filtering capability varies with time, growing in thickness during filtration but being partially or wholly removed by cleaning (Crittenden *et al.* 2005).

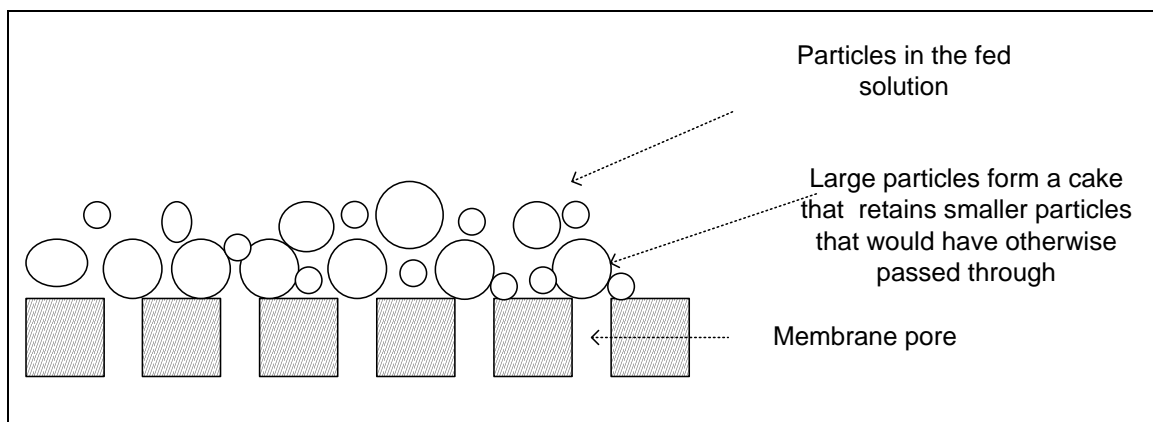


Figure 2- 10: Schematic representation of cake filtration in MF and UF processes

3. Adsorption

This mechanism results when material small enough to enter pores adsorbs to the walls of the pores. If the particles and the membrane are oppositely charged or if their zeta potentials are appropriate the particles will adhere to the membrane matrix resulting in removal of the particles smaller than the pores of the membrane (Madaeni 1999). This means that soluble materials may be rejected even though their physical dimensions are much smaller than the membrane retention rating (Figure 2-11). Adsorbed material can reduce the size of voids throughout the membrane. This will therefore, increase the ability of the membrane to retain smaller material by straining while increasing the chances of membrane fouling (Crittenden *et al.* 2005).

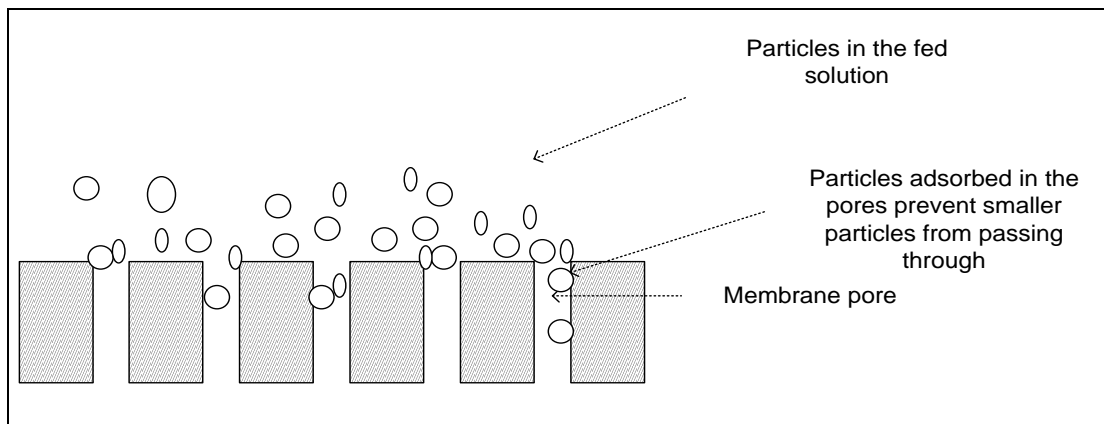


Figure 2- 11: Mechanism of adsorption of particles on membrane pores resulting in the removal of particles much smaller than the membrane rating

2.4.3 Transport in MF and UF membranes

MF and UF processes involve the application of a pressure difference across the membrane in order to achieve separation of particulate matter from the feed (Figure 2-12). The nature of the membrane itself controls which components permeate and which component is retained (Cheryan 1986). An important aspect of determining the performance of MF and UF systems is the rate of solute or particle transport towards the membrane which is measured in terms of flux. The permeate flow through the membranes

can be described by Darcy's law, whereby the flux (J) through the membrane is directly proportional to the applied pressure (Mulder 2003):

$$J = k \cdot \Delta P \quad (2.1)$$

Where,

k is the permeability constant containing structural factors such as porosity, viscosity

ΔP is the applied transmembrane pressure (TMP)

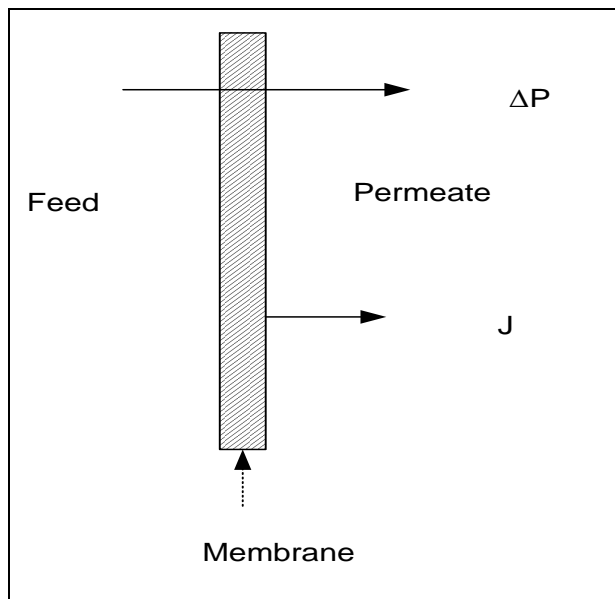


Figure 2- 12: Schematic representation of transport in MF and UF membranes

The flux or permeation rate of the membrane can also be obtained using the expression,

$$J = \frac{V}{A \cdot t} \quad (2.2)$$

Where,

V is the permeate volume (L)

A is the membrane filtration area (m²)

t is the period over which permeate is collected (h)

One of the widely used theories for modelling flux in pressure-independent, mass transfer controlled systems is the film theory shown in Figure 2-13. As the feed is filtered, solute is brought to the membrane surface by convective transport at a rate, J_s ,

$$J_s = J C_b \quad (2.3)$$

Where,

J is the permeate flux (LMH)

C_b is the bulk concentration of the rejected solute

The resulting concentration gradient causes the solute to be transported back into the bulk of the solution due to diffusion effects (Cheryan 1986). The rate of back-transport of solute (J_s) is given by,

$$J_s = D \frac{dC}{dx} \quad (2.4)$$

Where,

D is the diffusion coefficient

dC/dx is the concentration gradient over a differential element in the boundary layer

At steady state, the rate of solute deposition is equal to the rate of solute back transport and the two mechanisms balance. Hence equations 2.3 and 2.4 can be equated and integrated over the boundary layer to give,

$$J = k \ln C_g/C_b \quad (2.5)$$

Where,

k is the mass transfer coefficient

C_g is the gel concentration at the membrane surface

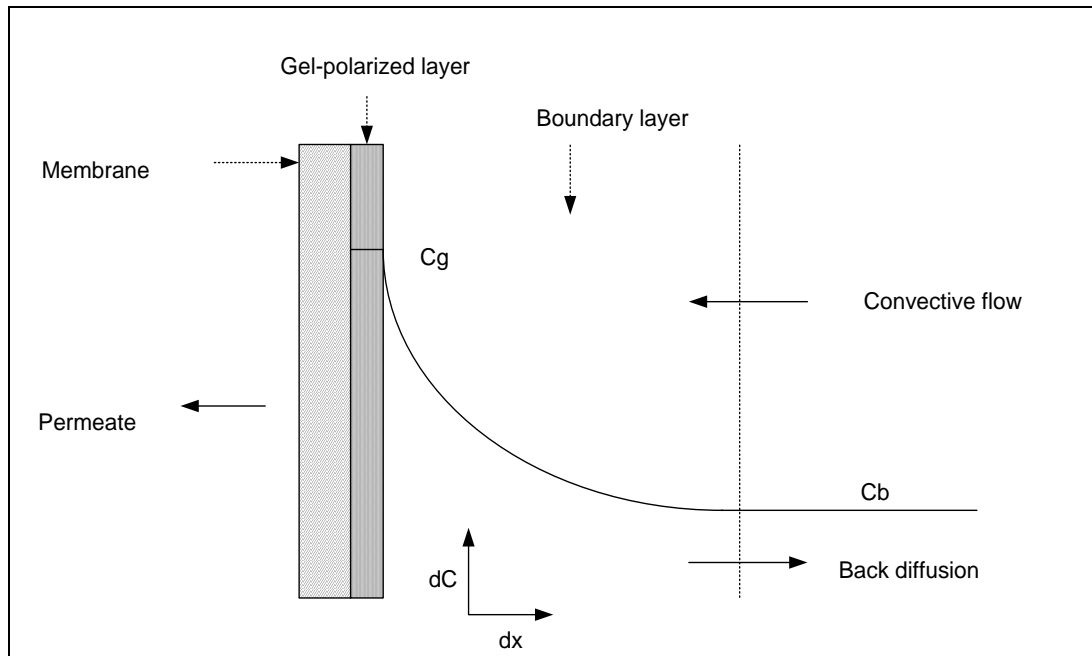


Figure 2- 13: Schematic representation of concentration polarization showing the gel-polarized layer and the associated boundary layer

2.4.4 Membrane module configurations

Membranes can be operated using different module configurations, such as flat sheet, spiral wound, hollow tube and tubular. Spiral wound membranes are made of rolled up layers of flat membrane sheets around a central permeate collection pipe. Hollow fibre configurations usually consist of a group of many tubes that are themselves constructed of membrane material. A summary of the configurations is shown in Figure 2-14 and Table 2-4.

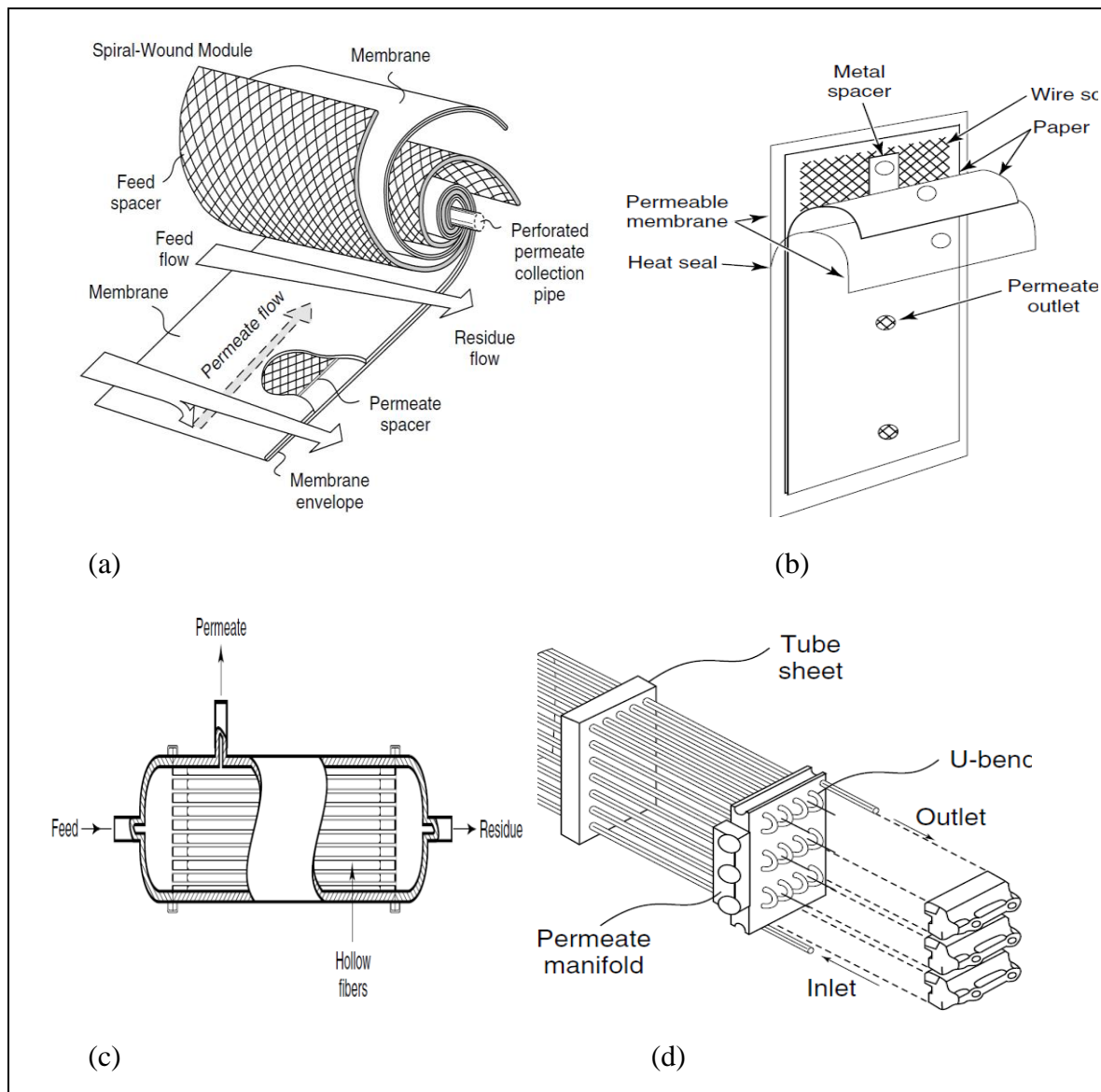


Figure 2- 14 : Membrane module configurations, (a) spiral wound, (b) flat sheet, (c) hollow fibre and (d) tubular (Baker 2004)

Table 2- 4: Merits and demerits of different membrane module configurations

Module configuration	Advantages	Disadvantages
Flat sheet	<ul style="list-style-type: none">• Low hold-up volume• Permeate collected from individual membranes	<ul style="list-style-type: none">• Difficult to clean• Replacing the membrane is time consuming
Spiral	<ul style="list-style-type: none">• Compact• Low energy requirement• Low capital requirement	<ul style="list-style-type: none">• Dead spaces• Difficult to clean• If faulty, whole membrane is replaced
Hollow fibre	<ul style="list-style-type: none">• Low hold-up volume• Backwashing is possible• Low energy requirement	<ul style="list-style-type: none">• Not suitable for viscous fluids• Damage to one fibre leads to replacement of whole module
Tubular	<ul style="list-style-type: none">• Easy to operate and clean• Can be used for viscous and non-Newtonian fluids	<ul style="list-style-type: none">• High energy consumption• High hold up volume• Large space demand

2.4.5 Membrane filtration modes

Pressure-driven membranes may be operated in different modes of filtration:

1. Dead end filtration

The entire feed flow is forced through the membrane under pressure (Figure 2-15). As particles accumulate on the membrane surface or in its interior, the pressure required to maintain the required flow increases due to increased cake resistance (Baker 2004). The increased resistance to filtration causes the permeate flux rate to decline if the pressure drop is held constant, or causes the pressure drop to increase if the flux rate is held constant (Davis 1992). Therefore, at some point the membrane must be cleaned or replaced due to the cake layer.

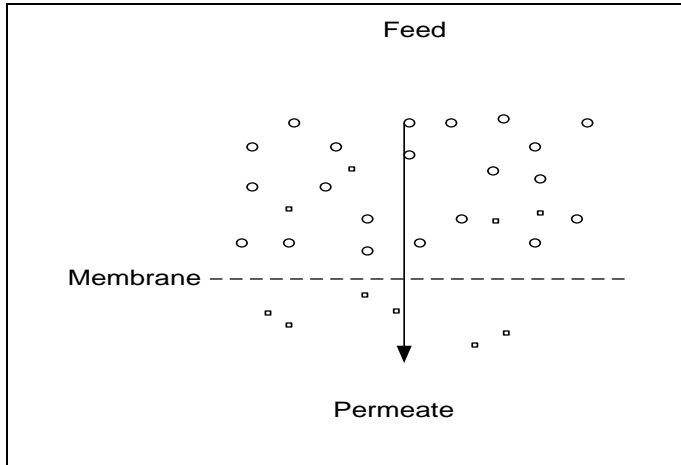


Figure 2- 15: Schematic representation of dead end filtration.

The behaviour of permeate flux and cake thickness for constant pressure is shown in Figure 2-16. The flux decreases with time as a result of increase in the resistance to filtration due to the increasing cake thickness. After the membrane is cleaned, the cake layer is removed and the flux is regained.

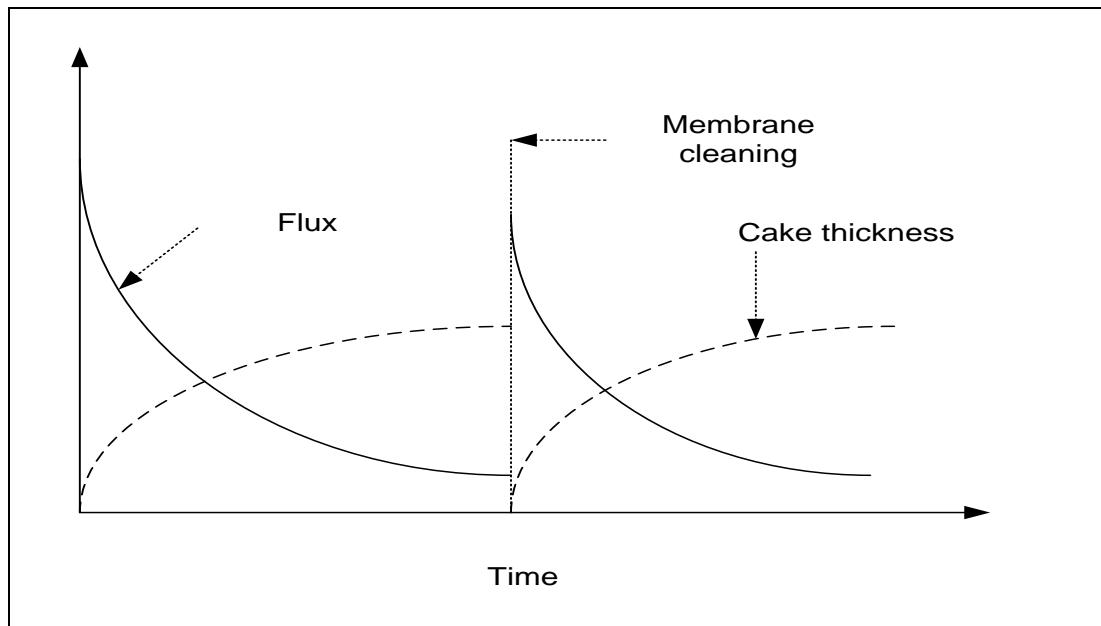


Figure 2- 16: Schematic representation of flux and cake thickness for constant pressure dead end filtration (Ho and Sirkar 2001)

The behaviour of ΔP and cake thickness for constant flux dead end filtration is shown in Figure 2-17. The ΔP increases with time as a result of increase in the resistance to filtration due to the increasing cake thickness. After the membrane is cleaned and the cake layer removed, the ΔP decreases due to the low resistance to filtration.

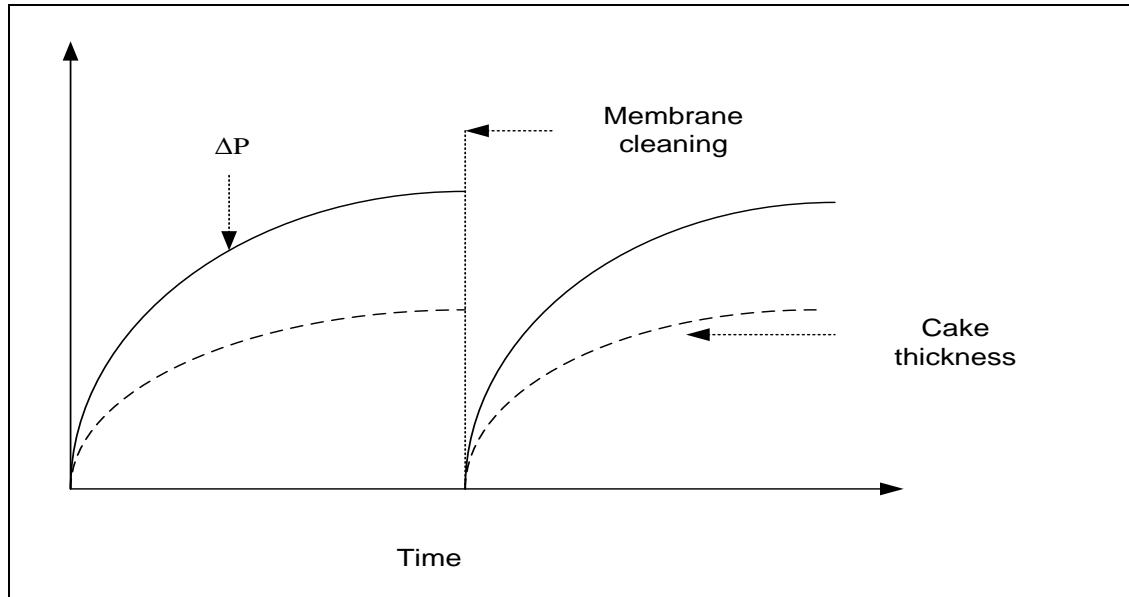


Figure 2- 17: Schematic representation of TMP and cake thickness for constant flux dead end filtration (Ho and Sirkar 2001)

2. Cross flow filtration

The feed solution is circulated across the surface of the filter, at a high velocity parallel to the membrane surface (Figure 2-18). This is done in order to reduce the collection of retained species at the membrane surface and hence the formation of the cake layer. The liquid being filtered is pumped tangentially across the membrane surface at the filtration pressure and at a right angle to the permeate flow direction. The deposited solids thus are sheared from the membrane surface and carried away with the feed solution. It produces two streams, permeate and a concentrated retentate containing the rejected particles. The equipment required for cross-flow filtration is more complex, but the membrane lifetime is longer than with dead end filtration (Baker 2004).

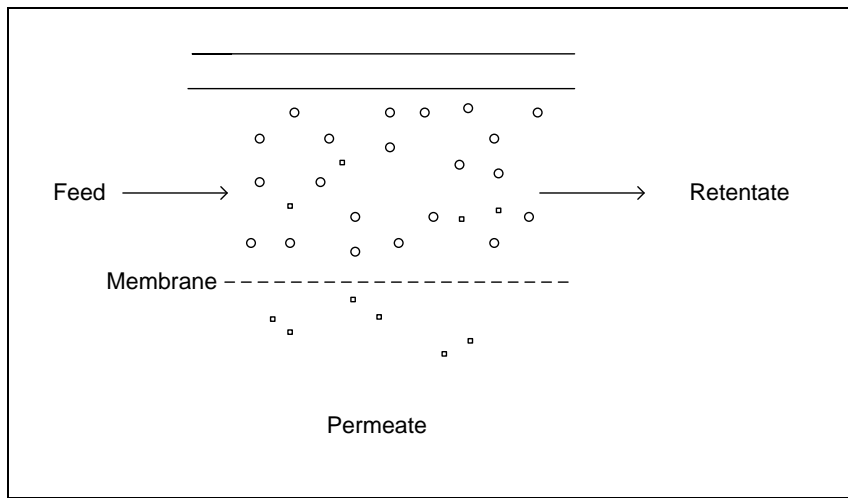


Figure 2- 18: Schematic representation of cross flow filtration.

Unlike in dead end filtration, the cake layer does not build up indefinitely. Instead, the high shear exerted by the feed flowing tangentially to the membrane surface sweeps the deposited particles towards the filter exit so that the cake layer remains thin (Davis 1992). This makes it possible for high fluxes to be maintained over prolonged periods of time and as shown in Figure 2-19, a steady state flux is achieved once the cake layer has reached its steady state thickness.

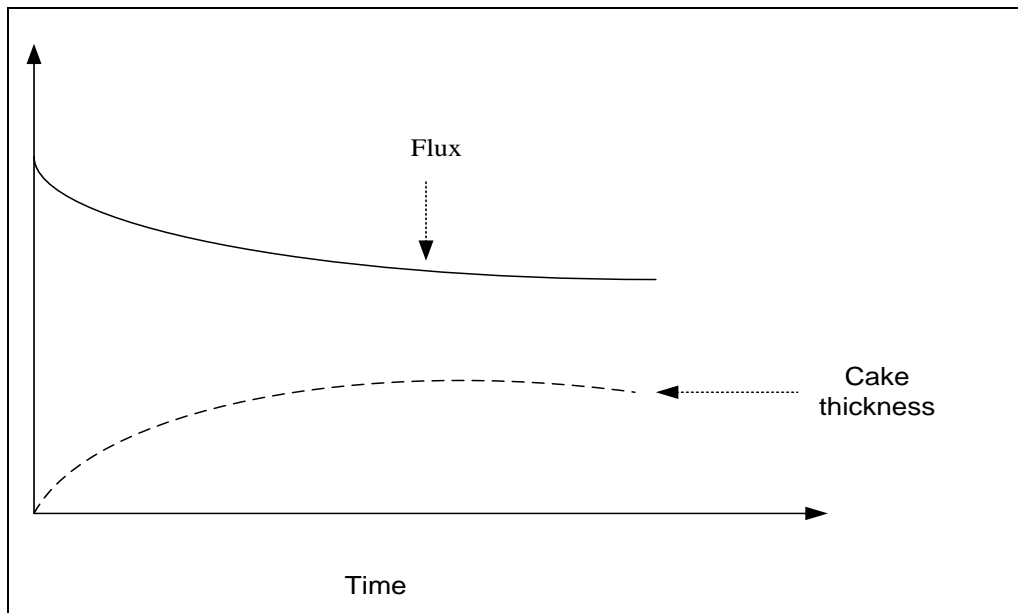


Figure 2- 19: Schematic representation of the behaviour of the flux and cake thickness during cross flow filtration (Ho and Sirkar 2001)

3. Immersed membrane filtration

This mode is commonly employed in membrane bioreactors for waste water treatment. The membranes are immersed in the feed solution contained in the process tank filtration occurs either inside-out or outside-in. The principle of submerged gravity driven membrane filtration is illustrated in Figure 2-20.

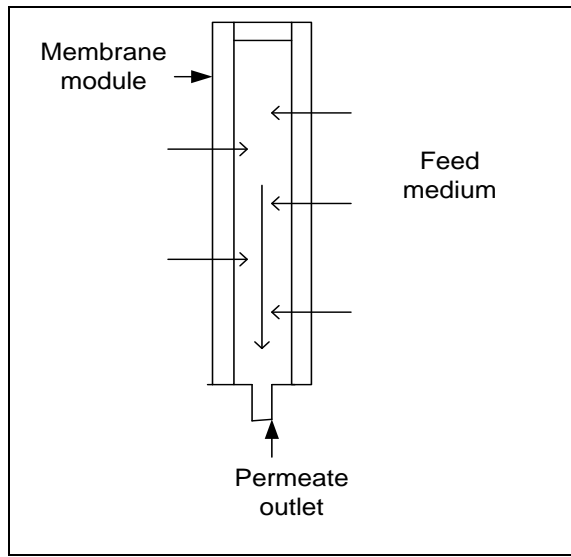


Figure 2- 20: Schematic representation of outside-in immersed membrane filtration

2.4.6 Membrane Fouling

Despite advances in membrane science and technology, the application of membrane processes continues to be derailed by the persistent problem of membrane fouling. Fouling refers to the deposition, adsorption, and/or accumulation of rejected species on, or within the membrane, causing loss of flux and altered rejection (Madaeni 1999). This significantly reduces the performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pores or within its pores (Crittenden *et al.* 2005). Fouling affects membrane filter performance by gradual deterioration of the system's performance in terms of flux as shown in Figure 2-21.

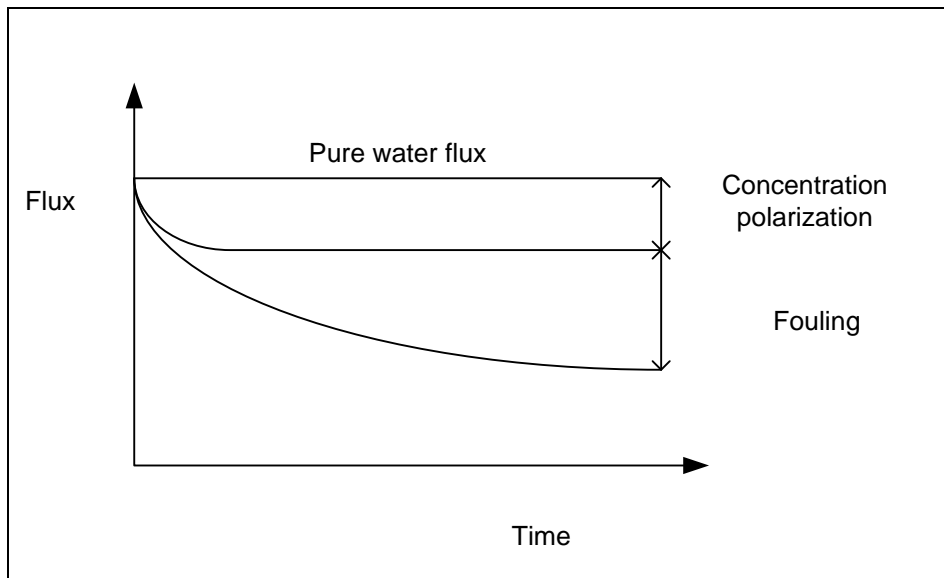


Figure 2- 21: Representation of membrane fouling and concentration polarization during membrane filtration (Mulder 2003)

A typical filtration process includes a period of rapid decline of flux followed by an asymptotic limit at steady state. Membrane performance is thus affected by a decrease in the permeate flux, increase in TMP and a decrease in rejection. These changes often continue throughout the process and eventually necessitate extensive cleaning or replacement of the membrane.

The pressure –flux behaviour observed during MF and UF processes can be expressed using the following equation (Cheryan 1986):

$$J = \frac{(\Delta P - \Delta \pi)}{\mu(R_m + R_f)} \quad (2.6)$$

Where,

ΔP is the applied pressure (TMP)

$\Delta \pi$ is the osmotic pressure

μ is the feed viscosity

R_m is the intrinsic membrane resistance determined using pure water as feed

R_f is the fouling layer resistance due to pore clogging, gel layer, and adsorption

For MF and UF processes the $\Delta\pi$ term is negligible because the osmotic pressure of the molecules is negligible compared to the applied pressure. Equation 2.6 can then be expressed as,

$$\boxed{J = \frac{\Delta P}{\mu R t}} \quad (2.7)$$

Where,

R_t is the total resistance composed of R_m and R_f

Concentration polarization arises due to the membrane retaining solute molecules near the membrane surface. If the feed solution contains proteins, a gel layer can be formed on the membrane surface. Moreover, if solutes penetrate into a porous membrane, they can lead to pore blocking and finally, if solutes are adsorbed on the membrane surface and within the pores they can increase the resistance to filtration.

Generally, two types of membrane fouling can be obtained. Firstly, surface fouling, also known as reversible fouling, occurs when the foulant appears as an evenly deposited layer on the membrane surface. This can be easily removed by physical cleaning and hence the permeation rate of the membrane can be regenerated. Secondly, pore fouling, also referred to as irreversible fouling whereby, particulate matter diffuses into the membrane pores causing internal membrane fouling. The flux cannot be regenerated by cleaning and ultimately this limits the lifetime of the membrane (Baker 2004).

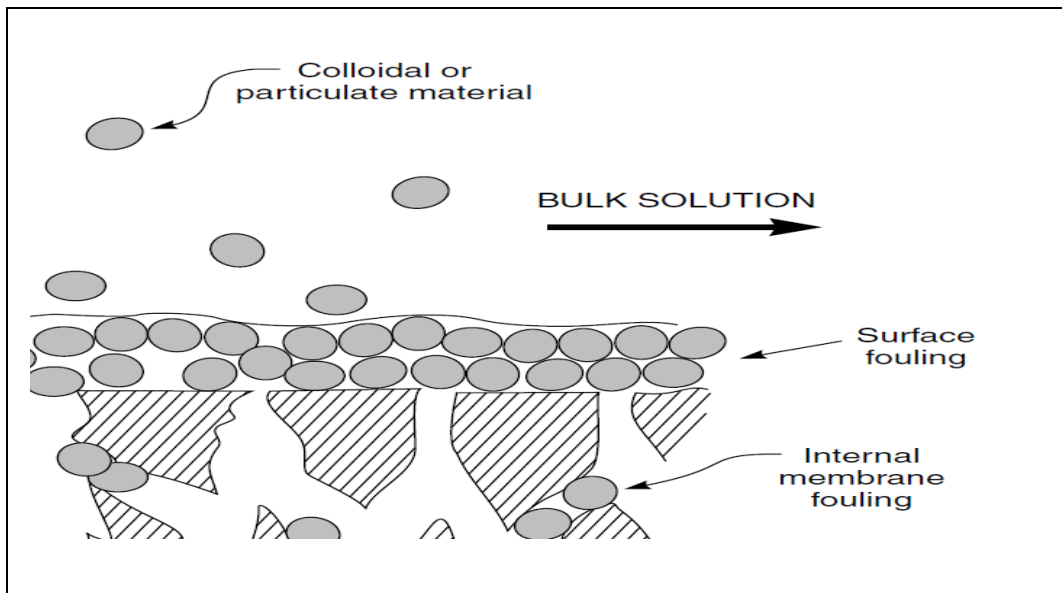


Figure 2- 22: Schematic representation of membrane fouling, showing both surface fouling and internal pore fouling (Baker 2004)

Fouling has other serious implications on the membrane filtration performance. For instance, it leads to increased energy consumption due to higher TMP, reduces the duration of continuous operation before cleaning, it significantly decreases the membrane durability and hence affects the overall economy of the membrane process.

Therefore, control of fouling is of utmost importance and the techniques involved include (Madaeni 1999):

- Preventive measures such as, pre-treatment of feed to reduce the amount of particulate matter reaching the membranes and therefore reduce fouling.
- By adjusting the operating conditions, e.g. pressure, cross flow and backwashing velocities, fouling can be controlled.
- Membrane regeneration by cleaning the membrane with or without using chemicals can reduce fouling.

The modification of the membranes by incorporation of metallic nanoparticles has the potential to impact antifouling capability on the membranes improving the membrane

properties, making the membranes reactive instead of simply a physical barrier (Li, Q *et al.* 2008; Zodrow *et al.* 2009).

2.4.7 Membrane Cleaning

Fouling necessitates that the modules be cleaned periodically to remove the fouling matter from the surface and pores of the membrane. Flux recovery to the pure water flux after cleaning is normally an indication of a cleaned membrane. The choice of cleaning method depends on: the module configuration, the type of membranes, the chemical resistance of the membranes, and the type of fouling matter in the feed (Wenten 2008). The cleaning methods are classified as follows:

- Hydraulic cleaning includes back flushing, alternate pressurizing and depressurizing and changing the flow direction at a given frequency. This technique, however, has limitations such as, it reduces the effective operation time, and results in loss of permeate to the feed solution (Wenten 2008).
- Mechanical cleaning involves the physical removal of the fouling matter. It can be done using oversized sponge balls, ultrasonic waves and air scouring.
- Chemical cleaning is the most commonly used method for reducing fouling, employing a number of chemicals either separately or in combination. Depending on the membrane material, chemicals such as sodium hydroxide, sodium hypochlorite and other detergents and disinfectants can be used (Madaeni 1999).
- Electrical cleaning is done by applying an electric field across a membrane. This makes the charged particles or molecules to migrate in the direction of the electric field hence, separating them from the membrane (Wenten 2008).

2.4.8 Application of MF and UF processes in large scale water treatment

Membranes have been applied in the processing of groundwater, surface water, and wastewater to levels that are now competitive with conventional techniques (Kochubovski 2007). Membranes are increasingly being used in large scale water treatment for the removal of particulate matter, chemical and microbiological

contaminants, desalination of sea water using RO, and treatment of waste water using membrane bioreactors.

MF and UF are commonly used in potable water treatment. The application of membranes in potable water treatment has been spurred by the increasing demand for high quality water from poorer water sources, the decreasing costs of membranes and the high demand by regulators and customers who expect effective barriers to water quality threats. The use of membrane processes in large scale water treatment systems has been motivated by its advantages over conventional processes shown in Table 2-5.

Table 2- 5: Comparison of conventional and membrane based water treatment

Conventional treatment	MF and UF processes
Requires a multiple barrier approach	Provides a once-off physical barrier to microorganisms
Requires large pieces of land for new plants and for expansion of existing plants	Compact footprint often allowing for major capacity expansion in existing footprint
Labour and chemical intensive	Automated with greatly reduced chemical use

2.4.9 MF and UF based small scale systems for rural areas

2.4.9.1 Potential advantages of MF and UF in rural areas

The use of membrane technology systems in rural areas has the following potential advantages (Jackson *et al.* 1999; Madaeni 1999; Crittenden *et al.* 2005; Guo 2011):

- Membranes produce very high water quality with significantly reduced or no chemical consumption.
- The quality of the product is fixed by the membrane, and does not vary as the raw water quality varies nor does it depend on the skills of the operator.

- Membrane systems are very simple to operate; they can be fully automated and do not require highly skilled operators.
- Membrane systems are modular, and the capacity of treatment units can be increased easily. Furthermore, they are amenable to easy scale up and scale down or even hybridize with other processes.
- Membranes have high process-intensity i.e., small land area per unit volume of water processed, hence allowing for smaller footprint.

2.4.9.2 Existing MF and UF small scale systems for rural areas

The same membranes used for large scale water treatment can be adapted for small scale systems (SSSs). SSSs are of larger capacity than POU systems, but smaller than centralized systems. Typically, SSSs treat the water consumed by several families in a community and hence are called community based systems. These systems can also be adapted for household use. Existing small scale membrane systems include:

1. Sky Hydrant and Sky box Units

The Sky Hydrant water filtration unit developed by Sky Juice Foundation in Australia is a SSS intended for community water supply in developing countries. It is a low pressure, high flow UF unit. It may be operated under gravity although high water pressures set up options are available. It produces approximately 700 L/ h of clean drinking water. It significantly removes turbidity and pathogens from water including bacteria, viruses, protozoa, cysts and parasites. The membrane has to be backwashed manually regularly and chemically cleaned using 10 per cent hypochlorite solution. Thus, the system requires a skilled operator (Peter-Varbanets *et al.* 2009) . Another system developed by the Sky Juice Foundation is the Sky box unit which can produce 20-25 L/h of safe potable water for three years. It makes use of a low cost bio-UF membrane. The unit requires no chemical cleaning and relies entirely on gravity.



Figure 2- 23: Photographs of the Sky hydrant unit (*left*) and the Sky box unit (*right*) (www.skyjuice.com)

2. LifeStraw Personal and LifeStraw Family filters

LifeStraw Personal and LifeStraw Family are both POU water interventions developed by Vestergaard Frandsen in order to provide safe drinking water at household level. The LifeStraw, is 25 cm long and weighs about 122 g and consists of a UF module with a pre-filtration system for reducing turbidity. During use, the user sucks through the straw, and the water flows through textile and iodine filters, which disinfect it. The unit also has a chamber consisting of granulated active carbon which absorbs residual iodine, in order to prevent it from affecting the taste of the water (Mincer 2008). Previous assessment of this system showed stable operation and high efficiency of bacteria and virus reduction (Peter-Varbanets *et al.* 2009).

Operation of the Lifestraw Family unit involves pouring raw water into the feed water bucket equipped with a prefilter which removes coarse particles larger than 80µm. The water flows by gravity to the purification cartridge which contains a hollow-fibre UF membrane (pore size, 20 nm) which removes turbidity and microbes. The pressure applied by the 1 m long plastic hose, corresponds to 0.1 bars and it forces the water through the pores of the UF membrane. Purified water can be collected from the blue tap (www.lifestraw.com).

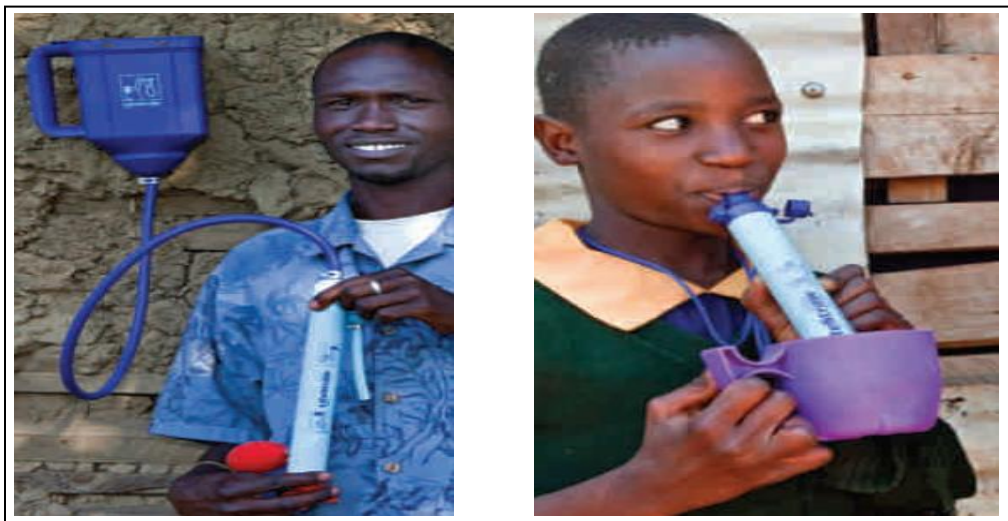


Figure 2- 24: Photographs of the LifeStraw Family filter and LifeStraw Personal filter respectively in use (www.lifestraw.com)

3. Ceramic filters

Ceramic microfiltration is one of the membrane technologies recommended by the WHO for use in potable water treatment. The filters produced are normally in the form of clay pots as shown earlier (Figure 2-7). Potters for Peace (PFP), has been heavily involved in the development and use of ceramic filters. The filters used have a pore size of between 0.6 µm and 3 µm. This has the potential to remove a significant portion of bacteria, protozoa and helminthes and some viruses (Lantagne 2001).

The PFP pore size goal is 1.0 µm, in order to remove *E. coli* without the need for a disinfectant (Lantagne 2001). This is rarely achieved, and in order to increase the disinfection efficacy and prevent biofilm formation on the filter surface, ceramic filters

are impregnated with colloidal silver (Sobsey 2002). The clean water flow rates for these filters is 1-2 L/h and when filtering turbid water, the flow rate decreases due to pore blocking and the filters have to be scrubbed by a brush to recover the flux. This often leads to the loss of silver from the coated filters and hence have to be recoated in order to maintain their disinfection efficacy (Halem 2006).

4. Eawag, KWB and Opalium system

This SSS is based on a gravity-driven bio-UF process using flat sheet modules (Figure 2-25) developed by Eawag, KWB and Opalium. The unit requires to be fed with raw water at a height of 2 m and can be operated without cross flow, back flush, aeration or chemical cleaning of the membranes. The unit's design specification in terms of water production is 5000 L/d as long as the turbidity of the raw water is less than 160 NTU, with a filtration flux of around 4 to 6 LMH. The system was run in Ogunjini in the region of Durban, South Africa and showed excellent performance producing permeate with no pathogenic bacteria. However, residual chlorine should be added in order to prevent recontamination of permeate (Boulestreau and gGmbH 2010).



Figure 2- 25: Photograph showing a pack of flat sheet UF membranes in a feed tank used in the Eawag, KWB and Opalium system (Boulestreau and gGmbH 2010)

2.4.9.3 Problems with use of current membranes in rural areas

Rural areas pose unique challenges to the establishment of conventional water treatment systems as noted earlier in section 1.1.2. In addition, the use of large scale membrane based systems in these areas is difficult because of lack of finances. This necessitates the development of decentralized membrane based water treatment systems that meet the following criteria for rural areas: robust in operation; low cost of production; require minimal skills to operate and maintain; adaptable for small scale use; high product quality and quantity; less energy requirement; and potential for remote operation (Peter-Varbanets *et al.* 2009).

According to Pillay *et al* (2009), despite the significant developments in membrane technology such as wide acceptance and reducing costs, the current commercial membranes available do not lend themselves to small water treatment systems that would be sustainable in rural areas of developing economies because of the following reasons:

- In terms of robustness, most of the current membranes are delicate and are easily damaged when left to dry out or even scratched.
- They are relatively expensive to install, use, and difficult to maintain. Many existing systems are simply too expensive for most of the rural poor who live on less than a dollar-a-day income.
- Once the membranes are fouled, they require sophisticated cleaning methods often using chemicals. The use of chemical cleaning produces good results in terms of flux recovery, except that often supply is limited especially in the remote villages thereby making it unreliable.
- Membranes such as ceramic filters are affordable and successful in water treatment. However, their low flow rates make them impractical for potable water provision for a household.

These challenges have necessitated the ongoing search for membrane based systems that can be adapted to rural areas. One such potential technology is the RRWTS which is investigated in this study.

2.5 The Remote Rural Water Treatment System (RRWTS)

2.5.1 Overview of the RRWTS

Researchers at DUT have previously developed the RRWTS as an interim solution for the provision of clean and safe water in remote rural areas. This is a gravity driven microfiltration system that overcomes most of the challenges facing current commercial membranes. The filtration unit is based on a polyester WFMF membrane which is robust and is produced locally in South Africa. The other accessories needed for the system can also be sourced locally hence making it easy to adapt it to the rural areas.

2.5.2 Development of the RRWTS

The core of the system is the WFMF membrane that is used to fabricate flat sheet modules. The membrane is robust and easy to work with. The construction of the module is easy and it involves fabricating a rectangular PVC support frame incorporating a permeate outlet. Two sheets of the WFMF membrane are glued to either side of the frame, and a mesh spacer is incorporated between the sheets in order to facilitate permeate flow to the outlet. The complete A4 size module is shown in Figure 2-26.

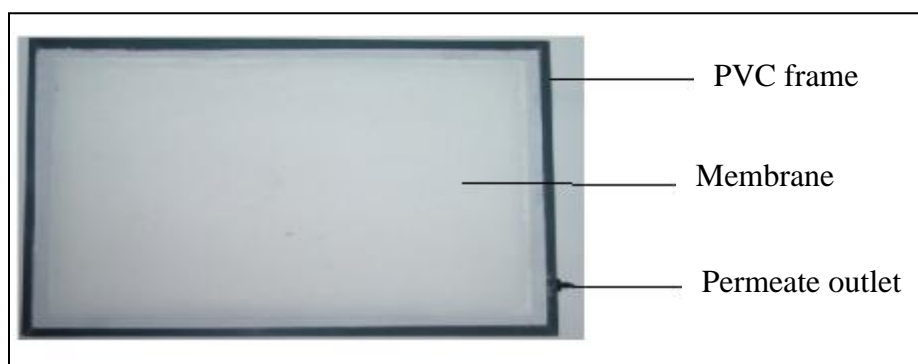


Figure 2- 26: A photograph of a flat sheet WFMF module (Pillay *et al.* 2009)

The modules are assembled and held together by threaded rods inserted through holes drilled in each module to form a membrane pack in order to increase the productivity as shown Figure 2-27. A permeate collection manifold is used to connect the individual

permeate outlets from each module to the permeate outlet tap (Figure 2-27). The membrane pack is immersed in a process feed tank containing the feed solution and permeate is collected from the permeate outlet valve (Figure 2-28).

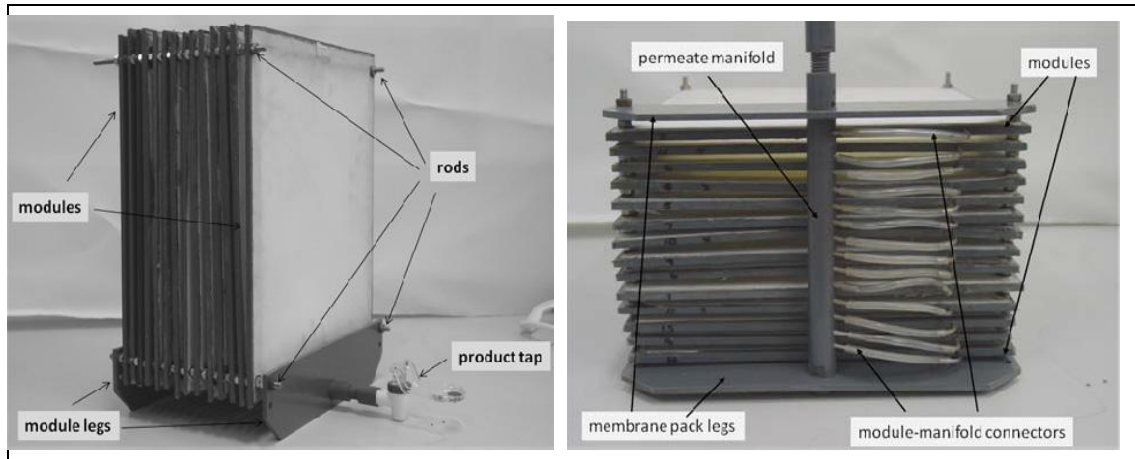


Figure 2- 27: Photographs of the RRWTS membrane pack showing the side view and bottom view respectively

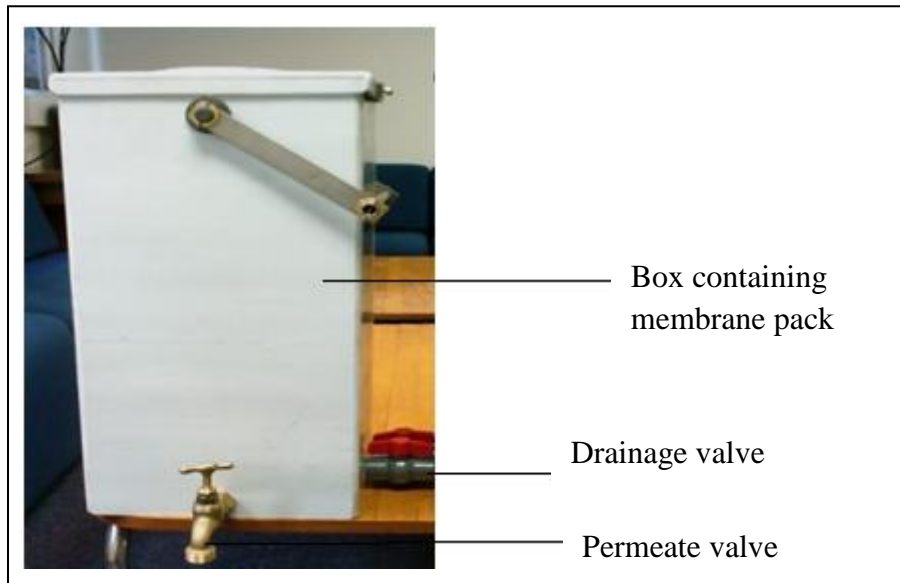


Figure 2- 28: A photograph of the assembled RRWTS showing the process feed tank containing the membrane pack, permeate valve and drainage valve

2.5.3 Advantages of the RRWTS

According to Pillay and Jacobs (2005) the advantages of the RRWTS include:

- The membranes are extremely robust and require little maintenance.
- The system operates under gravity, therefore, no need of electricity or pumps.
- It is simple to construct and is based on locally available materials.
- Membranes are not damaged when left to dry, it actually aids in cleaning them since the fouling material falls off.
- Membranes can be easily cleaned by brushing them and rinsing with clean water.
- Turbidity removal is good and comparable to that of commercial MF membranes.

2.5.4 Operation of the RRWTS

The operation of the unit is as follows (Pillay *et al.* 2009):

- The user pours raw water into the process feed tank.
- The permeate tap is then opened, and product is withdrawn and collected in a clean container.
- The user adds an appropriate amount of disinfectant to the product.
- The user then opens the drain valve and empties the unit to get rid of settled matter.

2.5.5 Performance of the RRWTS

Previous studies on the quality of permeate produced demonstrated the suitability of the RRWTS for potable water treatment in rural areas. The performance of the RRWTS in terms of permeate quality and product flow rate is reported in (Pillay *et al.* 2009; Pillay and Kalu 2010) and the following is a summary:

1. Water Quality

In field trials conducted, the RRWTS generally produced a product of less than 1 NTU, for raw water feed ranging from 20 NTU to 300 NTU (Figure 2-29). The permeate turbidity was not affected by feed turbidity, period of operation, or permeate flux. Furthermore, the *E.coli* removal was also good, the RRWTS on its own achieved 80 to 99 per cent, and the addition of the disinfectant ensured that the water contained zero *E.coli* per 100 mL of treated water (Table 2-6).



Figure 2- 29: Typical feed and permeate turbidities for the RRWTS (Pillay *et al.* 2009)

Table 2- 6: *E.coli* concentration in feed and permeate from the RRWTS and in the permeate collection container with disinfectant (Pillay and Kalu 2010)

Water source	<i>E. coli</i> if raw water (counts/ 100mL)	<i>E. coli</i> in permeate from RRWTS	<i>E. coli</i> in permeate from RRWTS with disinfectant added
River 1	4838	980	0
River 2	8160	185	0
River 3	11191	23	0

2. Product Flow Rate

A RRWTS unit containing 15 modules (A4 size) filtering raw water of 60 NTU produced 40 LMH of permeate on the first day of use, and about 10 LMH after one month of use, when used once a day, without cleaning. This showed that the system

could provide a household with 30 L of water each day, for one month without cleaning, depending on the feed turbidity.

2.5.6 Cleaning of the RRWTS

Studies by Pillay *et al* (2009) showed that depending on the raw water quality, the RRWTS could operate effectively for a month before cleaning was required. Thereafter, the system could still run but the flow rate progressively decreased if not cleaned. The modules could be cleaned by simply brushing them with a bottle brush (Figure 2-30), and rinsing them out with water. This proved to be adequate to remove the fouling layer. This routine maintenance requires no skill and can be done while the membranes are in the feed tank. The other option of cleaning the membranes was to allow the module to dry and the fouling matter to fall off. No chemical cleaning was required.



Figure 2- 30: Cleaning of the RRWTS modules using a brush. The brush is moved up and down between the modules while they are in the feed tank (Pillay *et al.* 2009)

2.5.7 Drawbacks of the RRWTS

The RRWTS overcomes several of the limitations of other existing membrane based methods for providing potable water to remote rural communities. However, its permeate does not meet international water standards, hence the need to add a disinfectant to the product. This necessitates a separate disinfection step often using chlorine and the user is depended on to add disinfectant to the product water (Pillay *et al.* 2009).

The use of a separate disinfection step often poses challenges. For instance, users may forget or sometimes ignore this important step, resulting in the consumption of water that may contain pathogens. Furthermore, users who do not understand the dosing requirements may overdose the disinfectant and lead to formation of DBPs that are carcinogenic and can cause adverse effects on their health.

This calls for ways to reduce the risk associated with the user adding the disinfectant such as incorporating disinfection capacity on the membrane. Indeed, the ability to manipulate the structure, surface chemistry and reactivity of matter, especially at the nanoscale has provided researchers with new strategies to address such a problem (Hotze and Lowry 2011). Silver is such a material with antimicrobial properties and with potential for application in water disinfection especially by being incorporated in water filters.

2.6 Use of silver nanoparticles for water treatment

2.6.1 History of silver and its applications

Silver is a transition metal element having an atomic mass of 107.87 and its medicinal value has been exploited for many centuries (Singh *et al.* 2008). Silver has been used in currencies and as a precious commodity in ornaments and jewellery, among others. One of the most important uses of silver has been as a potent antibacterial agent. Silver has long been used as a disinfectant for example in treating wounds and burns; silver vessels have been utilized for the preservation of perishable items as well as for disinfection of water because of its wide range of toxicity to bacteria as well as its limited toxicity to humans. The advent of nanotechnology has renewed interest in silver due to its unique properties at the nanoscale. Nanosilver is nowadays used in a large number of consumer and medical products mainly for disinfection purposes (Pradeep, T and Anshup 2009; El-Badawy *et al.* 2010). Silver is available in different forms as shown in the Table 2-7.

Table 2- 7: Forms of silver and their characteristics (Kulinowski 2008)

Type of silver	Size	Characteristics
Elemental	0.288 nm	Not found as a single atom in nature but rather as an aggregate. It has no oxidation state.
Ionic	0.258 nm	Toxic, may dissolve in water and have a positive or negative charge.
Nanosilver	1-100nm	May release silver ions and/or be toxic as nanoparticles.
Colloidal silver	1-1000 nm	May contain nano particulate or ionic silver or both.

The oligodynamic effect of silver is well recognized, with low concentrations such as, 10^{-9} to 10^{-6} mol/L Ag^+ ions reportedly showing effectiveness against a broad range of

microorganisms including bacteria, fungi, protozoa and viruses (Russell and Hugo 1994). The antimicrobial activity of silver especially is related to the biologically active silver ion. The antimicrobial properties of silver are utilized in form of silver salts and complexes that break down to release Ag^+ ions (Schierholz *et al.* 1998).

2.6.2 Uses of nanosilver as an antimicrobial agent

As an antimicrobial agent, silver has been used alongside copper in hospital and hotel distribution systems to control infectious agents such as *Legionella* and to sterilize recycled water aboard the space stations and space shuttles (Silver 2003). Microdyn (colloidal silver in gelatin) has been used drinking water treatment using ceramic filters (Lantagne 2001). Similarly, due to its antimicrobial effect on diverse microorganisms, silver based topical dressing has been widely used in the treatment of infections due to burns, and injuries resulting in open wounds (Singh *et al.* 2008).

In recent times, AgNPs are increasingly being incorporated into various substrates in order to extend their utility in materials and biomedical applications. They have been incorporated in health related products such as bandages, catheters, to prevent infection (Maneerung *et al.* 2008; Ravishankar and Jamuna 2011). Another prominent application is the synthesis of composites for use as water disinfecting filters (Pradeep, T. and Jain 2005; Zodrow *et al.* 2009; Dankovich and Gray 2011). Furthermore, systems supported with AgNPs are effective in reducing the presence of target microorganisms in a wide variety of water disinfection applications (Guo 2011). The AgNPs are also gaining increasing application in textiles, cosmetics, and even domestic appliances in order to impart antimicrobial properties to different materials (Lara *et al.* 2011).

2.6.3 Toxicity of silver

According to the WHO (2011b), silver is one of the chemicals used in water treatment which occurs naturally, and it has occasionally been found in groundwater, and surface water at concentrations above 0.005 mg/L. Silver is generally regarded as a safe and

effective bactericidal metal (Zhao and Stevens 1998) and is said to be of low toxicity to humans. However, it has been reported to cause *argyria* (irreversible pigmentation of the skin and hair) or *argyrosis* (irreversible pigmentation of eyes) after chronic ingestion of colloidal silver leading to deposition in the tissues (Hurt and Liu 2010).

Among the different antimicrobial agents, silver is probably the most powerful antimicrobial agent that exhibits a strong toxicity toward a broad range of microorganisms, while showing remarkably low human toxicity (Dallas *et al.* 2011). *Argyria* is not harmful, but rather a cosmetic issue that many people may find undesirable. The discolouration depends upon the route of silver delivery (mouth, nose, skin), and the individual's ability to excrete silver (Nowack *et al.* 2011).

However, for situations where silver derivatives may be used to disinfect water for drinking purposes, the WHO recommends that higher levels of silver, up to 0.1 mg/L could be tolerated in such cases without risk to health (WHO 2011b). Application of polymeric materials incorporated with AgNPs in drinking water filtration system has been on the increase due to the enhanced performance of such systems. This however, may cause the leaching of AgNPs into the drinking water resulting from physical damage or improper nanoparticle incorporation techniques (Ng *et al.* 2010). Therefore designers of such systems should ensure effective control of silver leaching to prevent the risk of argyria among consumers. According to Nowack *et al.* (2011) silver impregnated water filters have been safely used for domestic water applications and that no reports about any health or environmental effects have been reported.

The toxicity of AgNPs depends on the particle size, as size decreases; there are more atoms on the surface available to interact with microorganisms or to release more silver ions. In addition, particle stability has a significant effect; higher stability produces well dispersed particles and hence higher antimicrobial properties. Lastly, the shape of the particles is important. For instance, particles with (111) facets contain larger atom densities thus more atoms available for interaction (Jones and Hoek 2010).

2.6.4 Methods of production of AgNPs

2.6.4.1 Overview of methods

The diverse applications of AgNPs have led to the development of versatile methods to synthesize them. The approaches used can be broadly classified as conventional or unconventional. Conventional synthesis methods include the reduction of silver solutions using reducing agents such as, chemical agents (Sondi *et al.* 2003; Dankovich and Gray 2011), plant extracts (Kaviya *et al.* 2011), biological agents (Varshney *et al.* 2009), or irradiation methods (Jiang *et al.* 2004; Kora, A J *et al.* 2009b; Darroudi *et al.* 2011) that provide the free electrons needed to reduce silver ions (Ag^+) and to form AgNPs (Tolaymat *et al.* 2010; Kora, A J and Arunachalam 2011). Green approaches use environmentally friendly agents such as sugars (Panigrahi *et al.* 2004; Filippo *et al.* 2010; Bai *et al.* 2011) and plant extracts to form and stabilize AgNPs. However, when using green approaches it is more difficult to control the morphology of the produced nanosilver (El-Badawy *et al.* 2010). Unconventional methods include laser ablation, radio-catalysis, vacuum evaporation of metal among others (El-Badawy *et al.* 2010). A review of the conventional methods is presented in the following sub sections.

2.6.4.2 Chemical reduction in solution

This is the most versatile and simple approach for preparation of metal nanoparticles and especially AgNPs. It generally involves the reduction of relevant metal salts, mostly silver nitrate, in the presence of a suitable protecting agent known as a stabilizer, for example polyvinyl pyrrolidone (Song *et al.* 2006). The stabilizer is necessary in controlling the growth of nanoparticles through agglomeration. This method offers advantages such as, high yield of non-aggregated nanoparticles and ease of performance. Examples of reducing agents include sodium borohydride (Kim, JS *et al.* 2007; Dror-Ehre *et al.* 2009; Dankovich and Gray 2011), sodium citrate (Ratyakshi and Chauhan 2009), hydrazine (Shrivastava *et al.* 2007), ascorbic acid (Sondi *et al.* 2003), and formaldehyde (Song *et al.* 2006).

The most important parameters of this method are: starting concentration of AgNO_3 ; ratio of molar concentrations of reducing agent to AgNO_3 ; and the concentration of the stabilizer (Sun *et al.* 2004; Pulit *et al.* 2011). The purity of water and reagents, cleanliness of the glassware reaction temperature, concentrations of the metal salt and reducing agent, reaction time all are important considerations and influence the nature of particles obtained (Šileikaitė *et al.* 2006).

2.6.4.3 Photochemical reduction

This method is valuable as it allows the blending of all the reacting substrates before the reaction is initiated. It can be used to produce silver nanostructures using UV irradiation at room temperature (Park *et al.* 2011). The core of the method is the fast reduction of silver cations, and production of small-size nanoparticles (Pulit *et al.* 2011).

2.6.4.4 Laser ablation method

It involves the superficial reaction between liquid and a solid body suspended in it. In this process a pulsating laser beam directed at the surface of a solid body causes a discharge of material from the surface of the solid body, which then migrates to the surrounding liquid in a bubble form (Pulit *et al.* 2011). Ultra short laser pulses enable the easy conversion of the bulk material into nanoparticles in liquid media without changing their property. The main advantage of synthesizing nanoparticles in liquid media is the *in-situ* stabilization of nanoparticles produced through ablation. Moreover, laser ablation is a simple and easy technique to generate pure nanoparticles of high stability and resistance to aggregation (Christopher *et al.* 2011).

2.6.4.5 Electrochemical method

This method is based on the dissolution of metal on an anode, and then the reduction of the obtained transitional metal salt on the cathode, which leads to the formation of metal particles. The major advantage of this method is the high purity of particles and the control of their size through the compensation of the current density, with no need to add surface active agents (Pulit *et al.* 2011). By changing the current density, it is possible to

obtain different silver particle sizes (Rodríguez-Sánchez *et al.* 2000). Furthermore, it does not require expensive equipment and instrumentation.

2.6.4.6 Microwave irradiation

A microwave beam is passed through the dielectric coating of the material, radiation energy transforms into thermal energy and the material's temperature increases (Pulit *et al.* 2011). The penetration property of microwave electromagnetic radiation through solution results in a uniform heating for the reaction solution, thereby achieving better control on the size of nanoparticles than in thermal heating (Yin *et al.* 2004). Advantages of microwave irradiation over conventional heating include: rapid initial heating process; uniform heat transfer to the solution; and significant reaction rate enhancement (Phong *et al.* 2009).

2.6.4.7 Green synthesis

Green synthesis of nanoparticles can be done using the following methods (Sharma *et al.* 2009; Jones and Hoek 2010; Sahayaraj and Rajesh 2011):

- The polysaccharide method in which AgNPs are prepared using water and polysaccharides as a capping agent. In some cases polysaccharides serve as both a reducing and a capping agent.
- The Tollens method involves the reduction of Ag^+ ions by saccharides in the presence of ammonia. It gives AgNPs with a controlled size in a one step process. The irradiation method using laser irradiation of an aqueous solution of a silver salt and surfactant can fabricate AgNPs with a well defined shape and size distribution. No reducing agent is required in this method.
- The biological method, extracts from organisms may act both as reducing and capping agents in AgNPs synthesis. The reduction of Ag^+ ions by combinations of bio-molecules found in these extracts such as enzymes, amino acids, polysaccharides, and vitamins is environmentally benign, yet chemically complex (Durán *et al.* 2007).

- The poly oxometalates method uses poly oxometalates that have the potential of synthesizing AgNPs because they are soluble in water and have the capability of undergoing stepwise, multi electron redox reactions without disturbing their structure.

2.6.5 Antimicrobial mechanism of AgNPs

Antimicrobial action of AgNPs has been extensively studied and demonstrated against a broad spectrum of microorganisms such as *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Pseudomonas aeruginosa* and especially *E.coli* (Lv *et al.* 2009; Heidarpour *et al.* 2010b; Kheybari *et al.* 2010; Maria *et al.* 2010; Parameswari *et al.* 2010; Li, W *et al.* 2011) along with a lack of negative effects on treated water such as taste, odour, colour and formation of disinfection by products (Hotze and Lowry 2011).

The mechanism of the bactericidal effect of silver and AgNPs has nevertheless not been fully elucidated despite numerous studies. There are three most common mechanisms of AgNPs antimicrobial action proposed to date. Firstly, the uptake of free silver ions by the microorganism followed by disruption of adenosine triphosphate (ATP) production and DNA replication. Secondly, AgNPs and silver ions generate reactive oxygen species (ROS) which interacts with the microorganism. Lastly, AgNPs can directly damage the cell membrane thus making it more permeable (Jones and Hoek 2010).

Some studies propose that AgNPs due to their size may attach to the surface of the cell membrane disturbing permeability and respiration functions of the cell (Sharma *et al.* 2009). Smaller AgNPs have a large surface area available for interaction which provides better contact with microorganisms (Rai *et al.* 2009); hence have a higher bactericidal effect than the larger AgNPs (Martínez-Castan˜o˜n *et al.* 2008). In addition, the AgNPs can also penetrate inside the bacteria and interrupt the cellular processes (Raffi *et al.* 2008; Jin *et al.* 2010).

AgNPs are easily dissolved and oxidized in aqueous and biological media forming partially oxidized nanoparticles with ionic silver such that both ionic and metallic silver

appear to contribute to the total antibacterial activity (Ju-Nam and Lead 2008; Lalueza *et al.* 2011). Thus AgNPs behave as Ag^+ carriers leading to a stable and slow ion release for long times (García-Barrasa *et al.* 2011).

Moreover, it has also been suggested that the mechanism of action of AgNPs is similar to the one displayed by silver salts, but using much lower concentration than the salts (García-Barrasa *et al.* 2011). The effect of nanoparticles' size on the antimicrobial activity of AgNPs has been reported against Gram-negative bacteria (Morones *et al.* 2005) and Gram-positive bacteria. Smaller sized AgNPs with a large surface area to volume ratio provide a more efficient means for antibacterial activity even at very low concentration (Wijnhoven *et al.* 2009). The size dependence of chemical reactivity is mainly due to the presence of a large number of atoms at the surface of smaller sized particles (Pradeep, T and Anshup 2009).

The effect of the shape of nanoparticles on the antimicrobial activity of AgNPs has also been reported against Gram-negative bacteria. AgNPs of different shapes have differences in the exposed surfaces, which lead to differences in atomic distribution across the nanoparticle surface. As a result of this, the electron transfer rate kinetics between the AgNPs and the corresponding adsorbed species varies for the different shapes (Pradeep, T and Anshup 2009).

Truncated triangular AgNPs are found to pose stronger antimicrobial action against Gram-negative bacterium *E. coli* than the spherical and rod shaped nanoparticles (Pal *et al.* 2007). This is due to the differences in terms of reactivity of the different crystallographic facets of the different nanoparticles (Lalueza *et al.* 2011). The top basal plane of truncated triangular silver nanoplates, (111) facet, is a high-atom-density surface which favours silver reactivity. Spherical AgNPs have (100) facets along with a small percentage of (111) facets, whereas rod-shaped AgNPs have side surfaces with (100) facets and end with (111) facets (Morones *et al.* 2005). Therefore, the strong antibacterial activity of truncated triangular AgNPs could be due to their large surface area to volume ratios and their crystallographic surface structures (Wijnhoven *et al.* 2009).

2.7 Summary

Conventional disinfection methods for water treatment such as chlorination often produce harmful DBPs and some are inappropriate for use in rural areas of developing nations due to cost implications and the need for specialized skills. Membrane technologies especially MF and UF have potential benefits in the provision of potable water in rural areas. Since these membrane processes may not guarantee complete disinfection of water, the incorporation of antimicrobial nanoparticles such as AgNPs in membranes offers an alternative method of disinfection.

From the review of literature on the application of AgNPs in water treatment; it becomes apparent that there is still a lot of unknown information with regard to the incorporation of AgNPs in membranes such as the WFMF membranes and their disinfection efficacy. Some of the unknown information which this study will investigate is as follows:

- Most studies have concentrated on the synthesis of AgNPs and showing their antimicrobial efficacy, which is well known. Not many studies have investigated the antimicrobial performance of materials containing AgNPs for water treatment. This study will investigate the incorporation of AgNPs on WFMF membranes, and the effect of this on the filtration and disinfection efficacy.
- The few studies that have attempted to investigate the use of AgNPs in filters have not done so for long term performance. This study will investigate the disinfection performance of the coated filter and determine the lifespan of the filter. Moreover, it will also investigate the possibility of silver leaching from the filter with use and its effect on the filter performance.
- There is still no agreement on the mechanism of action of AgNPs and materials incorporating AgNPs for disinfection. This study will investigate the mechanism of antimicrobial action of AgNPs coated WFMF membranes during water treatment.

3 SYNTHESIS AND CHARACTERIZATION OF COATED MEMBRANES

3.1 Introduction

This chapter presents the investigation of the incorporation of AgNPs on the WFMF membranes. The specific objectives of this chapter are:

- i. To investigate the incorporation of AgNPs on the WFMF membrane.
- ii. To investigate the characteristics of the coated membrane.
- iii. To investigate the fabrication and integrity testing of the filter modules.
- iv. To investigate the filtration performance of the coated membranes.

3.2 Incorporation of AgNPs on materials

3.2.1 Overview

The immobilization and coating of metal nanoparticles with bactericidal activity on materials has found application in medical materials and devices, water treatment systems and food processing (Ruparelia *et al.* 2008). Application of nanotechnology to develop filter media incorporating nanoparticles for disinfection is a prime area of research. Such a passive disinfection system has great advantage over conventional chemical disinfection systems using chlorine resulting from lack of formation of harmful DBPs. The filters can also be engineered to adsorb harmful organic substances and/or oxidize harmful organics (Schutte, CF and Focke 2007).

The incorporation of AgNPs into polymeric membranes has become a key area of research in order to improve the performance and effectiveness of the membranes in fouling mitigation, (Zodrow *et al.* 2009) improvement of permeate quality, flux enhancement (Kim, J and Bruggen 2010) and for disinfection (Dankovich and Gray 2011). Efficient design of antibacterial materials incorporating AgNPs should ensure low cost of fabrication and high efficacy (Porel *et al.* 2011).

There are two important aspects to be considered in order to enhance the bactericidal activities of silver based materials. Firstly, the materials should be based on AgNPs in order to provide a larger surface area to volume ratio. This provides a high fraction of surface atoms, which enhances the antimicrobial activity of silver, even at a low concentration. Secondly, the AgNPs should be immobilized in the substrate in order to gain long-term antimicrobial activity and decrease the nanosilver leaching rate (Akhavan and Ghaderi 2009).

3.2.2 Methods of incorporation of AgNPs on materials

3.2.2.1 Impregnation by chemical reduction

This is one of the earliest methods used for particle immobilization on materials. It involves the addition of an aqueous solution of the metal precursor such as AgNO_3 to the cleaned supports such as porous materials. Subsequently, the solution is subjected to a reducing medium such as NaBH_4 , sodium citrate or thermal decomposition. Thereafter, the solution is subjected to high temperature heating for surface activation (Pradeep, T and Anshup 2009).

The advantage of using AgNPs for impregnation is that there is continuous release of silver ions and the devices can be coated by both the outer and inner side. This enhances the antimicrobial efficacy (Rai *et al.* 2009). The process involves chemical reduction and its effectiveness is based on reaction kinetics such as: the ratios of the reactants; times of reaction; and the surface activation conditions. For the case of ceramic materials, the silver solution is applied on the ceramic using a brush or the ceramic is dipped in the silver solution and later heat treated in order to attach the silver (Halem 2006; Oyanedel-Craver and Smith 2008; Bielefeldt *et al.* 2009).

3.2.2.2 Electrospinning

The incorporation of inorganic components such as AgNPs to polymer systems allows the fabrication of nanofibers with special functionalities. Electrospinning is a simple and

effective technology to produce polymer nanofibers. It makes use of electrostatic forces to stretch the solution or melt as it solidifies (Wang *et al.* 2009). The polymer solution or melt is placed into a syringe with a nozzle and subjected to an electric field. Under the applied electrostatic force, the polymer is ejected from the nozzle and deposited on a collector (Hong *et al.* 2006).

3.2.2.3 Physical vapour deposition (PVD)

This refers to a vacuum deposition method used to deposit thin films by the condensation of a vaporized form of the desired film material onto various surfaces. The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation. For example, Heidarpour et al (2010a) produced AgNPs using electron beam bombardment of silver metal, which were subsequently deposited on the polypropylene filter evenly. This method requires specialized equipment in order to use.

3.2.3 Selection of method for coating the WFMF membrane

A number of factors should be considered for efficient application of antimicrobial nanomaterials in drinking water treatment. Chief among them concerns the dispersion and retention of nanomaterials and the sustainability of antimicrobial activity. The high reactivity achieved by nanoparticles due to high specific surface area, is negated by aggregation in aqueous medium. Similarly, leaching of nanoparticles from the filtration medium to the treated water can have dire effects on consumers if the concentration is beyond the stipulated levels (Li, Q *et al.* 2008). This therefore calls for the use of a method that can minimize or eliminate these challenges.

Based on the above mentioned factors, selection of method for incorporating AgNPs on the WFMF membrane was done using the following criteria:

- The structure of the substrate to be used (WFMF membrane).
- Effectiveness of incorporating AgNPs on WFMF membrane.
- Availability of materials and equipment required.

- Cost of the process.

The structure of the WFMF membrane is a network of woven fibres. The method chosen should be effective in order to ensure that the AgNPs are coated uniformly on the surface and within the woven network structure. Furthermore, the overall intention of this coating was to produce a membrane filter that is cost effective for use in rural areas for water treatment. The materials for use should also be readily available. Electrospinning and PVD methods require special equipment which is not readily available. This makes them expensive to use. Conversely, the chemical reduction method is relatively cheaper and could be easily implemented in the laboratory without the need of specialized equipment. Furthermore, it is a well established method of producing and attaching nanoparticles on supports. Therefore, it was selected for this project.

There are two broad approaches of incorporating AgNPs on the membrane using the chemical reduction method. The nanoparticles can be formed separately prior to incorporating them into the membrane (*ex situ*), or by the reduction of silver ions present in the formed membrane (*in situ*). Whereas, *ex situ* formation allows for more control of particle size and morphology characteristics, *in situ* formation allows for more control over homogeneous distribution of the particles within the membrane which is a key factor for a water filter (Hotze and Lowry 2011). *In situ* synthesis also results in better accessibility of immobilized nanoparticles to reactants in the feed (Taurozzi *et al.* 2008). The *in situ* synthesis was used to incorporate AgNPs on the WFMF membrane.

3.2.4 Description of the *in situ* synthesis process

The equation for the reaction is expressed as,



The process entails the reduction of AgNO_3 using NaBH_4 and it can generate AgNPs of approximately 10 nm (García-Barrasa *et al.* 2011). The use of reducing agents, such as NaBH_4 , increases the rate of nanoparticles formation typically resulting in spherical particles with Surface Plasmon Resonance (SPR) absorption maxima around 400 nm.

The application of this method in this study was accomplished by immersing the membrane in the precursor AgNO_3 solution. NaBH_4 was then used to reduce the absorbed silver ion (Ag^+) inside of the fabric to metallic AgNPs. The membrane absorbs the Ag^+ ions into its matrix to form a polyester- Ag^+ complex. The Ag^+ ions are then reduced to AgNPs (Yang, G *et al.* 2012).

An excess of the reductant (ratio of NaBH_4 to AgNO_3 , 10:1) was used in order to obtain more uniform and smaller nanoparticles and result in deposition in the fabric rather than in the bath (Maneerung *et al.* 2008; Dankovich and Gray 2011). The structure of the woven polyester fabric, readily allowed the penetration of silver ions when it was immersed in the aqueous AgNO_3 . The absorbed Ag^+ ions were bound to the fabric by electrostatic interactions. Rinsing by ethanol effectively removed those Ag^+ that were not bound (Maneerung *et al.* 2008). NaBH_4 was used for reduction because it is a strong reductant and it results in almost uniform size distribution of particles, without the use of any capping agent and produces small particles that are monodisperse, as opposed to generation of larger particles that are difficult to control (Sharma *et al.* 2009; Pasricha *et al.* 2012). The immobilization of AgNPs on the WFMF membrane host controls the release of silver ions and is therefore expected to make this system suitable for use in disinfection of water especially for long term use (Yang, F *et al.* 2009).

3.3 Experimental methods

3.3.1 Incorporation of AgNPs on WFMF membranes

3.3.1.1 Materials and equipment

All chemicals used were obtained from Laboratory Supplies Co. South Africa. The chemicals were of analytical grade and were used as received without further purification. All dilutions were done using deionized water. Silver nitrate was stored in a dark container to prevent photo oxidation. All reagents were freshly prepared in “A” grade volumetric flasks and used. Deionized water was drawn from Pure lab option Q system delivered at a conductivity of 0.055 μ S/cm. The WFMF membranes were obtained from Gelvenor Textiles Company in Durban, South Africa. A list of the materials, chemicals and equipment used is shown in Table 3-1.

Table 3- 1: Materials, chemicals and equipment used for coating the WFMF membranes

Materials	Chemicals	Equipment
Uncoated WFMF membranes	Silver nitrate	Oven
	Sodium borohydride	Fume chamber
	Ethanol	Volumetric flasks and measuring cylinders
		Pan

3.3.1.2 Experimental procedure

The procedure was based on a method found in the literature (Dankovich and Gray 2011) for the production and incorporation of AgNPs on substrates with a few modifications.

The process is illustrated in the flow diagram in Figure 3-1.

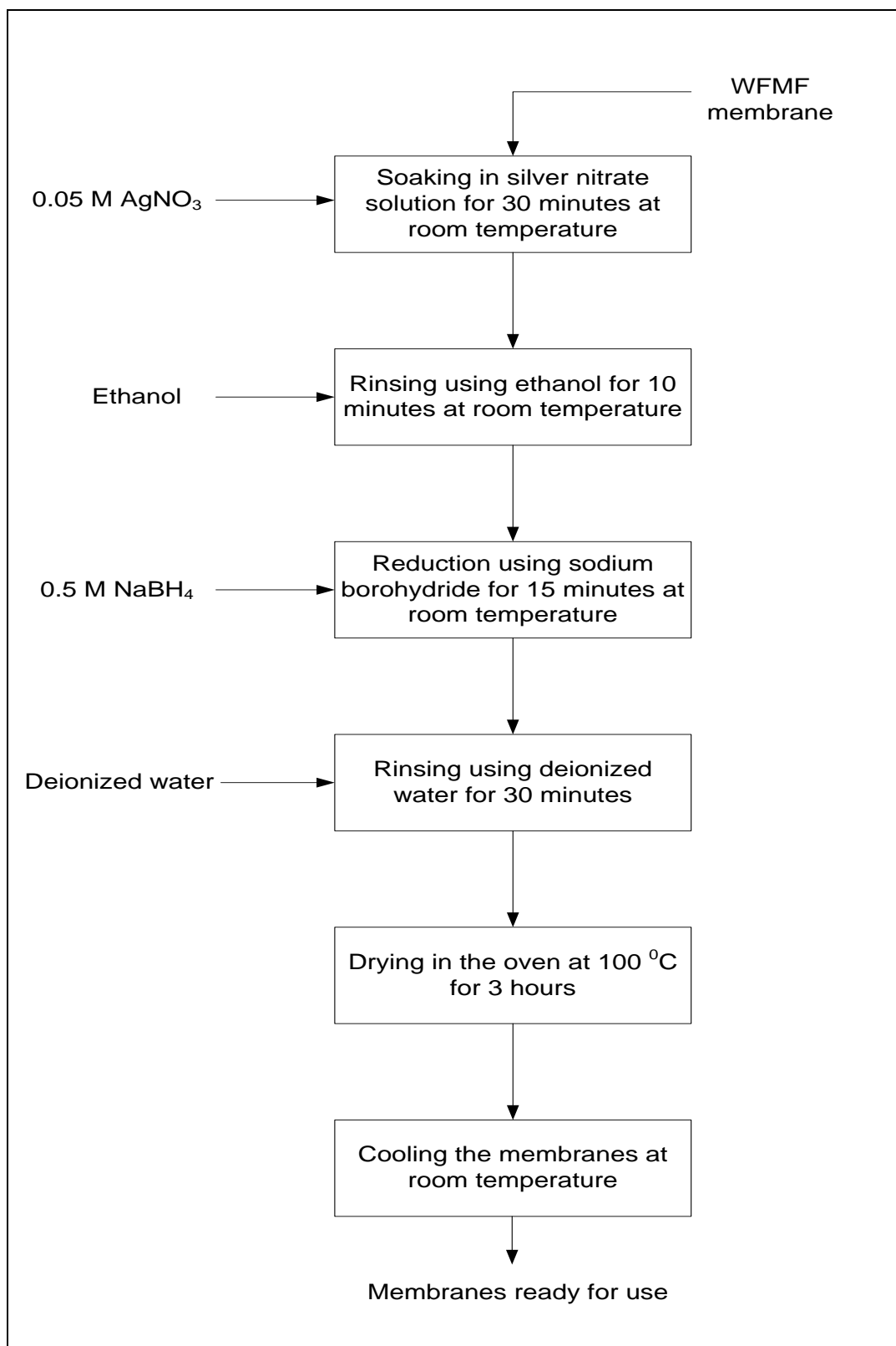


Figure 3- 1: Flow diagram of the process for the incorporation of AgNPs in the WFMF membranes

3.3.2 Membrane characterization

3.3.2.1 Objectives of membrane characterization

The characterization of the coated membrane was necessary for the following reasons:

- i. To investigate the presence of AgNPs on the coated membrane.
- ii. To investigate the effect of the coating on the structure of the WFMM membrane.
- iii. To investigate the effect of the coating on the properties of the membrane such as hydrophilicity.
- iv. To determine the silver content of the coated membrane.

3.3.2.2 Overview of membrane characterization tests performed

a) Membrane morphology

The scanning electron microscope (SEM) is used to determine the surface structure of materials. The microscope images a sample by scanning it with a beam of electrons. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, structure and composition (Kwakye-Awuah 2008; Childress *et al.* 2012). SEM was used to determine the structure of the uncoated and coated membranes.

b) Acid digestion

Acid digestion is employed in the determination of elements present in solids samples. The objective of digestion is the complete solution of the analyte together with the decomposition of the solid matrix. This however, should be done properly to avoid loss or contamination of the analyte. In this study, the membranes were digested using nitric acid and the silver concentration determined using Inductively Coupled Plasma- Atomic Emission Spectrophotometer (ICP-AES).

c) Membrane hydrophilicity

The most commonly used measure of hydrophilicity is the water contact angle. It can be readily measured by placing a drop of pure water on the surface of a solid of interest,

and measuring the angle through the aqueous phase at the three-phase contact between the solid, liquid and vapour/gas phases (Childress *et al.* 2012). Contact angle measurement characterizes the interfacial tension between a solid and a liquid drop. A droplet of a polar liquid on a hydrophilic surface has a low contact angle because the surface energy is greater than the liquids surface tension. In this case, the liquid likes the surface, therefore spreading out to make more contact with it. Therefore, the lower the contact angle, the higher the surface energy. The measurement of the contact angle is illustrated in Figure 3-2.

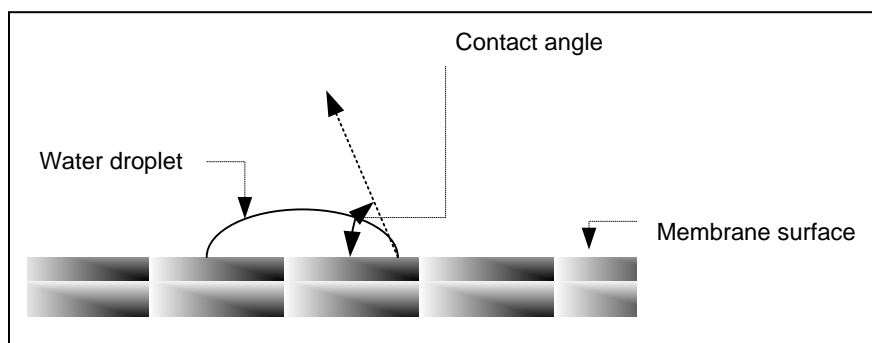


Figure 3- 2: Measurement of the contact angle

The interpretation of the contact angle is that an angle above 90^0 means lower likeness towards water and hence more hydrophobic, but an angle less than 90^0 means the membrane is more hydrophilic. The Sessile Drop method was employed to determine the hydrophilicity of the uncoated and coated membranes.

d) Identification of membrane functional groups

Infrared (IR) spectroscopy measures the molecular vibrations of molecules. When a sample absorbs infrared radiation at a given wave number, there is a corresponding decrease in the radiation intensity, which can be mathematically transformed into an absorption band. The IR spectrum presents the absorption characteristics of a molecule, in form of bands or peaks (Laot 1997). Each of the functional groups of a molecule has a wave number at which it absorbs IR radiation. IR spectroscopy is, therefore, used to characterize molecular structure, and to identify the presence of intermolecular

interactions which sometimes cause frequency shifts (Laot 1997). The IR region occurs between 4000-400 cm^{-1} .

Polymers and fibres are usually analyzed as pressed films although solid samples can be analyzed directly if the Fourier transform infrared (FTIR) apparatus has an appropriately attached microscopic unit (Ugbolue 2005). FTIR spectrometers measure absorbance. Different bonds have different vibrational frequencies, and the presence of these bonds can be detected in an organic molecule by identifying this characteristic frequency as an absorption band in the infrared spectrum. FTIR is used in membrane characterization studies to check the functional groups of components in the bulk of the membrane. This can help identify forces that attract foulants and also predict the tensile strength of the components. FTIR was employed to identify the functional groups in the uncoated and coated membranes.

e) Presence of AgNPs on membrane

UV-Vis spectrophotometry refers to absorption or reflectance spectroscopy in the UV-visible spectral region. It is used for the determination of different analytes, such as transition metal ions and organic compounds. The measurement of absorbance of radiation is used for the qualitative and quantitative analysis of chemical species. Absorption in the UV-visible region leads to excitation of bonding electrons. Thus the absorption peak can be correlated with the kind of bonds existing in the species. This technique was used to determine the presence of AgNPs on the coated membrane.

f) Structure of AgNPs

X-ray diffraction (XRD) is used to investigate long-range order of atoms and molecules in the solid state in order to reveal information about the crystal structure, chemical composition, and physical properties of materials (Kwaky-Awuah 2008). It is based on the scattering of X-rays by crystals and can be employed to identify the crystal structure of various solid compounds. Different elements and compounds have unique structures; therefore, XRD can be used to investigate the presence of a given element in the sample. XRD was used to determine the presence of AgNPs on the coated membrane.

g) Thermal properties

Thermo gravimetric analysis (TGA) is a method for the continuous measurement of the weight of a material as a function of time or temperature as it is heated in order to determine its thermal properties (Shao 2005). This analysis entails determining the change in sample mass as a function of temperature. The resulting change in mass versus temperature curve provides information concerning the thermal stability and composition of the sample, and that of any intermediate compounds that may be formed. It also provides information about the composition of the residue if any (Matsuda *et al.* 2002). TGA was used to investigate the thermal properties of the membranes.

3.3.2.3 Experimental procedures for the characterization tests

a) Membrane morphology

The test was carried out in triplicate using the following procedure:

- Clean pieces of the uncoated and coated membranes measuring 0.5 cm by 0.5 cm were dried in an oven at 70° C for 1 hour to remove moisture.
- The pieces were coated using gold in an inert environment containing Argon gas.
- The surface structure of the membranes was observed using SEM, at an accelerating voltage of 5.0 kV. This was done at magnifications of 150X and 2000X.

b) Silver content in the coated membrane

The test was carried out in triplicate employing the following procedure:

- Clean samples of the coated membrane were dried at 70° C for 1 hour in an oven, and cooled at room temperature.
- The dry weights of the samples were measured.
- The samples were placed in three separate beakers each containing a 50: 50 nitric acid/ water mixture making a total volume of 50 mL.

- The beakers were placed on hot plates with continuous magnetic stirring until the membrane pieces were disintegrated.
- The mixtures in the beakers were thereafter cooled in a water bath at room temperature and filtered through a Millipore membrane filter (0.45 μm).
- Deionized water was added to each of the filtered samples to obtain a total volume of 50 mL in order to make up for the amount evaporated during heating.
- The solutions were analyzed for silver concentration using ICPE-9000, Shimadzu ICP-AES.

The mass of silver on the membrane was calculated using equation 3-2.

$$\text{Mass of silver (mg)} = (\text{Concentration of silver (mg / L)} \times (0.05 \text{ L})) \quad (3-2)$$

Details of the process are presented in Appendix A.

c) Membrane hydrophilicity

The procedure for the Sessile Drop test was as follows:

- The uncoated and coated membrane samples were dried in an oven at 70° C for 1 hour to remove moisture and cooled to room temperature before use.
- They were placed in turns on the holding cap of the Data Physics contact angle measuring equipment.
- For each of the membrane pieces, a drop of pure water was deposited on the membrane using a Gilmont syringe located directly above the membrane.
- Water droplets were contacted with the membrane at different locations on each membrane sample for repeatability.
- A high resolution camera was used to capture a picture of the droplet as it came into contact with the membrane surface.
- The results were analyzed using software called SCA_U.
- The average values of the contact angles and surface energies were recorded.

d) Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) Spectroscopy

FTIR spectra were collected from the Perkin Elmer 100 FTIR-ATR spectrometer using the following procedure:

- Clean and dry pieces of the uncoated and coated membranes were taken.
- The sample holder was cleaned using acetone.
- The Spectrum software was launched.
- The membrane sample was placed in the sample holder for observation.
- Spectra were obtained for a range of wave numbers ($4000\text{--}650\text{ cm}^{-1}$).
- The data was processed using the equipment software.

e) UV- Visible Spectrophotometry

The UV-2540, Shimadzu Corporation, Kyoto, Japan spectrophotometer was used employing the following procedure:

- Clean and dry pieces of the uncoated and coated membranes were taken.
- The equipment mode was set to read absorbance.
- Two disk cuvettes were used, one containing barium sulphate powder (standard) and the other having a piece of the membrane (sample).
- The disk cuvettes were placed in the appropriate sample holders.
- The uncoated and coated membranes were analysed in turns.
- They were scanned and the absorption spectra of the samples recorded in the range of 900-200 nm

f) XRD Spectroscopy

The XRD for the coated membrane was conducted in the angle range of $5^{\circ} < 2\theta < 80^{\circ}$ using the following procedure:

- Clean and dry pieces of the coated membranes were taken.
- The membrane sample was placed in the sample holder.

- The equipment voltage and current were set at 40 kV and 40 mA respectively.
- The sample was scanned and the information processed by the software.

g) Thermo Gravimetric Analysis (TGA)

The Perkin – Elmer Thermal Analysis system was used and the procedure was as follows:

- Clean and dry pieces of the uncoated and coated membranes were taken.
- The equipment was switched on and the nitrogen gas supply connected.
- Approximately 10 mg sample was taken in an aluminium pan and loaded in the sample holder.
- The sample was heated at a rate of 10° C/min from 30° C to 800° C.
- The weight loss of the sample at different temperatures was recorded.

3.3.3 Filter assembly and integrity testing

3.3.3.1 Objectives of integrity testing

Integrity testing of the assembled filters was done for the following reasons:

- To investigate whether the filters were free from leaks and hence fit for use.
- To investigate whether the coating of the filters had an effect on the gluing of the filter on the PVC frames.

3.3.3.2 Module assembly

The flat sheet modules were assembled using the following procedure:

- Pieces of PVC were cut to A4 size with 45° joints at the ends.
- The pieces were joined using megabond glue to form rectangular frames and allowed to dry for 6 hours.
- Permeate outlets were drilled on the frames, one outlet for each rectangular frame.

- Two A4 size membrane sheets were cut and glued to the frames. Mesh spacers were inserted between the membranes.
- The modules were left for 12 hours in order for the glue to stick well.

3.3.3.3 Integrity testing of the modules

Integrity testing was performed using the air pressure method in order to ensure that the modules were free from leaks using the following procedure:

- Each of the modules was completely immersed in a container of deionized water.
- The immersed module was taken out of the water and air blown into it through the permeate outlet using an air blower.
- The permeate outlet was closed in order to prevent air from escaping.
- The module was completely immersed in the water and the release of air bubbles observed.
- If no bubbles were released from the points where the fabric was glued to the PVC frame, then the module was deemed to be in good condition.

3.3.3.4 Assembly of the filtration units

The assembly of the filtration units was done as follows:

- The membrane pack was made by joining four modules using rods and nuts. Two membrane packs were made using the uncoated and coated membranes.
- The permeate outlets were connected to a central manifold, which was connected to a tap at the outlet.
- Two feed tanks were used. They were rectangular boxes made of PVC each with a capacity of 30 L.
- The feed tanks were fitted with two taps, one for permeate collection from the membrane pack and a drainage tap for the residual water.
- The membrane packs were placed in the feed tank and the necessary connections to the drainage valve and permeate tap made.

3.3.3.5 Permeability test

The pure water flux is an important test that is used to investigate the initial performance of a membrane. It is defined as the volume of permeate per unit time, per unit area, per unit of TMP ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$). As such it gives an indication of the effort required to generate permeate for a membrane. The pure water fluxes of the uncoated and coated filters were determined by filtering deionized water through the filters in dead end mode under gravity. The experimental rig for the pure water flux is shown in Figure 3-3. The test was done in triplicate using the same rig.

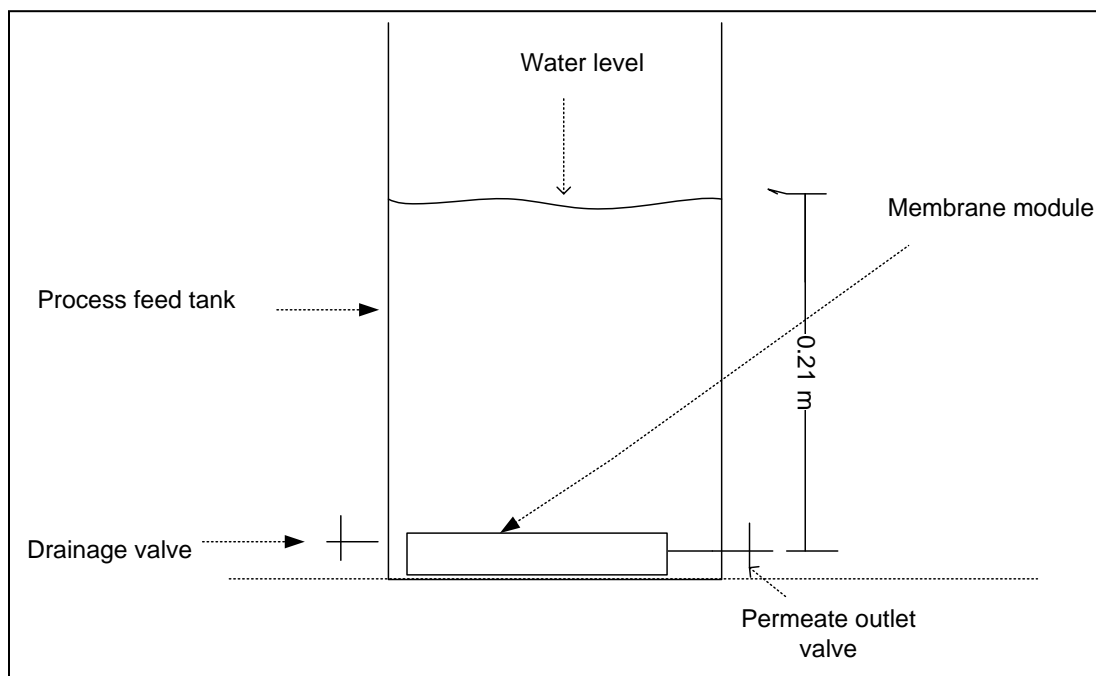


Figure 3- 3: Laboratory rig for the determination of the pure water flux using uncoated and coated membranes filtering deionized water

Procedure for the pure water flux:

- The filtration unit was flushed with deionized water and the drainage valve and permeate outlet tap opened to drain the water.
- The drainage valve and permeate tap were closed.
- Deionized water was poured into the feed tank to a height of 0.21 m.

- The permeate outlets of the coated and uncoated filters were opened and permeate collected in beakers.
- The volume of permeate collected with time was recorded, as well, as the corresponding water level in the feed tank.

The flux (J) was calculated using equation 2-2.

The transmembrane pressure (TMP) was calculated as follows:

$$\text{TMP (N/m}^2\text{)} = h\rho g \quad (3- 3)$$

Where,

h = height of water in the feed tank (m)

ρ = density of water at room temperature (1000 kg/m³)

g = acceleration due to gravity (9.81 m/s²)

3.3.3.6 Filtration performance

The filtration unit was used to filter turbid water and permeate turbidity was monitored with time in order to determine the filtration performance of the membranes. Two units were constructed, each consisting of a membrane pack containing four modules of the uncoated and coated filters respectively. Therefore, the turbidity of permeate collected was an average value for four modules. The filtration unit is illustrated in Figure 3.4.

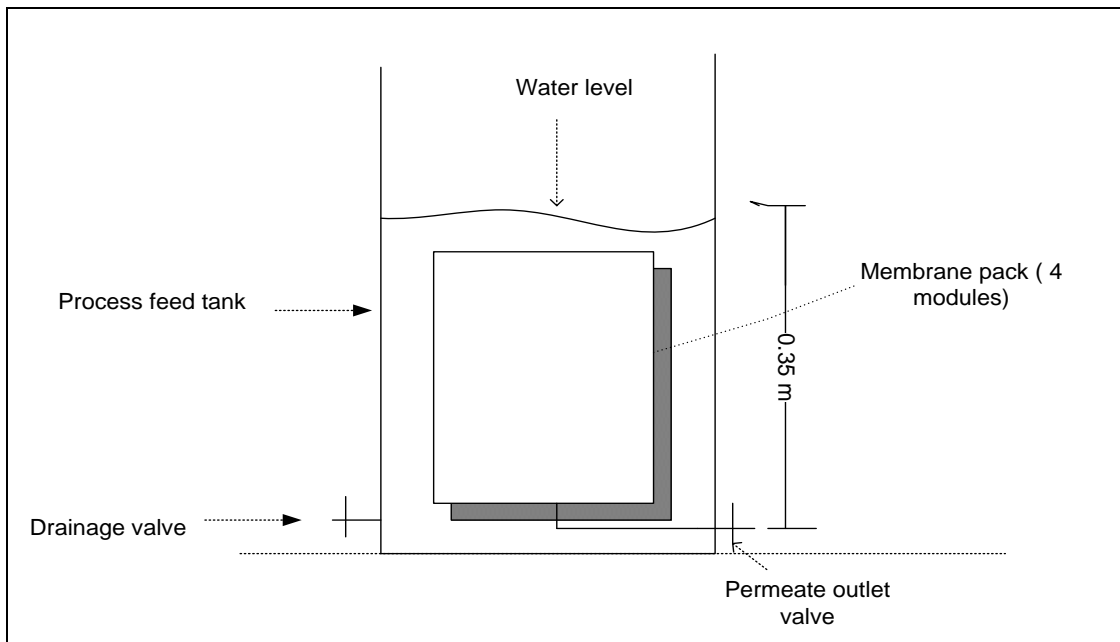


Figure 3- 4: Schematic representation of the RRWTS unit used for filtering water of different turbidities

Feed water with different turbidities was filtered using the submerged pack of membrane filters under gravity. The feed water samples used had turbidities of 700 NTU, 100 NTU, and 40 NTU.

The procedure for the filtration test using the three feed samples was as follows:

- The filtration units were flushed with tap water and the drainage valve and permeate outlet tap opened to drain the water.
- The drainage valves and permeate taps were closed.
- Feed samples (20L) were poured into the filtration units.
- The permeate taps were opened and permeate was collected from each of the two filtration units in clean bottles.
- The turbidities of the samples over time were measured using a Hach 2100P turbidity meter and recorded.

3.4 Results and Discussion

3.4.1 Incorporation of AgNPs on the WFMF membrane

3.4.1.1 Visible effects of membrane coating

Figure 3-5 shows photographs of the coated membrane and the complete filter module:



Figure 3- 5: Photographs of the coated membrane and the coated filter module respectively

The colour of the WFMF membrane changed from white to brown-yellow indicating the formation of AgNPs by reduction of silver ions (Ag^+) to elemental silver (Ag^0) (Voigt 2009). The brown-yellow colour is a scientifically well established characteristic of AgNPs.

This observation was in agreement with a previous study by Pradeep and Jain (2005) who coated polyurethane foam with AgNPs and the colour changed from white to yellow. This colour is due to the SPR of AgNPs under the range (390-420 nm) for AgNPs (Dankovich and Gray 2011) as a result of the interaction of light waves on the surface of a particle.

This indicated that AgNPs were incorporated on the WFMF membrane.

3.4.2 Membrane characterization

3.4.2.1 Morphology

Figures 3-6 and 3-7 show the SEM micrographs of the uncoated and coated membranes at a magnification of 150X.

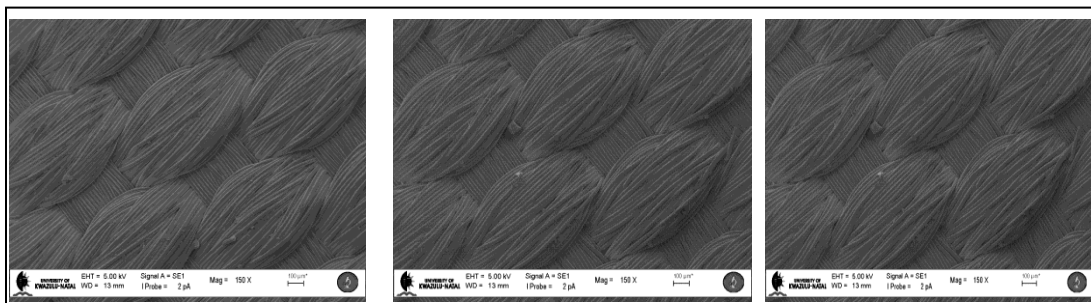


Figure 3- 6: SEM micrographs of the uncoated membrane at 150X

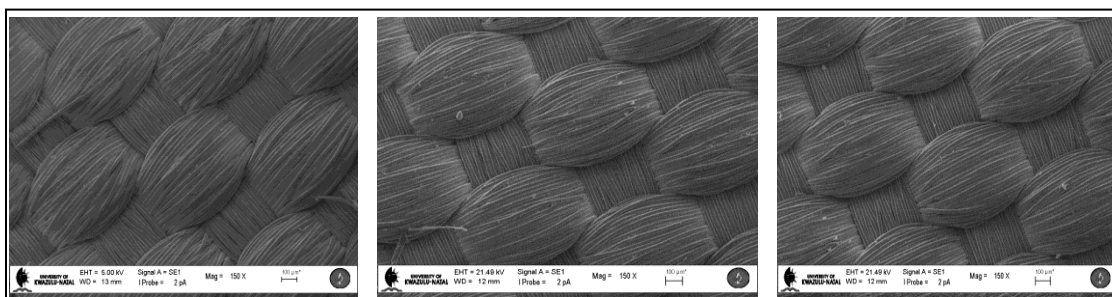


Figure 3- 7: SEM micrographs of the coated membrane at 150X

The woven structure of the membranes was visible in both sets of micrographs. There appeared to be no significant difference in the morphology of the uncoated and coated membranes at this magnification.

The micrographs for the membranes at a magnification of 2000X are shown in Figures 3-8 and 3-9.

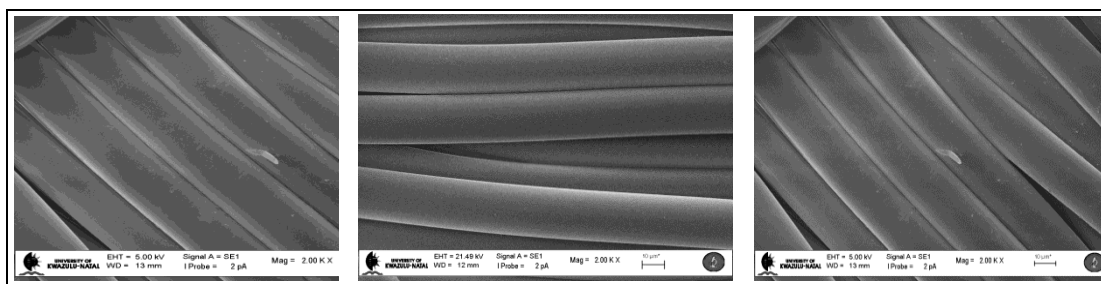


Figure 3- 8: SEM micrographs of the uncoated membrane at 2000X

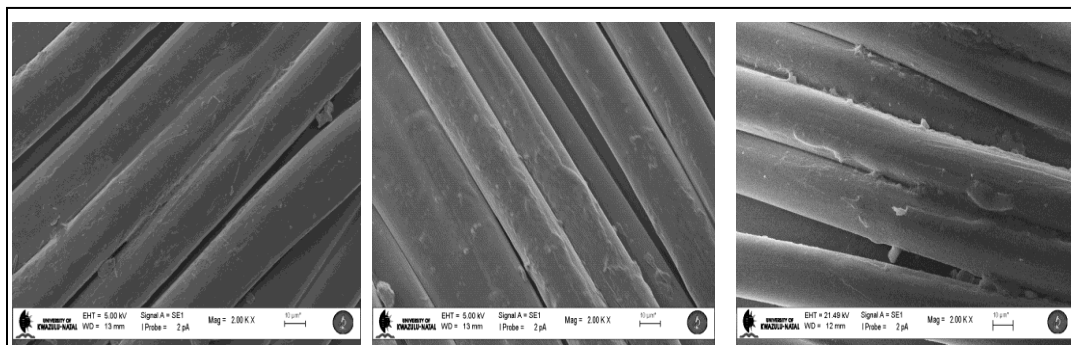


Figure 3- 9: SEM micrographs of the coated membrane at 2000X

There appeared to be no significant difference in the structure of the uncoated and coated membranes. However, some matter was observed on the surface of the coated membranes that was postulated to be the AgNPs.

In a previous study (Savage *et al.* 2009), using porous membranes it was shown that the AgNPs seemed to be preferentially concentrated along the internal pore surface of the membrane. Another study using AgNPs coated polyurethane foams showed that the polyurethane retained its structure even after coating with AgNPs (Pradeep, T. and Jain 2005). Similarly, Zhu et al (2011) investigated the immobilization of silver on propylene membranes and reported that the silver did not significantly affect the original pore structures of the membrane on the macroscopic scale.

The current study showed that the morphology of the WFMF membrane did not change upon coating with AgNPs.

3.4.2.2 Concentration of silver on the membrane

The results of the acid digestion of the membrane samples are shown in Table 3-2.

Table 3- 2: Silver concentration in acid digested fabrics

Sample	Mass of sample (mg)	Area of sample (m ²)	Silver content (mg/L)
1	340	0.00075	0.508
2	134	0.00030	0.218
3	235	0.00053	0.360

The amount of silver incorporated to the membranes as determined from equation 3-2 is shown in Table 3-3.

Table 3- 3: Mass of silver per unit area of the three modules

Sample	Mass of silver in sample (mg)	Mass of silver in A 4 size module (mg)	Mass of silver per cm ² of membrane (mg/cm ²)
1	0.0254	14.000	0.0139
2	0.0109	14.520	0.0144
3	0.0180	13.600	0.0135

The amounts of silver on the membranes were almost similar and this indicated that the silver coating was fairly uniform for the three samples. The average amount of silver on the coated module was calculated to be 14.04 mg AgNPs per 120 g of A4 size WFMF membrane module. This represented 0.0117 wt. % in the module and corresponded to an average amount of silver per surface area of the membranes of 0.0139 mg/ cm².

In another study (Zodrow *et al.* 2009) polysulfone UF membranes were impregnated with 0.9 wt. % AgNPs and depicted improved antifouling and virus removal.

In the current study, there appeared to be no significant difference in the amount of silver on the three coated membrane samples tested and this indicated that the coating process was effective in uniformly attaching the AgNPs on the membrane.

3.4.2.3 Membrane hydrophilicity

The average values of the contact angles and surface energies are shown in Table 3-4.

Table 3- 4: Contact angles and surface energies of the WFMF membranes

Sample	Contact angle (°)	Surface energy (mN/m)
Uncoated	76.3±18.5	34.32
Coated	17.6±2.8	69.45

Photographs of water droplets on the surfaces of the uncoated and coated membranes are shown in Figure 3-10.

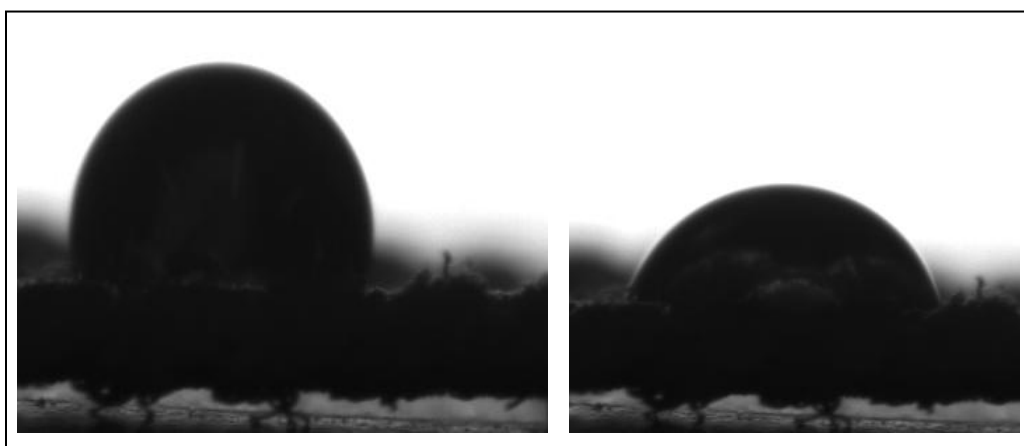


Figure 3- 10: Water droplets on the surfaces of the uncoated (*left*) and coated (*right*) membranes

The uncoated membrane had a higher contact angle than the coated membrane, while the coated membrane had a higher surface energy than the uncoated membrane. The average contact angle of the uncoated membrane was $76.3 \pm 18.5^\circ$ and the corresponding surface energy was 34.32 mN/m. The polyester fabric without silver coating is known to be hydrophobic in nature (Kusuktham 2010), and hence the large contact angle. The contact angle for the coated membrane was $17.6 \pm 2.8^\circ$ while the surface energy was 69.45 mN/m. There was a 77 per cent decrease in the contact angle due to coating.

The coated membrane was found to be significantly more hydrophilic than the uncoated membrane at 95 per cent confidence interval ($p < 0.05$). This is in agreement with the

findings from a study by Zodrow et al (2009) who coated polysulfone membranes with AgNPs. They concluded that the coated membrane was significantly more hydrophilic than the uncoated membrane due to its contact angle being 10 per cent smaller than that of the uncoated membrane. They suggested that this decrease in hydrophobicity can be potentially beneficial in preventing chemical fouling.

It has been proposed that the hydrophilic property may be because the immobilized silver on the membrane surface is hydrophilic (Zhu *et al.* 2011). Lower contact angles indicate that the membranes are more hydrophilic and such membranes will generally have better resistance to fouling by hydrophobic foulants (Gilron *et al.* 2001). Thus the coated membrane was more hydrophilic than the uncoated membrane as a result of the AgNPs coating.

3.4.2.4 FTIR Spectra

The FTIR spectra of the uncoated and coated membranes are presented in Figure 3-11.

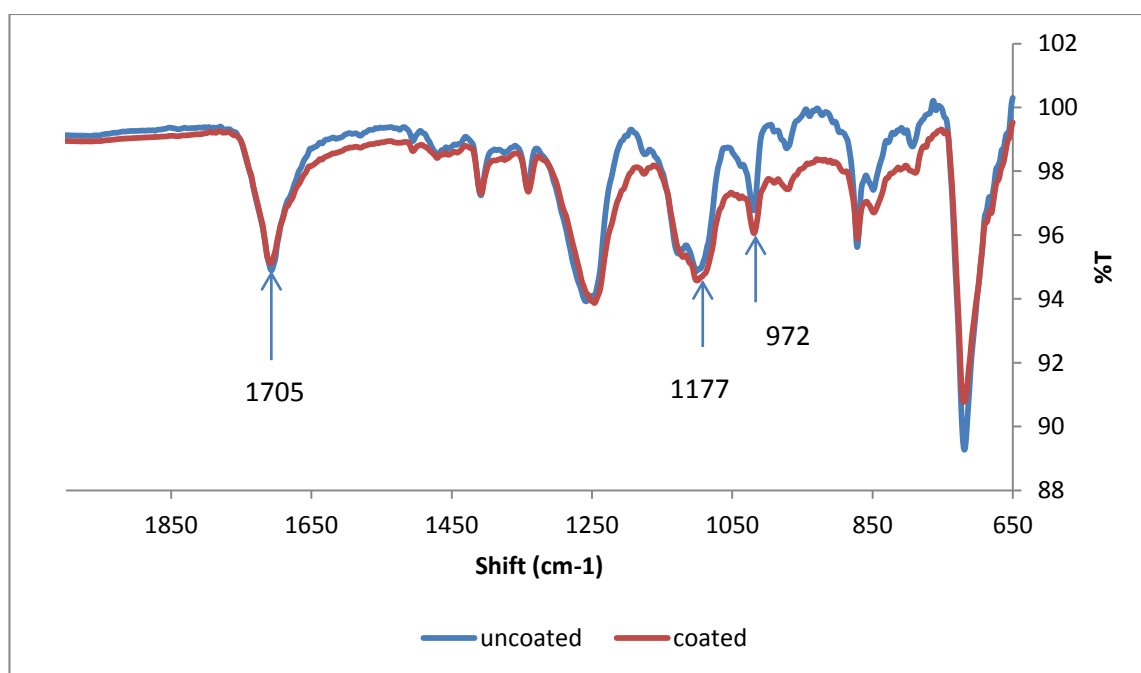


Figure 3- 11: FTIR spectra of uncoated and coated WMF membranes for shifts between 1900 and 650 cm^{-1}

The spectra of the uncoated and coated membranes indicated that both membranes have many similar IR band peaks mainly because of the similar composition of polyester. The presence of peaks at 972 cm^{-1} , 1177 cm^{-1} , and 1705 cm^{-1} in the spectra of both membranes showed that the membranes were polyester based (Derrick *et al.* 1999).

However, there were some notable differences in the intensity of the peaks between the spectra of both membranes. This shift in the peaks observed in the spectra of the coated membrane was postulated to be due to the coating with AgNPs arising from bonding interactions between polyester and silver. In another study (Pradeep, T. and Jain 2005), where polyurethane foam was coated with AgNPs for water filtration, the authors observed that there was a significant shift in the -N- peak upon nanoparticle coating, while all the other peaks remain unchanged.

The main absorption bands observed are presented in Table 3-5.

Table 3- 5: Interpretation of the FTIR Spectra of the uncoated and coated membranes

Shift (cm^{-1}) Uncoated	Shift (cm^{-1}) Coated	Probable assignment
720	722	Aromatic ring stretch or CH_2 rock
870	870	C-H deformation and double bond
972	973	Bending frequency of trans olefinic group
1011	1019	C-H aromatic bend
1088	1102	C-O stretching
1177	1177	C-CO-C stretch (ester)
1404	1404	C-H bend
1505	1505	C=C (aromatic)
1705	1707	C=O stretching

3.4.2.5 UV-Visible Spectrophotometry

The UV –visible absorbance spectra of the membranes is shown in Figure 3-12.

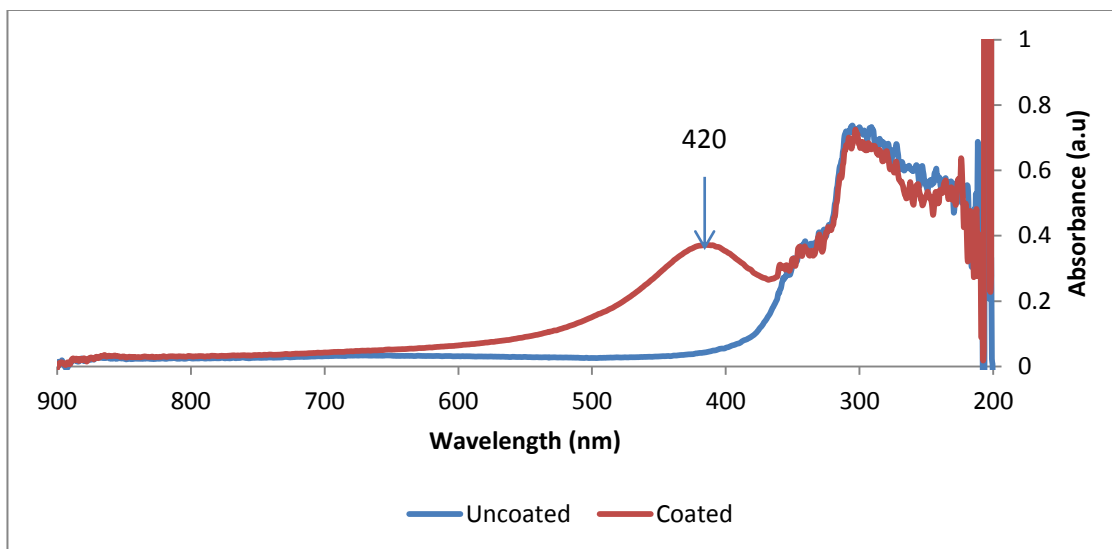


Figure 3- 12: UV Spectra of uncoated and coated WFMF membranes at wavelengths between 200 nm and 900 nm

The spectra of both membranes appeared generally similar except for the characteristic peak at 420 nm on the spectrum of the coated membrane. Metal nanoparticles such as silver display a very intense peak in UV-Vis spectroscopic analysis due to SPR of conducting electrons on the surface of AgNPs (Barud *et al.* 2011). The movement of free electrons between the conduction and valence bands of silver gives rise to SPR absorption band in UV-Vis spectroscopy analysis (Rathnayake *et al.* 2012).

The characteristic absorbance peak, approximately at 420 nm for the coated membrane (Giri *et al.* 2011) indicated the presence of AgNPs on the membrane. There was no characteristic peak at this position (420 nm) for the spectrum of the uncoated membrane as expected. This indicated that the coated membrane indeed contained the AgNPs.

3.4.2.6 XRD Spectra

The XRD spectra for the AgNPs coating are shown in Figure 3-13.

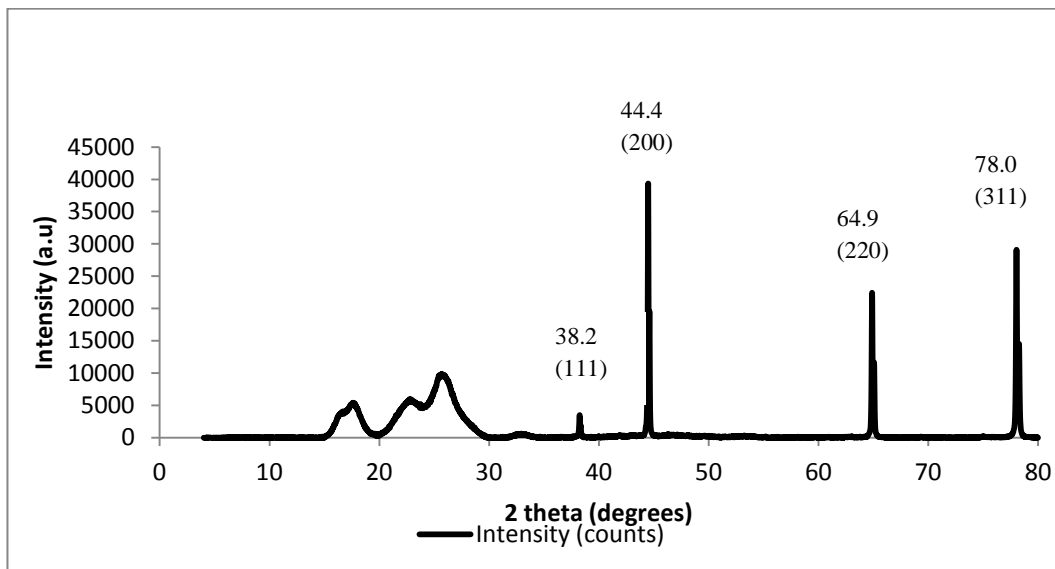


Figure 3- 13: XRD patterns of the AgNPs on the coated membrane for 2 theta angles between 0° and 80°

The diffraction pattern showed characteristic Bragg peaks at 2θ values of 38.2°, 44.4°, 64.9° and 78.0°. This diffraction pattern matches the face-centred cubic (fcc) structure of silver observed at 2θ angle. The characteristic Bragg peaks of the silver nano crystallites observed at 2θ values of 38.2°, 44.4°, 64.9° and 78.0° corresponding to the four diffraction peaks (1 1 1), (2 0 0), (2 2 0) and (3 1 1) respectively. These peaks indicated the presence of AgNPs on the coated membranes (Khan *et al.* 2011; Mthombeni *et al.* 2012).

The intensive peak located at $2\theta = 44.4^\circ$ corresponds to the diffraction of (200) lattice plane of fcc structure. This showed that (200) planes of AgNPs were highly oriented parallel to the WFMF membrane (Heidarpour *et al.* 2010a).

The peaks in XRD pattern are in good agreement with that of fcc form of metallic silver. Thus, the XRD spectra confirmed the crystalline structure of AgNPs on the coated membrane. No peaks of other impurity crystalline phases were detected, which showed that the coating did not introduce substances other than silver to the membrane.

3.4.2.7 TGA

Figure 3-14 shows the results of the Thermo Gravimetric Analysis.

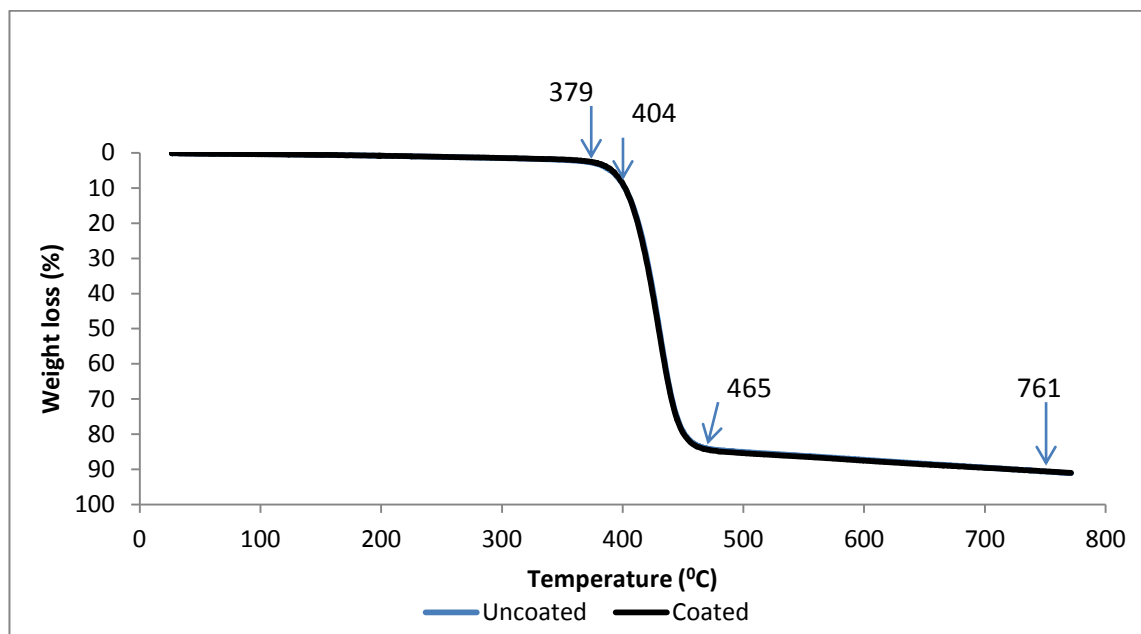


Figure 3- 14: TGA curves for the uncoated and coated membranes for a temperature range of 30° C to 800° C

The TGA curves were similar for both the uncoated and coated membranes; this may have been due to the dominant polyester structure. The initial decomposition occurred at 379° C due to thermal breaking of the double bonds ($-C=O-$). Furthermore, there was a 10 per cent weight loss at about 404° C, and the residual weight of less than 10 per cent at 761° C due to the presence of high aromatic rings in the polymer structure. The specimen experienced major decomposition and carbonization starting at 404° C and ending at 465° C.

In a previous study on polyester fibres it was found that the major decomposition started at 350° C and was complete at around 500° C. The initial degradation step occurred below 350° C in which there was a slight loss in weight of between 5 and 10 per cent (Talukdar and Achary 2010).

The current study indicated that the coating of the WFMF membrane did not compromise its thermal properties as shown by the similar thermal decomposition curve for the uncoated and coated membranes. This may have been as a result of the low amount incorporated on the membranes (0.0117 wt. %) which could not significantly change the thermal properties of the membrane.

3.4.3 Integrity testing

3.4.3.1 Air pressure test

The air pressure test indicated that the modules were free from leaks and therefore fit for use in the experiments. This also indicated that the coating of the membrane did not compromise the membrane's ability to be glued to the PVC frame.

3.4.3.2 Pure water flux

The results of the pure water flux are shown in Table 3-6.

Table 3- 6: The values of the pure water flux ($\text{Lm}^{-2}\text{h}^{-1}\text{Pa}^{-1}$) with time for both membranes

Time (minutes)	10	20	30	40	50	60
Uncoated	0.057	0.050	0.053	0.052	0.049	0.052
Coated	0.115	0.100	0.085	0.071	0.061	0.060

It was observed that the pure water flux was fairly constant for the uncoated membranes over time as expected. However, the pure water flux of the coated membrane decreased with time as the gravity head reduced. This change in flux with time could have been as a result of the AgNPs coating which increased the hydrophilicity of the membranes.

The flux versus TMP plot is shown in Figure 3-15.

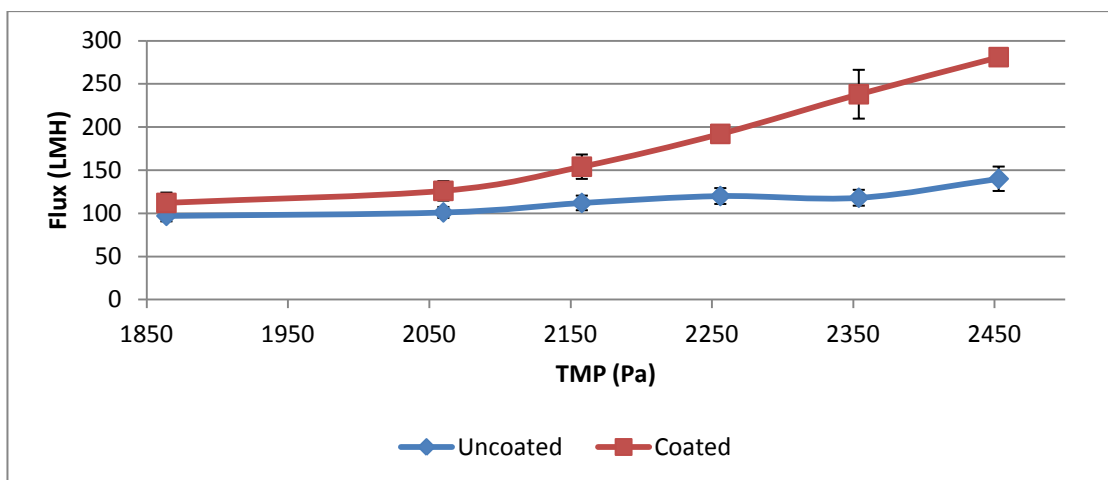


Figure 3- 15: Pure water flux of uncoated and coated membranes using deionized water under gravity filtration for selected TMP values. The error bars are based on the standard deviations

The flux increased with increase in TMP for both filters. The average flux of the uncoated filters was 115 ± 14 LMH while that of the coated filters was 184 ± 60 LMH. There was a significant difference in the fluxes of the two filters at 95 per cent confidence interval ($p < 0.05$). The statistical computation is shown in Appendix B. This was expected, because it is known that the specific flux increases with increasing hydrophilicity of the membrane material (Childress *et al.* 2012). The hydrophilicity of the WFMF increased as a result of coating with AgNPs as was shown in section 3.4.2.3. The fluxes obtained for both filters were typical of MF membranes.

Similar increase in hydrophilicity was observed in another study using polypropylene membranes coated with silver (Zhu *et al.* 2011). However, the results obtained in the current study were different from those obtained by Zodrow *et al.* (2009) who impregnated UF polysulfone membranes with 0.9 wt % AgNPs. They showed that the hydrophilicity of the coated membrane increased by 10 per cent and found that the coated membrane had similar permeability to the control polysulfone membrane without AgNPs at 95 per cent confidence interval.

The difference in results may have been due to the difference in the degree of hydrophilicity achieved. In the study by Zodrow *et al.* (2009) the water contact angle

decreased by 10 per cent while in the current study it decreased by 77 per cent. This study proposed that coating of the WFMF membrane resulted in a significant increase on the permeability and may have influenced the anomalous behaviour of the pure water flux of the coated membrane.

3.4.3.3 Filtration of turbid water

The results from the filtration using both the uncoated and coated filters are shown in Figures 3-16, 3-17, and 3-18.

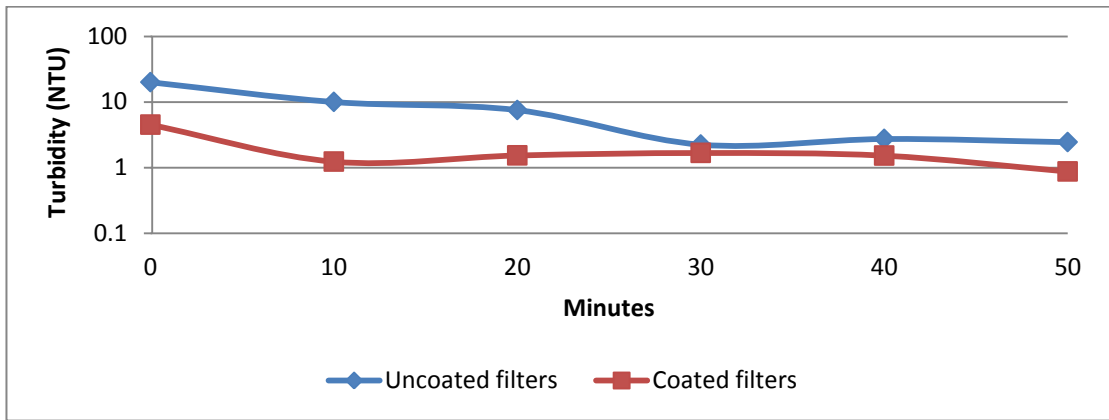


Figure 3- 16: Average permeate turbidities for clay suspension feed water (700 NTU) using uncoated and coated filters

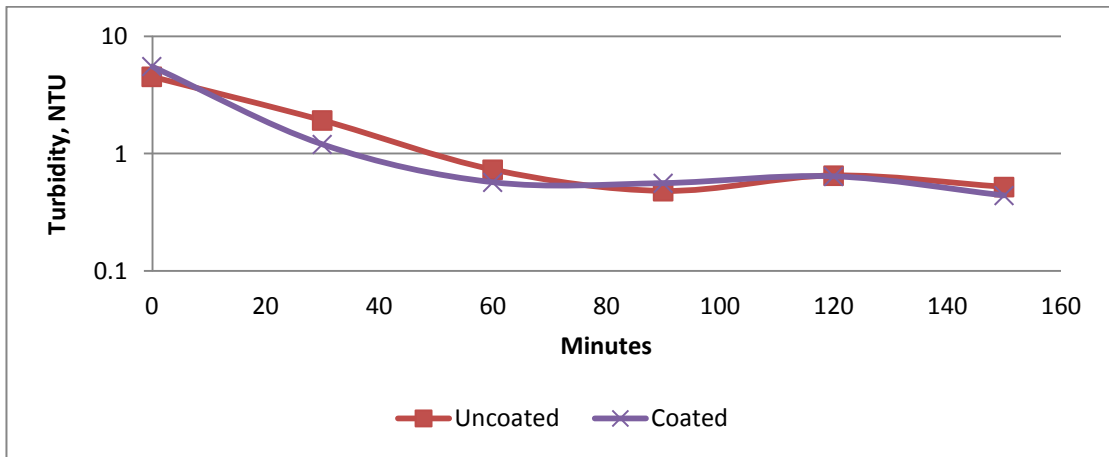


Figure 3- 17: Average permeate turbidities for raw river water (100 NTU) using uncoated and coated filters

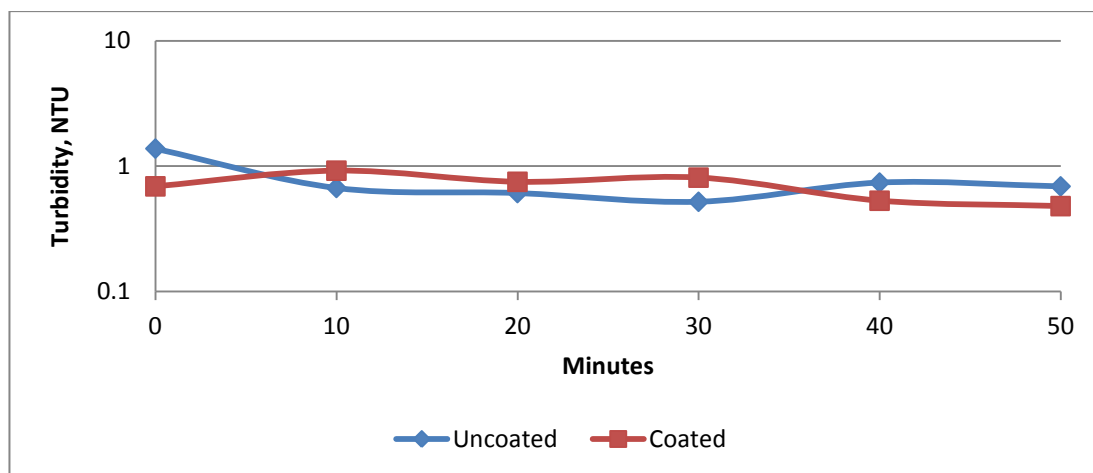


Figure 3- 18: Average permeate turbidities for raw river water (40 NTU) using uncoated and coated filters

Permeate from both the uncoated and coated filters had turbidities generally below 1 NTU irrespective of the turbidity of the feed water and therefore met the set guidelines for potable water (WHO 2011b).

The filtration performance of the uncoated fabric had been investigated previously and found to be satisfactory (Pillay *et al.* 2009). The WFMF filter is an absolute barrier to substances that are larger than the equivalent pore size of the fabric.

It was observed that the filtration performance was not compromised by the coating of the fabric with AgNPs as demonstrated by the satisfactory permeate turbidities obtained from the three tests conducted.

3.5 Summary

The main objective of this chapter was to evaluate the synthesis of AgNPs and their incorporation into the WFMF membranes. The review of the literature concerning the use of silver in potable water treatment filters indicated that the disinfection performance of the systems depends on the following:

1. The form of the silver. The use of AgNPs ensures increased surface area for interaction with microbial contaminants and therefore leads to better disinfection efficacy.
2. The method of incorporation of AgNPs on the support. Impregnation is a common method that has been used to attach AgNPs in medical devices and water treatment filters. It was chosen for his study because it is convenient and cost effective and produces excellent results.

The study successfully incorporated AgNPs in the WFMF membrane using the chemical reduction of AgNO_3 in the woven networks of the polyester membrane. The membranes were characterized using spectroscopic and analytical methods.

The main findings from the characterization tests are summarized as follows:

1. The presence of AgNPs on the coated membrane was indicated by the change of colour of the membrane from white to brown-yellow. This colour is due to the SPR of AgNPs. This was also confirmed by UV-Visible Spectroscopy, by the presence of a characteristic peak at a wavelength of 420 nm which is typical for AgNPs.
2. The morphology of the membranes was evaluated using SEM. At magnifications of 150X and 2000X, there appeared to be no significant difference in the structure of the uncoated and coated membranes. However, the coated membrane had some matter on its surface when observed at 2000X which was postulated to be the attached AgNPs.

3. The hydrophilicity of the WFMF membrane increased due to the coating with AgNPs as expected. This increase in hydrophilicity had a significant effect on the pure water flux of the coated membranes.
4. The structure of the AgNPs coating was also determined by XRD analysis; the spectra indicated peaks at 2θ values 38.2° , 44.4° , 64.9° and 78.0° which correspond to the four diffraction peaks (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes, respectively, indicating the presence of silver on the surface of the coated membranes. The 2θ values of the Bragg-peaks in the XRD pattern were in good agreement with that of fcc form of metallic silver.
5. The filtration performance of the membrane was not compromised by the coating; both the uncoated and coated filters produced permeate of less than 1 NTU for a range of feed waters (raw river water of 40 NTU, 100 NTU and clay suspension of 700 NTU), thereby treating water to the required drinking water standards.
6. The permeability of the membrane increased as a result of the coating. The difference in permeability between the coated and uncoated filters was significant ($p < 0.05$) probably as a result of hydrophilicity.

4 INVESTIGATION OF THE DISINFECTION PERFORMANCE OF THE COATED MEMBRANE FOR SHORT TERM TRIALS

4.1 Introduction

This chapter presents the investigation of the disinfection efficacy of the coated membrane using *E.coli* as the indicator organism. The feed samples used were raw river water and synthetic feed water. The specific objectives for this chapter are:

- i. To investigate the antibacterial efficacy of the coated membrane in contact with media containing *E. coli*.
- ii. To investigate the disinfection efficacy of the coated filter during filtration of water with different *E.coli* concentrations (Flow test).

The investigations in this section were done over short periods of time of up to one hour. The long term trials are reported in Chapter Five.

4.2 Selection of methods for determining disinfection efficacy

4.2.1 Introduction

The literature survey showed that a number of methods can be used to determine the disinfection efficacy of materials containing disinfecting agents and for quantifying microorganisms. The methods used for the detection of antimicrobial activity of materials are categorized into three groups: bioautographic; diffusion; and dilution methods. The bioautographic and diffusion methods are qualitative techniques since they only give an indication of the presence or absence of substances with antimicrobial activity. On the other hand, dilution methods are considered quantitative assays because they determine the number of micro-organisms (Valgas *et al.* 2007). The dilution methods are presented in section 4.3. This section presents the following qualitative methods that are widely used:

- Disk diffusion test
- Agar well diffusion test
- Glass bottle test

4.2.2 Disk diffusion test

This method is used for the screening of antibacterial materials, by diffusion of the antimicrobial agent through agar. The materials are placed on a lawn of the challenge bacteria to test their antibacterial properties. The principle of operation of the disk diffusion method is that when a disk impregnated with an antimicrobial chemical agent is placed on agar, the chemical will diffuse from the disk into the surrounding agar medium. The extent of diffusion around the disk will depend on the solubility of the chemical and its molecular size. If a microorganism that is susceptible to the chemical agent is placed on the agar medium, it will not grow in the area around the disk where the chemical has diffused to. This area without growth around the disk is therefore known as the zone of inhibition (Refat *et al.* 2012) and its diameter is measured by a ruler and expressed in mm. Bacterial sensitivity to antibiotics is commonly investigated using disk diffusion method, often employing antibiotic impregnated disks (Ruparelia *et al.* 2008).

4.2.3 Agar well diffusion test

This method is used to determine the microbial growth suppression especially using liquid agents. The antibacterial activity is tested by making wells of about 5 mm diameter solidified nutrient medium such as agar containing inoculums in a Petri dish. Then the agent being investigated is poured in the marked wells and incubated for a specific period under specified conditions. The principle of this method is that the antimicrobials present in the agent diffuse out into the nutrient medium and interact with the test organisms in the medium (Valgas *et al.* 2007). This forms a zone of inhibition around the well and its diameter can be measured using a ruler and expressed in mm.

4.2.4 Glass bottle test

This method is an adaptation of the conventional test for minimum inhibitory concentrations (MICs) of disinfectants on microorganisms. The MICs test involves batch cultures in flasks containing varying concentrations of the disinfectant, liquid media and a given concentration of the test organism. The flasks are placed in a shaker for a specified period of time. Thereafter the absorbance of the solutions in the flasks is measured to determine the degree of microbial growth inhibition (Ruparelia *et al.* 2008).

The glass bottle test is used to determine the disinfection efficacy of a material when immersed in a liquid media containing the target microorganism. The principle of operation of this test is that when a material impregnated with an antimicrobial chemical agent is placed on suspension for a certain period of time, the chemical will diffuse from the material into the surrounding liquid medium. After the end of the test period, the suspension is tested for the presence of the microorganism.

4.2.5 Selection of the indicator organism

Microbial indicators are microorganisms that while not themselves pathogenic, indicate potential threats to the microbiological quality of water. Examples of these microorganisms include, total coli forms, faecal coli forms and *E.coli*. Water contaminated with pathogenic species also has the normal inhabitants of the human intestine. A good indicator organism of faecal pollution should fulfil the following criteria (Health 2005; Cabral 2010):

- It should always be present when faecal pathogens are present.
- It should be present in faeces in large numbers so that the organisms can be detected.
- It should be relatively easy and quick to detect in environmental waters.
- It should survive in water at least as long as waterborne pathogens of faecal origin.

- It should be as sensitive as pathogens to disinfection, and not be pathogenic to humans.

No single indicator fulfils all these considerations, nor is any suitable for all cases. The most important point is that the presence of indicators of faecal contamination implies an increased risk of water borne disease. *E. coli* is a commonly used bacterial indicator organism for pathogenic contamination (Mangayarkarasi *et al.* 2012). The WHO guidelines recommend a value of zero *E.coli* per 100 mL of treated water (UNICEF 2008; WHO 2011b) as an indication of proper water treatment.

The justification for using *E. coli* is based on the following:

- It is a strict indicator of faecal contamination.
- It is an organism, whereas total coli forms and faecal coli forms are groups.
- It is most usually present when pathogens are present.
- It is amenable to rapid and accurate enumeration.

4.3 Methods used to quantify microbes

4.3.1 Introduction

Bacteria are normally assayed using either quantal or enumerative methods (WHO 2011a). Enumerative methods such as the standard plate count method usually are based on counting bacteria colonies on a solid medium such as, typically, an agar medium. Quantal assays, on the other hand, involve making serial dilutions of a sample, inoculating the samples and estimating the bacterial density as a most probable number (MPN) per unit sample volume.

4.3.2 Standard plate count method

This is an enumerative method used to determine quantitatively a bacterial population. The procedure is as follows:

- Making a suspension of the bacteria from fresh culture in a liquid.
- Serial dilution of the suspension to approximately 300 CFU/ mL.
- Sterile spreading of aliquots of the diluted sample over the surface of sterile nutrient medium such as solidified nutrient agar.
- Incubation of the plates at the appropriate conditions of temperature and for the required duration in order to induce the development of colonies.
- Counting of the resulting visible colonies.
- Calculation of the number of CFUs in the original package or suspension from the number of colonies on the plates and the dilution factor.

4.3.3 Most probable number method

The most probable number (MPN) technique is an important quantal technique used for estimating microbial populations. The MPN technique estimates microbial population sizes in a liquid substrate after dilution and incubation of samples. In addition, this technique relies on the pattern of positive and negative test results (presence/ absence test) following inoculation of a suitable test medium (usually with a reagent) using tubes or micro well plates. The identification of the microbe is done by observing the colour of the wells. The wells are enumerated and the microbial population is read from statistical tables.

One of the MPN methods used is the Colilert 18 method. It makes use of well plates to hold the sample during incubation. It detects total coli forms and *E. coli* in water. When total coli forms metabolize Colilert 18's nutrient indicator, the sample turns yellow,

while when *E.coli* metabolizes the nutrient indicator, the sample fluoresces (*E.coli* fluoresces under UV light to give a greenish blue colour).

The procedure for the Colilert 18 test is as follows (IDEXX Laboratories 2013):

- The sample containing the test organism is diluted using sterile water to the required dilution.
- The contents of one sachet of the Colilert reagent are added to 100 mL of the sample in a sterile bottle.
- The bottle is capped and the reagent is allowed to dissolve and mixed well.
- The sample is poured into a test bag referred to as a Quanti-Tray.
- The test bag is sealed using a Quanti-Tray sealer.
- The test bag is incubated at 37° C for 18 hours.
- The test bag is placed under a 6 watt, 365 nm UV light within 5 inches of the sample in a dark environment in order to count the wells containing *E.coli*.
- The number of *E.coli* is read from a standard statistical MPN table.
- The number obtained from the table is multiplied with the dilution factor in order to obtain the amount of *E.coli* in the sample.

4.4 Methods selected for this study

4.4.1 Basis of method selection

The criteria employed in the selection of methods for the evaluation of the disinfection efficacy were based on the following objectives:

- i. A method to investigate the antibacterial effect of the coated membrane when in contact with medium containing *E.coli*.
- ii. A method to evaluate the antibacterial efficacy of the coated filter during filtration of water containing *E.coli*.

Disk diffusion and glass bottle tests were selected for use to investigate the antibacterial efficacy of the coated membrane in contact with *E.coli* because the test material (WFMF membrane) is in solid form. The MPN method was selected to quantify the concentration of the indicator organism in the feed and permeate samples because it is more convenient to use and accurate in terms of quantification of microbes.

4.5 Determination of the extent of disinfection

4.5.1 Removal efficiency of *E.coli*

Removal efficiency of *E.coli* is obtained using the expression:

$$R (\%) = 100 (1 - C_p / C_f) \quad (4-1)$$

Where,

C_f = concentration of *E.coli* in the feed

C_p = concentration of *E.coli* in permeate

Disinfection efficacy can be expressed in terms of log removal values (Baker 2004),

$$LRV = \log_{10} (C_f / C_p) \quad (4-2)$$

Where, C_f and C_p have the same meaning as stated above.

In municipal water filtration, an LRV of 4 or 5 is recommended (Baker 2004).

4.6 The feed suspensions

4.6.1 Selection of test feeds

The feed suspensions studied were raw river water and synthetic feed made using de-ionized water spiked with *E.coli*. Raw river water was employed because the target population for the use of the RRWTS are people in rural areas who usually obtain water from rivers. However, the microbial populations in river water may vary depending on

the climate and the seasons. Furthermore, river water may have high turbidity which will lead to the formation of a cake layer on the filters. This will act as a precoat on the filter and aid in the removal of contaminants. Therefore, synthetic feed was employed especially for the long term disinfection tests which were aimed at determining the disinfection potential of the coated membrane without the formation of a cake layer. Long term disinfection performance tests are presented in Chapter Five.

4.6.2 River water

River water was obtained from River Umhlangane in Durban, South Africa and transported to the laboratory in a cooler box and analyzed within six hours after collection to prevent the death of *E.coli*. Properties of the raw river water used are shown in Table 4-1.

Table 4- 1: Properties of raw river water

Parameter	Value
Turbidity (NTU)	40-100
<i>E.coli</i> (CFU/ 100 mL)	2 500- 10 000

4.6.3 Synthetic feed water

E.coli inoculum was obtained from the Microbiology laboratory, department of Biotechnology at Durban University of Technology. Nutrient agar was obtained from Prestige Lab Supplies cc (PLS) in South Africa.

The pure culture of *E.coli* was sub-cultured on nutrient agar slants as follows:

- Nutrient agar was dissolved in sterile water (3.1 g agar in 100 mL of water) and autoclaved at 121° C for 30 minutes in order to sterilize the media.
- The media was cooled under a laminar flow to 40° C and then poured into sterile glass bottles each kept in a slanting position (60°) and allowed to solidify under laminar flow.

- A pure culture of fresh *E.coli* was streaked on the slants and kept in the refrigerator at 4° C. This was used for subsequent experiments.

Before the *E.coli* was used for spiking deionized water, inoculum was prepared from the above pure culture using the following procedure:

- Nutrient agar solution was sterilized by autoclaving and cooled to 50° C.
- The solution (15 mL) was poured into a Petri dish under sterile conditions and allowed to solidify at room temperature.
- To 15 mL of solidified nutrient agar in a Petri dish, a loop of culture was inoculated by streaking under a Bunsen burner flame.
- The plate was incubated for 24 hours at 35° C before use in the preparation of synthetic feed.

Preparation of the synthetic feed was done as follows:

- A loop of *E.coli* that had been incubated for 24 hours from the Petri dish was taken and mixed with 100 mL of deionized water.
- Two drops (0.1 mL) of the well mixed suspension were taken and added to 20 L of deionized water in a sterile bucket and mixed thoroughly to ensure uniform feed suspension.
- The feed suspension was poured into the process feed tank containing the membrane pack for treatment.

Properties of the synthetic feed are shown in Table 4-2.

Table 4- 2: Properties of synthetic feed

Parameter	Value
Turbidity (NTU)	0.6
<i>E. coli</i> concentration (CFU/ 100 mL)	77 000

From the literature, some bacterial challenge tests have employed *E.coli* concentrations in the order of millions of CFUs in order to demonstrate the disinfection efficacy of disinfectants (Guzmán *et al.* 2008). However, such high concentrations are not normally found in river water. The synthetic feed was prepared contained 77 000 CFU/ 100 mL which is higher than the concentrations found in the raw river water obtained.

4.7 Experimental methods

All materials and apparatus used in the following experiments were autoclaved at 121° C for 30 minutes to ensure sterility. All tests were conducted under sterile conditions.

4.7.1 Disk diffusion test

Uncoated membrane pieces were used as the control and the coated membranes as test samples. The test was done using the following procedure:

- Pieces of the uncoated (three) and coated (three) membranes measuring 0.8 cm by 0.8 cm were sterilized by autoclaving.
- The membrane pieces were cooled in a laminar flow at room temperature and were kept under sterile conditions.
- Synthetic feed containing three *E.coli* concentrations was prepared as explained in section 4.6.3. The three concentrations were 61 310 CFU/ 100 mL, 50 000 CFU/ 100 mL and 40 000 CFU/ 100 mL.
- Synthetic feed was transferred into the Petri dishes (1 mL in each dish). Six Petri dishes were used, two for each concentration of *E.coli*.
- To each of six Petri dishes, 15 mL of liquefied sterile nutrient agar was added and mixed well and allowed to solidify at room temperature.
- Sterile cotton swabs were used to transfer *E.coli* to the test plates. For each concentration, the swab was dipped into the *E.coli* solution and gently squeezed against the inside of the tube to remove excess fluid.

- The swabs were streaked on the nutrient agar plates. This was done using the three *E.coli* concentrations.
- The test filter pieces were placed on the lawn of bacteria at the centres of the plates using sterile forceps, each plate contained one membrane piece.
- The plates were incubated in an upside down position for 24 hours at 37° C.
- The inhibition ring formed after 24 hours served as an indicator of the antibacterial activity and was determined by visually inspecting the diameter of the inhibition zone around the filter piece.
- The zone of inhibition was measured using a ruler around the filter piece as stated in the literature (Maneerung *et al.* 2008; Yoon *et al.* 2008; Parameswari *et al.* 2010; Sadeghi *et al.* 2010).
- The plates were disposed in the biohazard waste box.

4.7.2 Glass bottle test

The test was done in triplicate using the following procedure:

- Synthetic feed water (100 mL) containing 61 310 CFU of *E. coli* was prepared and placed in sterile glass bottles.
- Pieces of the uncoated and coated membranes (0.8 cm by 0.8 cm) were sterilized by autoclaving at 121⁰ C for 30 minutes and cooled to room temperature.
- Six membrane pieces (three uncoated and three coated) were immersed in six glass bottles containing 100 mL of synthetic feed with intermittent shaking every 15 minutes for one hour.
- The membrane pieces were removed from the feed solutions and the solutions tested for the presence of *E.coli* using the Colilert 18 method.

4.7.3 Flow test

4.7.3.1 Experimental rig

The rig for the flow test is shown in Figure 4-1.

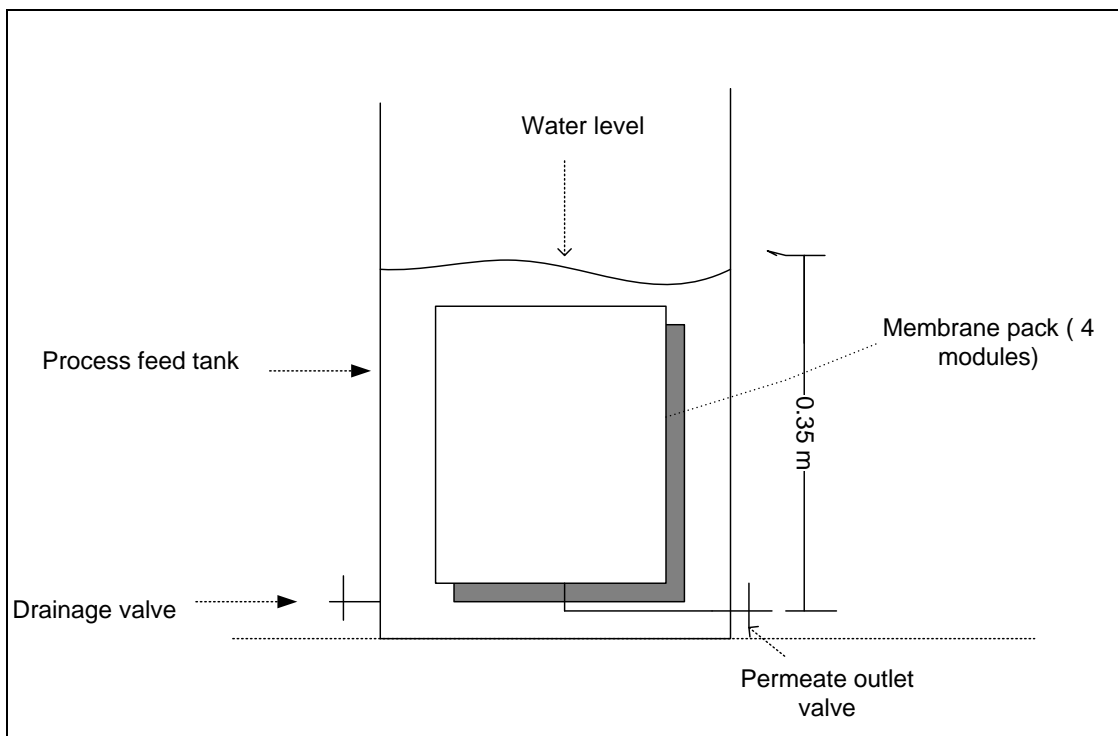


Figure 4- 1: Schematic representation of the rig used for the flow test

Two experimental rigs were assembled using the uncoated and coated membranes respectively. Each of the rigs consisted of a pack of four A4 size flat sheet membranes, immersed in a feed tank containing feed suspension. The rig consisting of the uncoated filters was used as the control. Three concentrations of *E.coli* were employed for this test using river water and synthetic feed. River water recorded *E.coli* concentrations of 2 500 and 10 000 CFU/100 mL while the synthetic feed had an *E.coli* concentration of 77 000 CFU/100 mL.

4.7.3.2 Procedure for the flow test

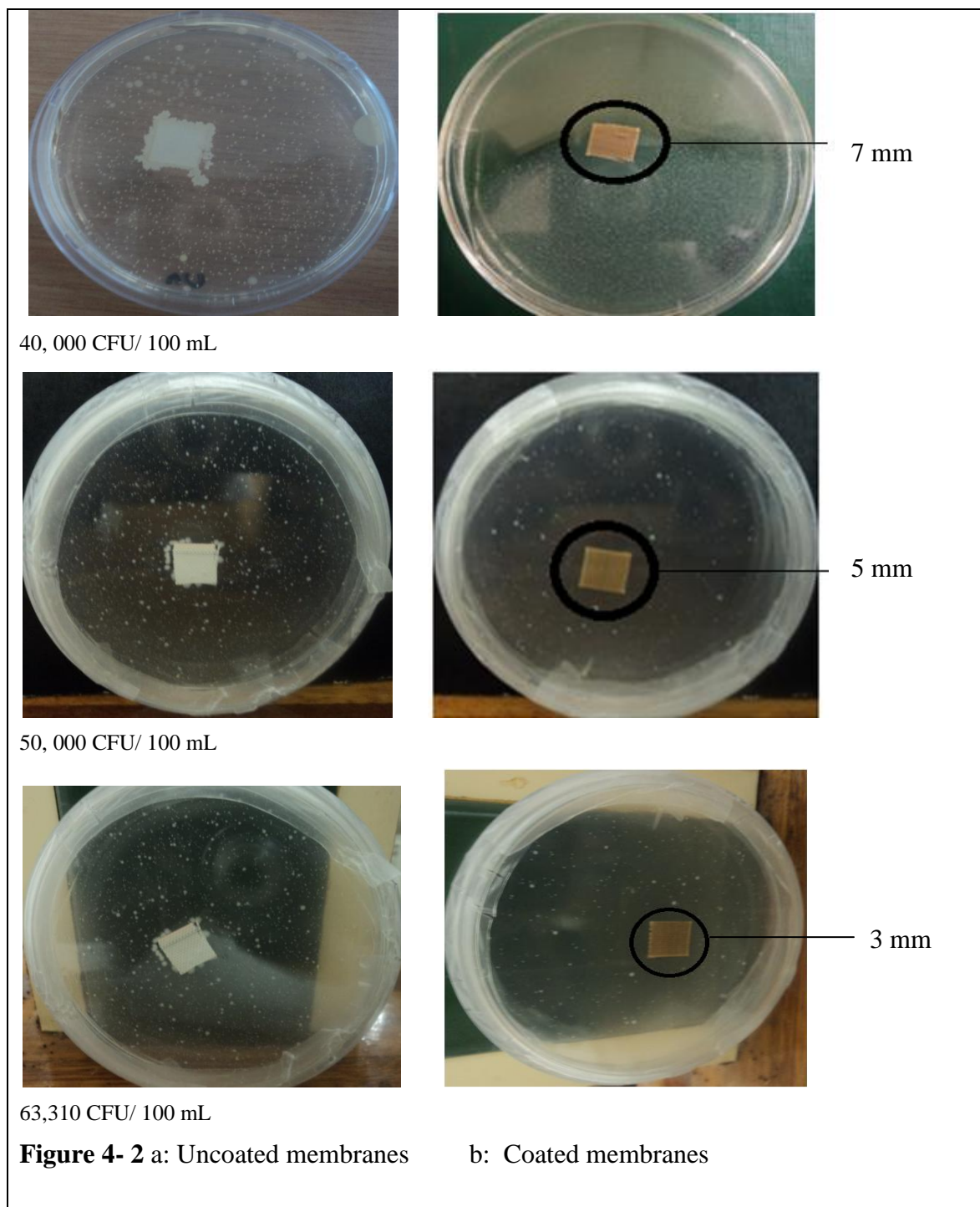
The three feed solutions were filtered in turns using the following procedure:

- The filtration unit was flushed with deionized water and the drainage valve and permeate outlet tap opened to drain the residual water.
- The drainage valve and permeate tap were closed and feed samples (20 L) poured into the filtration units.
- The permeate taps was opened and 100 mL of permeate was collected from each of the two filtration units in sterile bottles. For the sample with an *E.coli* concentration of 77 000 CFU/ 100 mL, this was initially done at 10 seconds, 30 minutes and 60 minutes after the start of filtration in order to test the effect of sampling time on performance.
- The samples were tested for the presence of *E.coli* using the Colilert 18 test method and incubated for 18 hours at 37°C.
- The results were recorded and the trays disposed in the biohazard waste box.

4.8 Results and Discussion

4.8.1 Disk diffusion

The results of the disk diffusion test are shown in Figure 4-2.



There was growth of *E.coli* observed all around the uncoated membrane and hence there was no zone of inhibition formed for the three *E.coli* concentrations used in the tests. However, there were clear zones of inhibition around the coated membrane pieces for the three tests done. The difference in the zones of inhibition was due to the different concentrations of *E.coli* used. The lowest feed *E.coli* concentration resulted in the largest zone of inhibition (7 mm) while the highest feed *E.coli* concentration resulted in the smallest zone of inhibition (3 mm). The presence of the zone of inhibition for all the three tests was an indication of consistency in performance of the coated membranes.

A clear zone of inhibition around the coated membranes was an indication of the antimicrobial effect. This demonstrated that the antimicrobial activity was only as a result of AgNPs impregnated in WFMF membrane and not due to membrane itself. This was in agreement with the findings of other studies that investigated the antimicrobial effect of bacterial cellulose impregnated with AgNPs (Maneerung *et al.* 2008) and silver coated polypropylene membranes (Zhu *et al.* 2011). The zone of inhibition shows the migratory effect of the disinfectant to the surrounding medium (Nirmala *et al.* 2010). The inhibition of bacterial growth around the disk is due to the release of diffusible elements from AgNPs into the surrounding agar medium (Kora, Aruna Jyothi *et al.* 2009a).

In the present study the WFMF coated membrane displayed a clear zone because it released silver ions into the media which imparted antimicrobial activity under humid environment. The AgNPs release Ag^+ ions to the medium (Feng *et al.* 2000; Lv *et al.* 2009). It has also been said that, for the case of AgNPs, the rates of dissolution and diffusion determine the amount of ionic silver released to the corresponding culture media (Lalueza *et al.* 2011).

This test demonstrated that the antibacterial effect of the coated membrane was due to the attached AgNPs. Furthermore, it indicated that the coating with AgNPs impacted disinfection ability on the membrane and enhanced its potential for use in the disinfection of water.

4.8.2 Glass bottle test

The results of the glass bottle tests are shown in Table 4-3 and Figure 4-3.

Table 4- 3: *E.coli* concentrations (CFU/ 100 mL) in the control and test samples

Sample	Control	Coated membrane
Test 1	63 310	0
Test 2	63 310	0
Test 3	63 310	0

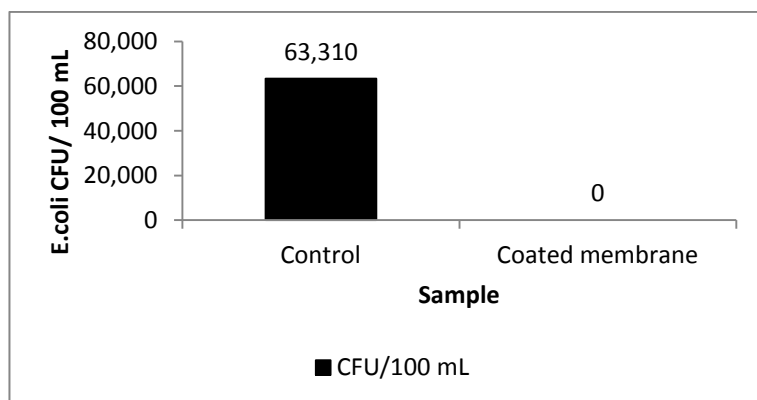


Figure 4- 3: *E.coli* concentrations for the control (uncoated) and test samples (coated)

The control did not display any disinfection ability when left in contact with synthetic feed for one hour; this is because its disinfection ability can only be as a result of size exclusion of bacteria during filtration (Pillay *et al.* 2009).

The coated membranes samples achieved zero *E.coli* when left in contact with synthetic feed for one hour with intermittent shaking of the feed. This was as a result of the migration of silver ions from the membranes due to the aqueous media and their deactivation of the *E.coli* (Juby *et al.* 2012). This mechanism of antimicrobial effect is used in the medical field whereby bandages containing AgNPs are used for wound dressing and when the AgNPs in the dressing come into contact with the humid environment of the wound, they release Ag^+ ions that kill germs (Percival *et al.* 2005; Maneerung *et al.* 2008).

This test further demonstrated the antibacterial effect of the coated membrane and its potential for use in the disinfection of water.

4.8.3 Flow test

4.8.3.1 Effect of sampling time on disinfection performance

E.coli counts at sample collection times of 10 seconds, 30 minutes and 60 minutes for feed of 77 000 CFU/ 100 mL are shown in Figure 4-4.

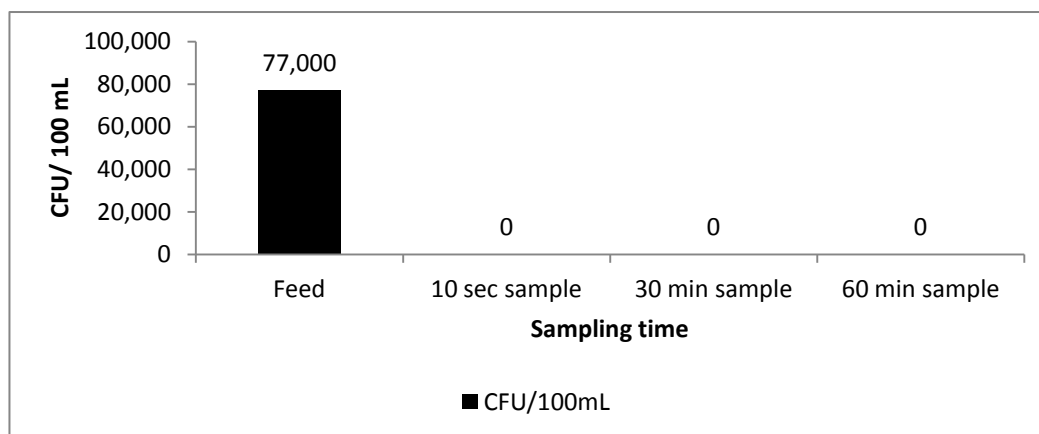


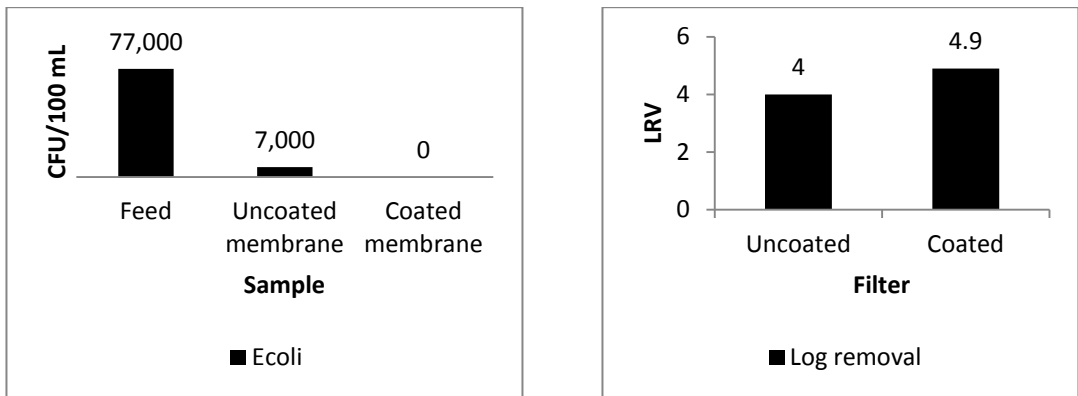
Figure 4- 4: Effect of sample collection time on the disinfection efficacy for synthetic feed of 77 000 CFU/ 100 mL

The results indicated that for a feed containing 77 000 CFU/100 mL of *E.coli*, there was zero *E.coli* in permeate for all the three sampling times used. Therefore, subsequent samples for the investigation of disinfection performance of the coated filters were taken from the first 100 mL of permeate collected from the unit. This volume was generally collected in less than five minutes of filtration. Since the sample was collected within five minutes of filtration, a significant cake layer was unlikely to form within such a short period for the raw river water. This study focused on determining the capability of the coated membrane to disinfect water without the influence of the cake layer. However, for practical application, the issue of formation of cake layer by suspended matter will have an effect on the disinfection performance of the coated membranes.

4.8.3.2 Disinfection efficacy

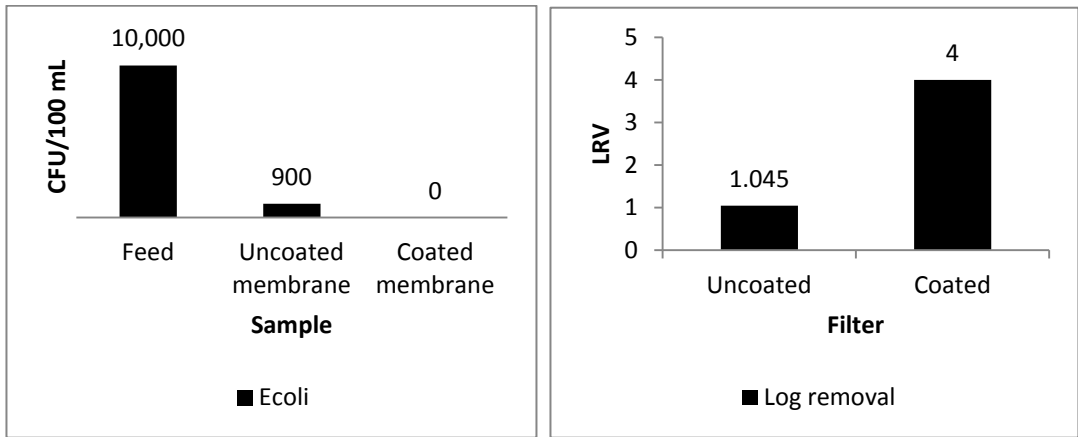
In this study the term disinfection refers to both physical removal of *E.coli* due to size exclusion by filtration and inactivation by AgNPs. The results of the effect of *E.coli*

concentration on the disinfection efficacy using both filters are shown in Figure 4-5 a-f with the corresponding log removal values (LRVs).



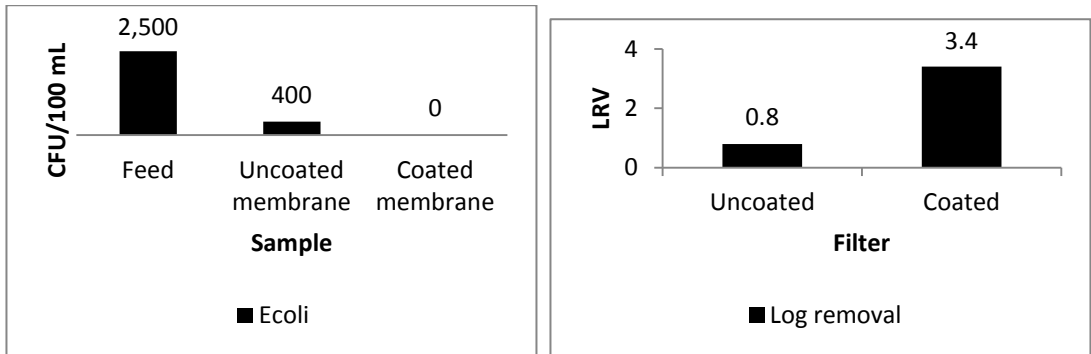
a) High *E.coli* concentration

b) LRVs for both filters



c) Medium *E.coli* concentration

d) LRVs for both filters



e) Low *E.coli* concentration

f) LRVs for both filters

Figure 4- 5: Disinfection performance of the uncoated and coated filters for different *E.coli* concentrations

The uncoated filters attained appreciable *E.coli* removal levels of between 84 per cent and 91 per cent in the three tests reported. The corresponding LRVs for the three *E.coli* concentrations (77 000 CFU/ 100 mL, 10 000 CFU/ 100 mL, 2 500/ 100 mL) were 4, 1.045 and 0.8 respectively. This indicated that the *E.coli* removal improved with increase in the amount of *E.coli* in the feed water probably due to the higher concentrations leading to more *E.coli* deposition on the filter surface and improving the removal efficiency.

The coated filters, on the other hand, achieved 100 per cent *E.coli* removal for all the three investigations. No *E.coli* was detected in permeate. The corresponding LRVs for the three *E.coli* concentrations (77 000 CFU/ 100 mL, 10 000 CFU/ 100 mL, 2 500/ 100 mL) were (4.9, 4.0 and 3.4), the difference was due to different *E.coli* concentrations in the feed; otherwise the removal was 100 per cent for the three tests.

Based on the results of the disk diffusion, glass bottle and flow tests, three possible antibacterial mechanisms for the coated filter were proposed. The first mechanism is separation by physical removal due to size exclusion. This is attributed to the separation of matter that cannot pass through the filter due to its large size. Secondly, that the bacteria are directly killed by the silver ions released from the coated filter and AgNPs penetrating the bacteria cell wall. Lastly, that any bacteria flowing out of the coated filter are contaminated with silver ions and AgNPs resulting from leaching, and therefore they cannot grow into colonies in the nutrient medium, because the silver ions affect the cells' ability to replicate in a culture environment.

Other studies have also shown that silver may inactivate pathogens that pass through the filter pores, or may prevent bacterial growth in the filter itself (Bielefeldt *et al.* 2009). This means that the main purification mechanism may not be the removal of bacteria from the feed water by filtration, but rather the deactivation of bacteria as they percolate through the coated filter by AgNPs (Dankovich and Gray 2011).

The current study postulates that the disinfection ability of the coated filter is probably due to a combined effect of size exclusion of bacteria during filtration, contact with AgNPs on the filter and continued disinfection of permeate resulting from the eluted

silver. The third mechanism proposed is in agreement with a previous study, which investigated the disinfection ability of residual silver in water (Pape *et al.* 2004). It has been reported that functional bactericidal nanocomposites that have both the ability to release chemicals to deactivate bacteria and also deactivate by means of being in contact with bacteria, have added advantages over any method consisting of either function alone (Gottesman *et al.* 2011). Therefore, this test demonstrated that the incorporation of AgNPs indeed significantly improved the disinfection efficacy of the WFMF membrane.

4.9 Summary

The objective of this chapter was to investigate the disinfection performance of the coated filter. The investigations carried out and the key findings are summarized as follows:

- The antimicrobial effect of the coated filter on *E.coli*. This was investigated using the disk diffusion method. The results indicated that there was a clear zone of inhibition all round the coated membranes while there was no zone around the uncoated membranes that were used as controls.
- The mechanism of disinfection of the coated membrane. The mechanism of disinfection using AgNPs has not been fully elucidated. In this study, based on the disk diffusion and glass bottle tests, it was postulated for the tests conducted that disinfection capability of the coated membrane was due to the release of silver ions by the AgNPs from the coated filter, which interacted with *E.coli* in the surrounding media and thus deactivating them.
- The flow test achieved 100 per cent *E.coli* removal for feed water containing a range of *E.coli* (2 500-77 000 CFU/100 mL). This was postulated to be due to size exclusion of *E. coli*, and interaction between the AgNPs on the filters and *E.coli* in the feed. Therefore, the AgNPs impregnated polyester membrane exhibited a strong antimicrobial activity against *E.coli*.

5 INVESTIGATION OF THE LONG TERM DISINFECTION PERFORMANCE AND SILVER ELUTION

5.1 Introduction

The disinfection ability of the coated filter was demonstrated in Chapter Four using the disk diffusion test, glass bottle test and flow test. However, the essential questions surrounding the effectiveness of the coated filter as a potential POU system for water treatment include:

- What will be the extent of silver elution from the filter to the treated water?
- Does the leaching of silver depend on the flow rate of permeate?
- For how long can the disinfection efficacy last?
- What will be the effect of silver leaching on the disinfection efficacy?

This chapter presents the investigation of the disinfection efficacy of the coated filter over a period of time, as well as silver elution from the filter over time and its impact on the disinfection performance. The specific objectives of this chapter are:

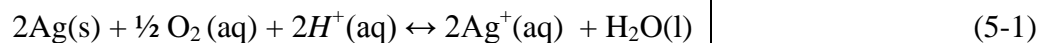
- i. To investigate the effect of time on leaching of silver.
- ii. To investigate the effect of time on disinfection efficacy.
- iii. To investigate the effect of permeate flow rate on leaching.
- iv. To investigate the effect of leaching on the disinfection efficacy of the filter.

5.2 Summary of previous work on AgNPs coated materials

5.2.1 Theory of silver elution

AgNPs when exposed to aqueous media, undergo dissolution leading to the formation of Ag^+ ions. The ion release from AgNPs is a combined oxidation process involving

protons and dissolved oxygen (Hurt and Liu 2010). In simple solutions containing no other oxidants, reductants, or organic matter, the silver ion release can be expressed using the following reaction equation,



Ionic silver can adsorb on AgNPs, hence, AgNPs in aqueous media coexist with Ag^+ ions and surface adsorbed Ag^+ . It has been shown by thermodynamic analysis that Ag^+ is the only equilibrium product in simple media (such as deionized water), so the prediction of the concentration of ions in AgNPs colloids is based on chemical kinetics (Hurt and Liu 2010). The important factor affecting the oxidation of the AgNPs is the presence of dissolved oxygen in the water. The release of Ag^+ is also determined by the presence of other oxidants, aggregation induced by multivalent electrolytes, precipitation by Ag-complexing ligands, regrowth of AgNPs by reducing agents and the readsorption of released Ag^+ onto particle surfaces (Li, X and Lenhart 2012).

5.2.2 Effect of time on silver elution from AgNPs coated materials

A major challenge in the development of water treatment systems employing the use of AgNPs and other nanomaterials is the concern about the leaching or elution of nanoparticles or ions into the treated water (Kwakye-Awuah 2008). The presence of nanomaterials in drinking water in concentrations beyond the stipulated levels is a health risk to consumers and is therefore unacceptable. For instance, for situations where silver derivatives may be used to disinfect drinking water, the WHO recommends that levels of silver, up to 0.1 mg/L can be used without risk to human health (WHO 2011b).

This calls for effective design of the disinfecting material in order to ensure that adequate disinfection is achieved in sufficient contact time and disinfectant concentration whilst ensuring that leaching of silver is kept within the stipulated levels.

Silver elution from substrates has been investigated previously (Zodrow *et al.* 2009; Diagne *et al.* 2012; Lorenz *et al.* 2012; Pasricha *et al.* 2012) but the studies done were aimed at determining whether leaching occurred and involved short term tests rather than investigating leaching over a long period in order to determine the trend and the effect on performance of the materials.

5.2.3 Effect of permeate flow rate on leaching of silver

Nagarajan investigated the effect of operating pressure (using a pump) on the leaching of silver from a fiber. The study established that the leaching value is 0 mg/L at 55 kPa and 0.001 mg/L at 690 kPa after a prolonged and continuous use for a period of 12 weeks. The study concluded that a higher operating pressure does not release the silver impregnations from the fiber, which means the silver embedded into the fiber is held very strongly by the fiber polymer (Nagarajan 2009). However, the author did not mention how the silver was incorporated in the fiber.

5.2.4 Disinfection efficacy over time

A number of researchers have investigated the antimicrobial efficacy of AgNPs and substrates incorporating AgNPs (Pradeep, T. and Jain 2005; Maneerung *et al.* 2008; Dankovich and Gray 2011). Many of these tests however, were not conducted over a long enough period in order to provide information about the long term performance of water filters incorporating AgNPs. They were mainly aimed at showing that the materials containing AgNPs had antimicrobial properties. These studies were also not extensive in terms of ascertaining the disinfection lifespan of the coated materials.

5.2.5 Effect of silver leaching on the disinfection efficacy

Studies using AgNPs coated materials have shown that there is a relationship between the silver elution and the disinfection achieved. For instance, Zodrow *et al.* (2009) reported that the antimicrobial and antiviral properties of AgNPs coated polysulfone membranes decreased significantly when 10 per cent of the silver on the membranes was

leached during filtration. Lorenz et al (2012) investigated the effect of the textiles coated with AgNPs on the growth of the Gram- bacterium *Klebsiella pneumoniae*. They found out that the textiles showed antibacterial activity (LRV of 3) before washing, but not after washing. The washing had resulted in 15 per cent loss of the silver content in the textiles. However, these studies were performed for a short duration of time (less than one hour) and hence could not provide insights into the performance of the materials over time.

5.2.6 Overview

The review of literature has indicated that the major gap in knowledge is that the studies conducted previously on silver elution from coated materials have all be short term in nature and therefore cannot provide enough information to determine the performance of filters containing AgNPs in water treatment. Moreover, these studies were aimed at ascertaining whether leaching occurred as opposed to investigation leaching over time. This necessitates long term studies and quantification of the amount of silver leached with time. In addition, the studies on the disinfection performance of filters containing AgNPs were not conducted over a long enough period of time in order to provide information about the long term performance of the filters. Lastly, only few studies have investigated the relationship between the rate of silver elution and disinfection performance and none of them were conducted for periods longer than a few hours.

5.3 Scope of the current study

5.3.1 Effect of time on silver elution from AgNPs coated materials

In this study, an attempt was made to test permeate from the coated filters for the presence and concentration of silver. This investigation was done over a period of 90 days of continuous operation in order to determine the trend of silver elution over time.

5.3.2 Effect of permeate flow rate on leaching of silver

This study was conducted to determine the relationship between silver leaching and permeate flow rate in order to determine an optimum flow rate for the operation of the RRWTS incorporating AgNPs. The filters were run at different pressure heads in order to obtain different permeate flow rates. This was done in order to obtain an optimum flow rate for the operation of the RRWTS at which there is minimum leaching of silver.

5.3.3 Long term disinfection performance

The present study endeavoured to investigate the following:

- i. The disinfection ability of the coated filter treating water containing different concentrations of *E.coli* over time.
- ii. Determination of the disinfection lifespan of the coated filter.
- iii. Testing of the disinfection potential of the coated filter without the formation of a cake layer by filtering synthetic feed over time.

Seeded challenge tests are often employed to assess microbial removal by filters. A pure culture of the microorganism is spiked in a process tank containing the filters and de-ionized water. Samples are collected from the feed tank and from permeate for testing in order to determine the removal efficiency. The use of seeded challenge study for this work was motivated by the fact that the concentrations of specific indicator organisms such as *E.coli* in natural waters is low and generally not sufficient for challenge tests that endeavour to determine the operational limits of the membrane treatment system.

The removal of microorganisms by a membrane is also dependent on the formation of a dynamic layer on the membrane by fouling matter. This cake layer will dramatically improve the removal efficiencies of some pathogens over the filtration cycle either by physical straining or by adsorption in the cake layer. This phenomenon makes it difficult to evaluate the true potential of the membrane without the cake layer. Previous tests using the uncoated filters had shown marked improvements in *E.coli* removal up to 99

per cent due to the fouling of the membrane (Pillay *et al.* 2009). The fouling matter forms a dynamic membrane that plays a significant role as it further limits, in terms of size of particles, the passage of particulate matter through the filter (Persadh 2003). The current study endeavoured to test the performance of the coated filters without formation of the cake layer by using synthetic feed.

The concentrations of *E. coli* employed for the long term disinfection tests in this study were between 10 000 and 85 000 CFU/100 mL. These concentrations were adopted based on the observation that the average *E.coli* amounts in samples obtained from river water which was within this range. Some challenge studies (Guzmán *et al.* 2008; Maria *et al.* 2010) have employed *E.coli* concentrations in the order of millions in order to demonstrate antimicrobial efficacy of disinfectants. However, such large amounts of *E.coli* are not generally found in river water and therefore were not used in this study.

The turbidity of the feed suspension before and after spiking with *E.coli* was also monitored in order to determine the potential of the *E.coli* to increase the turbidity of the feed water and thereby lead to the formation of a cake layer on the filter.

5.3.4 Effect of silver leaching on the disinfection efficacy

The present study attempted to investigate the relationship between the elution of silver from the coated filter and the disinfection efficacy achieved over time. One of the mechanisms proposed in Chapter Four for the disinfection efficacy of the coated filters was based on elution of silver from the filter to the treated water which deactivates the microorganisms hence disinfecting the water. This study sought to investigate this further.

5.4 Experimental methods

5.4.1 Investigation of the effect of permeate flow rate on silver leaching

The leaching of silver from the coated filter into permeate was investigated by filtration of deionized water for a period of time.

5.4.1.1 Design of the filtration unit

The experimental rig is shown in Figure 5-1.

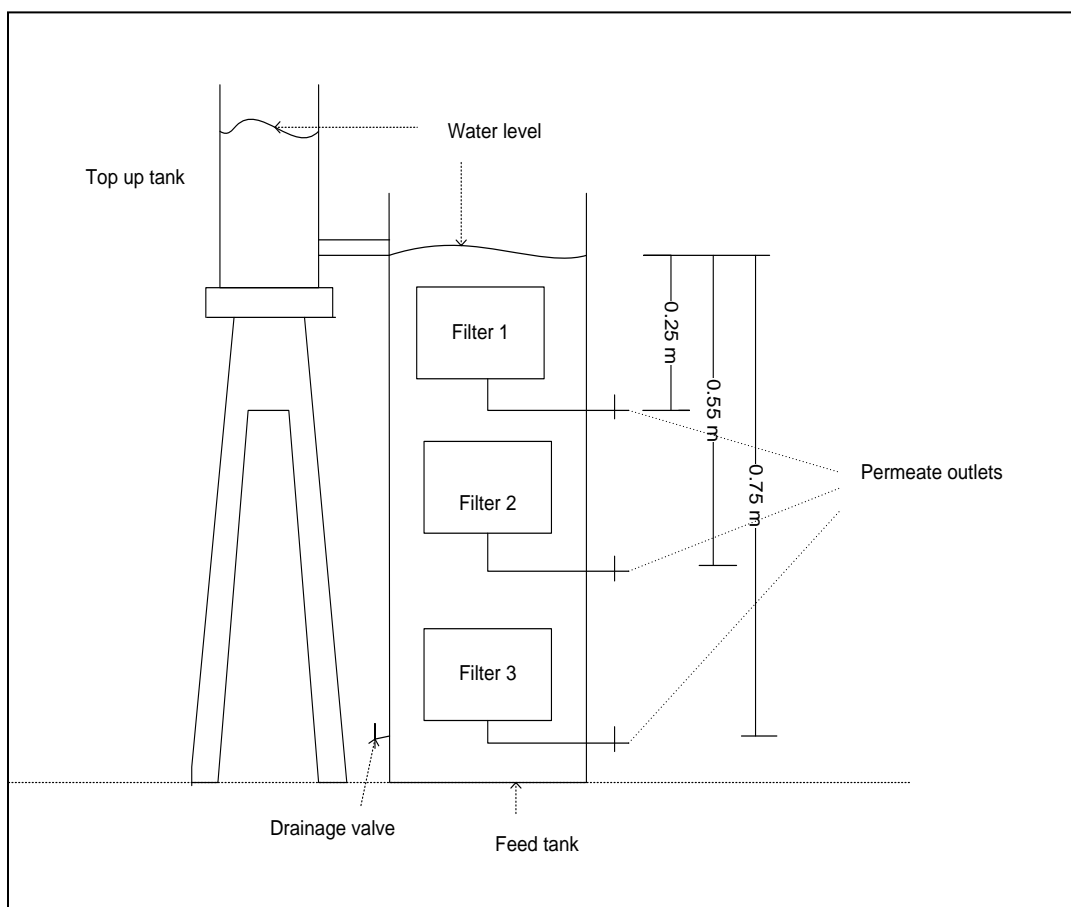


Figure 5- 1: Schematic representation of the silver elution test rig consisting of three coated filters located at different heights in the feed tank

The experimental rig consisted of a process feed tank, 1 m in height having a volume of 40 L and made from transparent Perspex. The tank was fitted with a level control in order to maintain the level in the feed tank at 0.75 m water. It was also fitted with a drainage valve. A top up tank with a volume of 10 L connected to the feed tank in order to ensure constant head. Three coated flat sheet modules were fabricated (their size was half of A4). The filters were positioned along the height of the feed tank in order to achieve different flow rates due to a difference in pressure heads.

The three filters and the corresponding positions along the tank were as follows:

- Filter 1 (0.25 m)
- Filter 2 (0.55 m)
- Filter 3 (0.75 m)

Each filter had a separate permeate outlet into separate permeate collection containers.

5.4.1.2 Operation of the unit

The feed was deionized water obtained from a pure lab Option-Q machine and the procedure was as follows:

- The feed was collected in a thoroughly cleaned container and poured into the feed tank to the 0.75 m level and also to the top up tank.
- The drainage valve was kept closed while the permeate outlets were opened and permeate collected into clean plastic bottles.
- The volume of permeate collected was recorded after every 24 hours.
- The top up tank was filled up daily in order to maintain the level of water in the feed tank.

5.4.1.3 Sample collection and analysis

- Samples of permeate (100 mL) were collected from each filter for silver leaching analysis after every three days for a period of 90 days.

- Samples were analysed using ICP-AES for the presence of silver.

5.4.2 Long term disinfection performance

The experimental rig for the investigation of the disinfection efficacy of the coated filter with time was almost similar to that used in the flow test in Chapter Four. However, since the objective of this investigation was to run the experiment continuously, a top up tank was included in order to ensure constant head of 0.35 m in the process feed tank as shown in Figure 5-2. The rig consisted of a pack of three coated filters (half of A4 size) in a process feed tank containing synthetic feed.

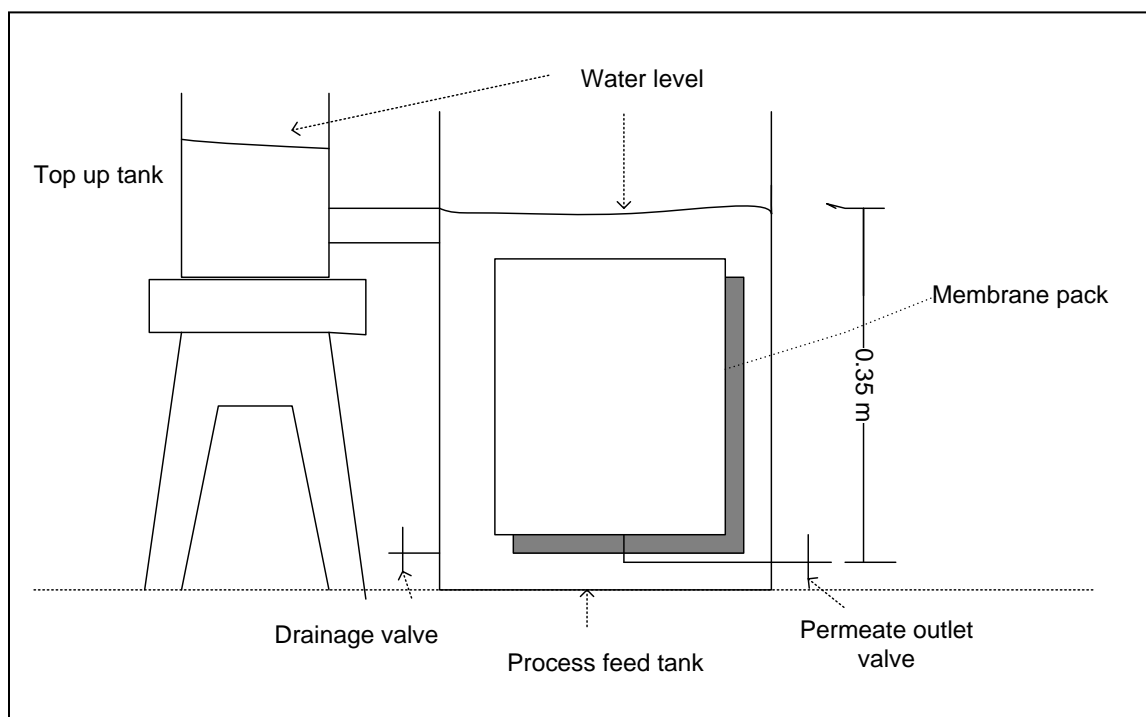


Figure 5- 2: Experimental rig for investigating the long term disinfection performance of the coated filters

5.4.2.1 Operation of the unit

The study was conducted over a period of 90 days with a daily introduction of fresh synthetic feed (10 000 to 85 000 CFU/100 mL of *E.coli*) after every 24 hours. The following procedure was used:

- The drainage valve was opened to drain the residual water. The permeate outlet was also opened to drain remaining permeate.
- The filtration unit was flushed with deionized water which was allowed to drain out through the drainage valve and the permeate outlet. This was done in order to get rid of the previous feed sample. Special care was taken to ensure that the permeate pipe was cleared of permeate. The dead volume of the pipe is approximately 10 mL.
- Synthetic feed (20 L) containing 0.1 mL of *E.coli* suspension was prepared following a procedure explained before in Chapter Four, section 4.6.3.
- This solution was mixed thoroughly to ensure uniform composition.
- The turbidity of the mixture was measured.
- The drainage valve and the permeate tap were closed and the feed was poured into the feed tank.
- As soon as the feed was poured into the feed tank, the permeate outlet tap was opened and 100 mL of permeate was collected into a sterile glass bottle over a period of less than 5 minutes.
- Permeate was diluted using sterile water and analyzed for the presence of *E.coli* using the Colilert 18 method.

5.4.3 Disinfection efficacy versus leaching rate

Samples of permeate from the filters from the long term disinfection performance rig were collected randomly and investigated for silver leaching using ICP-AES, Shimadzu, ICPE-9000. These results of silver leaching were compared with the disinfection results obtained from the Colilert 18 test method.

5.5 Results and Discussion

5.5.1 Permeate flow rate and flux

The results obtained from the investigation of the effect of permeate flow rate on the silver elution were not as expected. Deionized water was used as feed and it was expected that the flow rates and fluxes from the filters would remain constant with time and would vary with the pressure head. However, this was not so, instead, the flow rates and fluxes decreased with time and this indicated that the filters probably were fouling or the silver coating may have influenced this behaviour. Repeated attempts were made using deionized water from other sources and thorough cleaning of the feed tank but similar results were obtained.

The anomalous behaviour of the pure water flux using the coated membranes was noted earlier in section 3.4.3.2. Therefore, it was decided to continue with the investigation with an aim of determining the effect of time on silver leaching and not the effect of permeate flow rate on silver leaching.

The expected results and the results obtained are shown in Figure 5-3 and Figure 5-4 respectively.

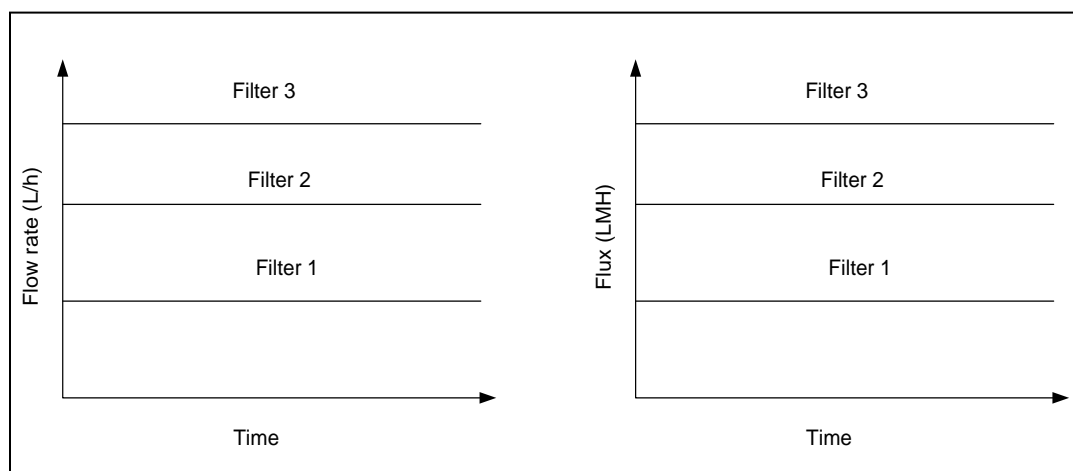


Figure 5- 3: Expected results for the effect of time on permeate flow rate and permeate flux when filtering deionized water (pure water flux)

During filtration of deionized water, the membrane is not expected to foul because the deionized water is free of particulate matter. Therefore the permeate flow rate and flux are expected to remain constant over time.

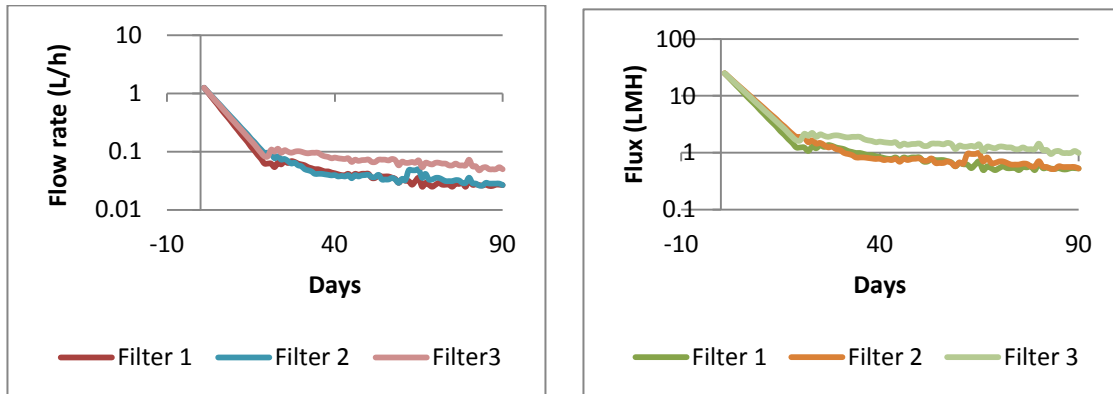


Figure 5- 4: Actual results for the effect of time on the permeate flow rate and flux

The permeate flow rates and fluxes showed similar trends for all the filters. There was a rapid decrease for 15 days. Thereafter, the decrease was minimal. Generally, Filter 3 appeared to have the highest flow rate and flux, as expected, and the flow rate and flux of Filter 2 were slightly higher than that of Filter 1 over time, also as was expected.

The permeate flux for the first 15 days is shown in Figure 5-5 in order to have a clearer picture of the trend in flux decline.

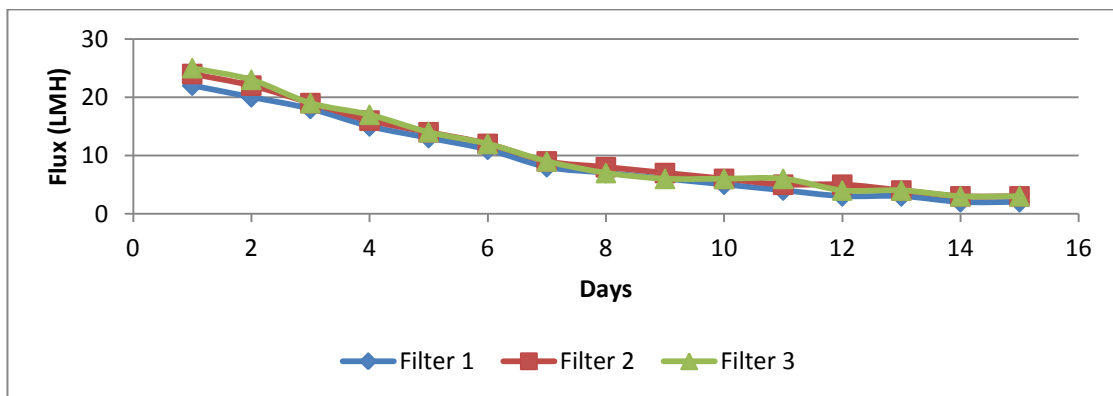


Figure 5- 5: Permeate flux for the first 15 days for the three filters

The fluxes of all the filters decreased with time. The cause of this behaviour could not be ascertained. Filter 3 initially had the highest flux (25 LMH) while Filter 1 had an initial flux of 22 LMH. It appeared that the difference in pressure head did not seem to have a

significant effect on the permeate flow rates and fluxes, this observation was not expected.

This was an interesting phenomenon, especially because it was repeatable for all the filters over the period of study. However, it is beyond the scope of this study to determine whether the decrease in flux was as a result of fouling or coating of the filters with AgNPs and therefore was not investigated further.

5.5.2 Concentration of silver in permeate over time

The concentration of silver in permeate from the filters is shown in Figure 5-6.

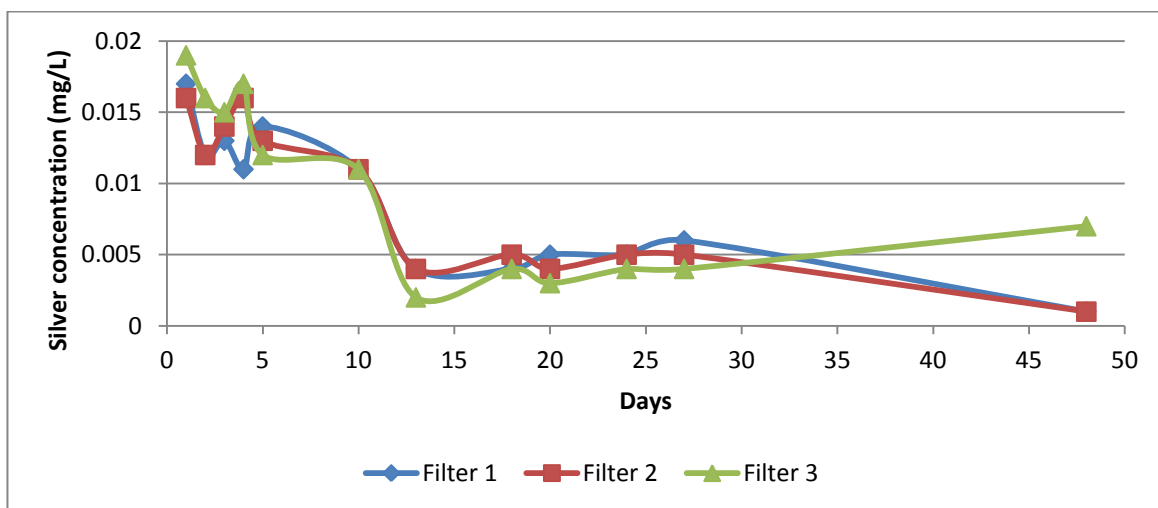


Figure 5- 6: A plot of silver concentration in permeate over time for the three filters

Silver elution decreased significantly after 13 days of continuous filtration for the three filters. This may have been due to the decrease in the rate of flux decline after the first 13 days of operation. The flux remained fairly constant between 15 and 35 days for the filters as seen in Figure 5.4. After 35 days, Filters 1 and 2 showed a decrease in silver elution while Filter 3 showed an increase. The cause of this drastic increase was not known. Generally, the three filters displayed a similar trend in the silver elution. After 48

days of continuous operation, the concentrations of silver in permeate for the three filters were below the detection limit of the ICP instrument (< 0.001 mg/L).

The silver elution is postulated to be mainly due to the weak adhesion forces between the AgNPs and polyester fabric matrix as well as the dissolution of nanosilver in water leading to release of silver ions (Basri *et al.* 2010). One of the main factors controlling the release of Ag^+ from composites is the concentration of the silver in the substrate (Kumar and Munstedt 2005). According to Pasricha et al (2012) who impregnated AgNPs on cotton, wool and nylon fabrics and investigated the elution of silver by washing the fabrics, they found that fundamental differences in the types of fabric controlled the amount of silver that could be loaded on to fabric and also leached in aqueous media. The silver elution was highest in the first wash and decreased as the number of washings increased. Additionally, they concluded that the fabrics released silver into the wash water at different rates.

In the present study it was found that, as more water was filtered through the filters, the amount of silver leached decreased. The decrease in silver elution was probably due to decrease in silver concentration on the filters that led to a decrease in the concentration gradient, which is the driving force for the dissolution. Furthermore, the decrease could also be due to the decline in flux over time that was observed.

The results of the concentration of silver in permeate were compared to the WHO guideline and are presented in Figure 5-7.

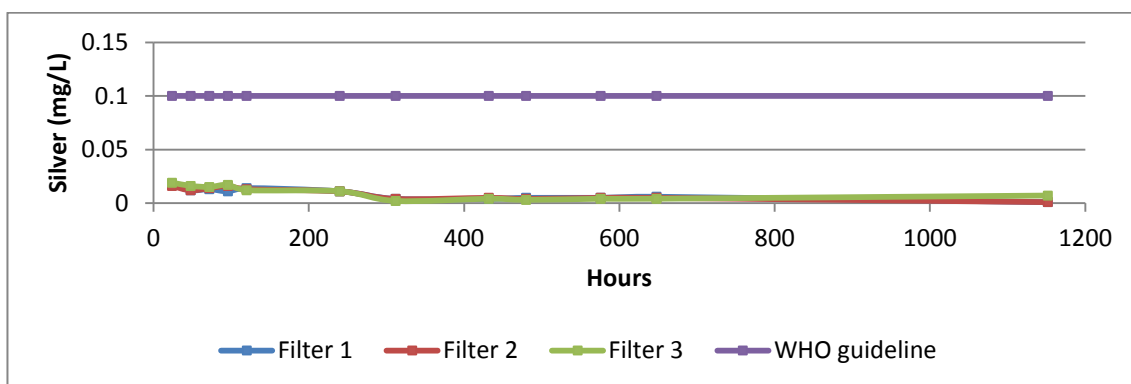


Figure 5- 7: Silver concentration in permeate compared to the WHO guideline

Since the silver leached from the filters was generally far below 0.1mg/L, it indicated that leaching of silver from the coated filter into permeate does not pose significant health risk to consumers (WHO 2011b). In a way the coated membranes can be regarded as a disinfection system providing low amounts of silver in permeate just like the slow release techniques for small scale water treatment such as chlorine and iodine tablets.

The cumulative mass of silver eluted over time was calculated using equation 5-2:

$$\text{Cumulative mass (mg)} = \int_0^t \{t * Q * Ag\} \quad (5-2)$$

Where,

t is the change in time (h)

Q is the average permeate flow rate (L/h)

Ag is the average silver concentration in permeate (mg/L)

Since the permeate flow rate was not constant over time, numerical integration using equation 5-2 was employed to determine the mass of silver eluted for the period of study. The detailed procedure and results are illustrated in Appendix C.

The cumulative mass of silver eluted from each filter is shown in Figure 5-8.

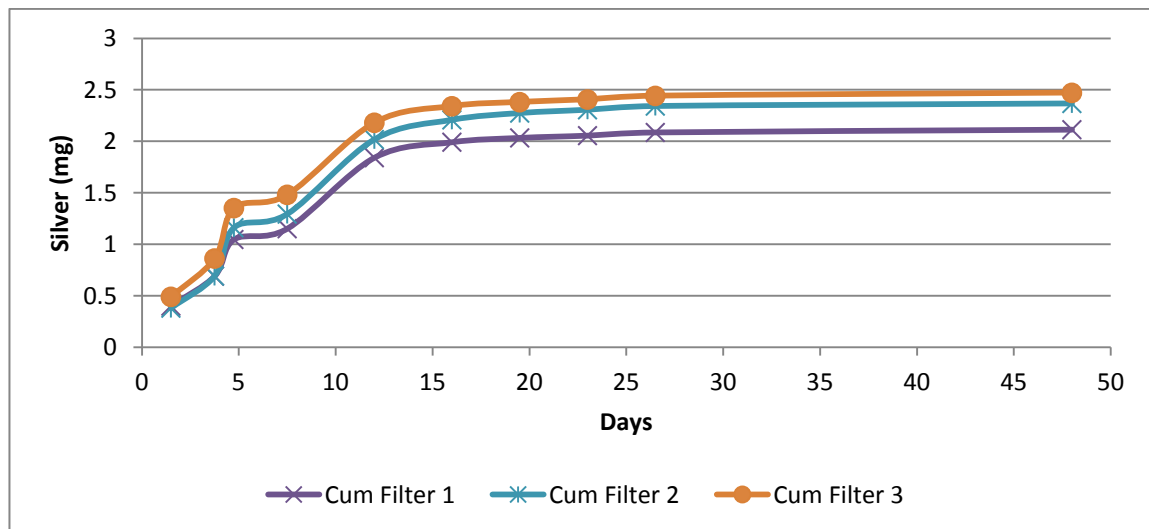


Figure 5- 8: Cumulative amount (mg) of silver leached from each filter over time

The cumulative amount of silver leached increased with time for the three filters. The increase was highest for the period between the start of the experiment up to 13 days. This could be explained by the high concentration gradient between the silver on the filters and the surrounding deionized water and also the generally high fluxes observed.

The total amount of silver eluted from each filter was found to be 2.1 mg (Filter 1), 2.4 mg (Filter 2) and 2.5 mg (Filter 3). For the membrane area employed in this experiment (section 5.4.1.1), the mass of silver eluted was 30.0 per cent for Filter 1, 34.2 per cent for Filter 2 and 35.7 per cent for Filter 3 of the original amount of silver loaded on the membranes (Table 3-3).

In a previous study that investigated silver elution from coated hollow fibre poly acrylonitrile filters, the authors reported that after 30 days of flushing with water, the silver content in the filters was between 21 per cent and 58 per cent. They also observed that the silver content in the hollow fiber decreased with the increase of the permeate effusion time. The decrease was very sharp in the first four days and then gradual thereafter (Yu *et al.* 2003). According to Li and Lenhart (2012) who investigated the dissolution of AgNPs in natural water system, the cumulative concentration of dissolved silver increased with increasing filtration time.

In the current study, the use of ICP-AES to determine the silver concentration could not distinguish between AgNPs or Ag⁺ ions and thus the study could not ascertain whether it was AgNPs or Ag⁺ in permeate.

5.5.3 Long term disinfection performance

5.5.3.1 Effect of *E.coli* on the turbidity of the synthetic feed

The deionized water used to prepare the synthetic feed had an average turbidity of 0.5 NTU. The average turbidity for the *E.coli* stock solution was 3.5 NTU, however, only 0.1 mL of this was used for spiking 20 L of deionized water. The average turbidity of the resulting feed was 0.6 NTU. Therefore, the spiking of the deionized water did not appear

to significantly change the turbidity of the feed and hence would not be expected to form a significant cake layer on the filter and influence its disinfection efficacy.

5.5.3.2 Disinfection efficacy over time

Disinfection performance of the coated membranes over a period of 90 days of continuous operation is shown in Figure 5-9 and Figure 5-10.

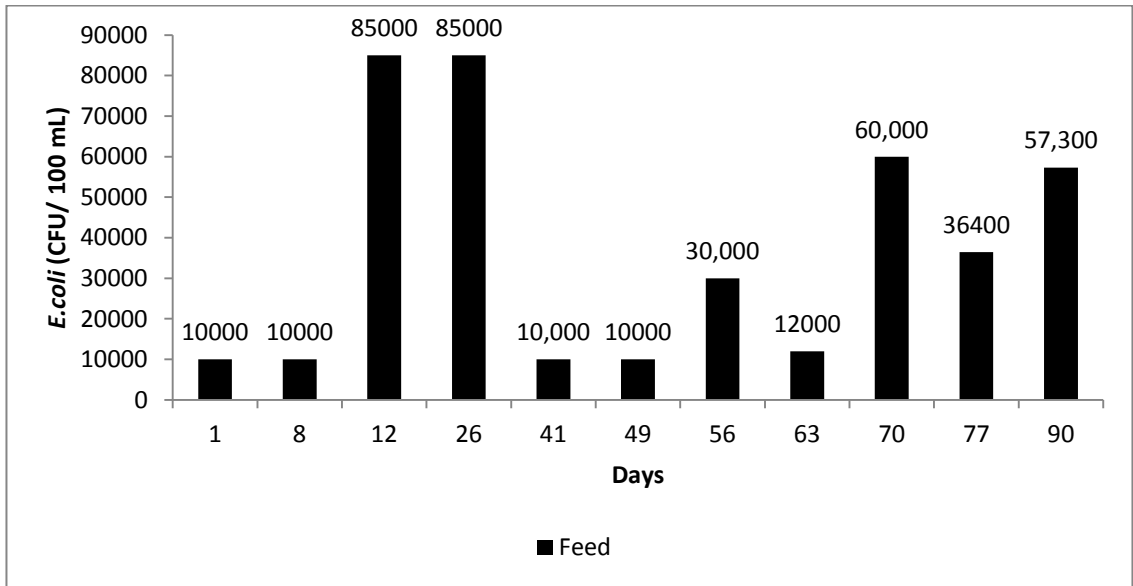


Figure 5- 9: *E.coli* concentration in the synthetic feed over time for 90 days of continuous operation

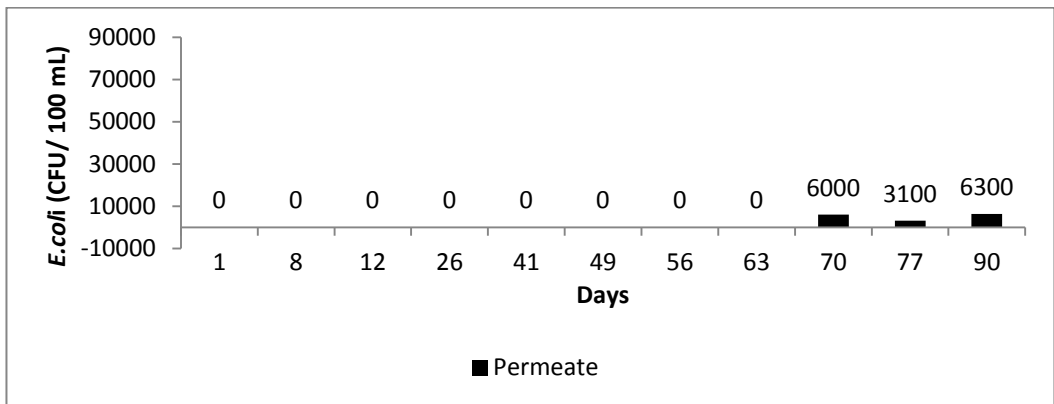


Figure 5- 10: *E.coli* concentration in permeate over time for 90 days of continuous operation

The coated filters achieved 100 per cent removal efficiency of *E.coli* when filtering synthetic feed for a period of 63 days for a range of influent feed concentrations (10 000-85 000 CFU/100 mL). This showed that irrespective of the *E.coli* concentration in the feed, the filter treated water to the expected standards. Thereafter, from the 70th day onwards the removal efficiency dropped to below 100 per cent. This was postulated to be as a result of loss of silver from the filters due to elution and hence decreased amount of silver on the filters. It could also be due to the decreased residual silver in permeate.

The corresponding log removal values for the same period are shown in Figure 5-11.

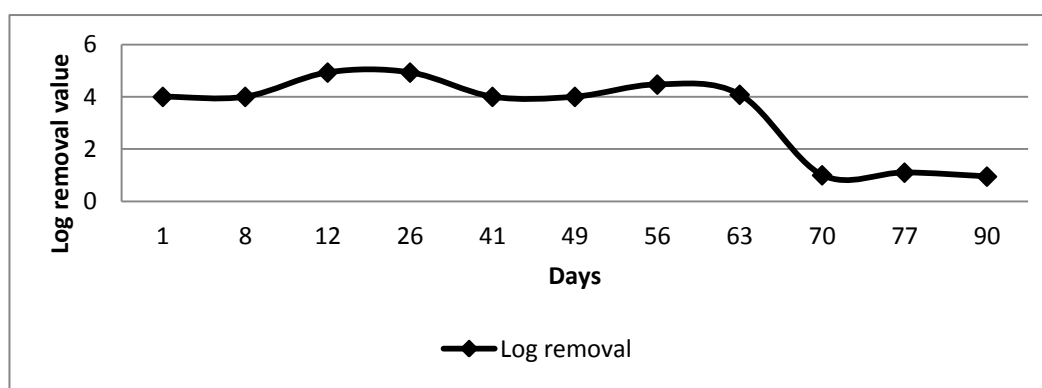


Figure 5- 11: A plot of LRVs for 90 days of continuous operation

The coated filters achieved LRVs of between 4 and 5 for 63 days of continuous operation which is appropriate for municipal water treatment (Baker 2004).

5.5.3.3 Permeate flow rate and flux over time

For completeness, the effect of time on permeate flow rate and flux is shown in Figure 5-12.

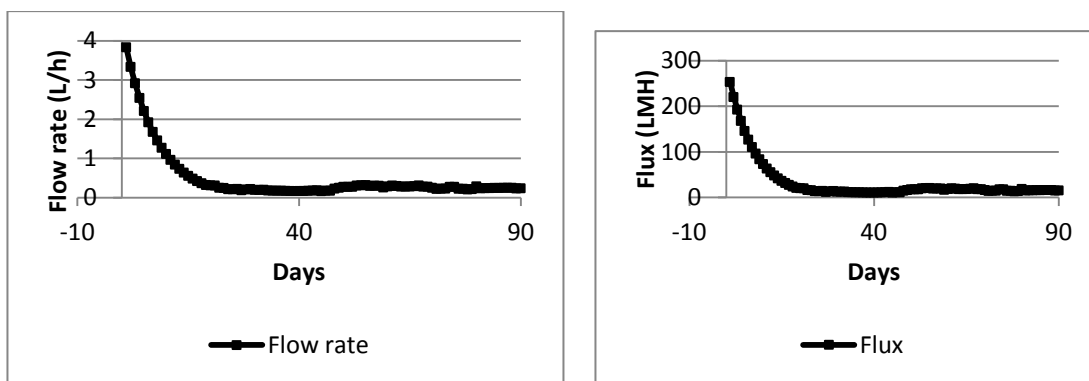


Figure 5- 12: Plots of permeate flow rate and flux from the membrane pack with time

The trends of permeate flow rate and flux were similar to those presented in section 5.5.1. The cause of the flux decline over time could not be explained especially since the synthetic feed employed had an average turbidity of 0.6 NTU and was not expected to cause membrane fouling. This phenomenon was not investigated further since it is beyond the scope of the current study.

5.5.4 Disinfection efficacy versus leaching rate

Figure 5-13, shows the concentration of silver in permeate over time from the long term disinfection rig.

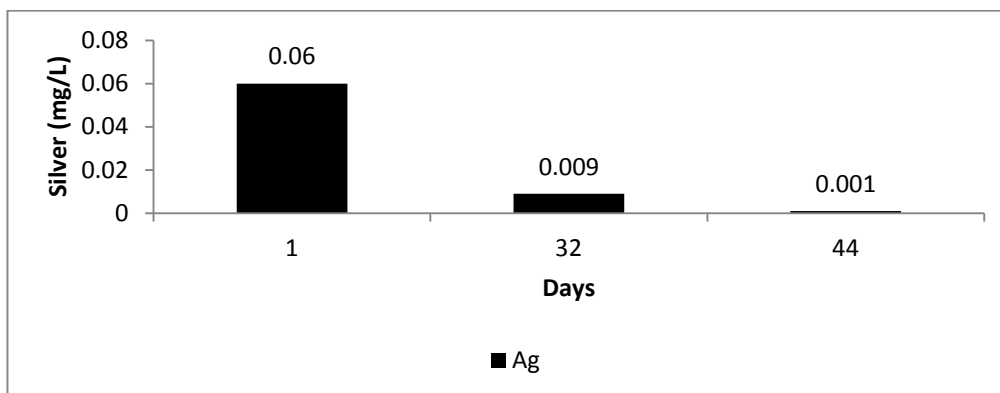


Figure 5- 13: Silver concentration in permeate over time for long term disinfection test

The silver elution decreased steadily with time to 0.001 mg/L after 44 days of operation, thereafter the silver concentration in permeate was below the detection limit of the ICP instrument (0.001 mg/L). The trend of leaching was in agreement with the findings of the study of silver elution presented earlier in section 5.5.2 where the silver concentration reached below 0.001 mg/L after 48 days of continuous operation. The permeate samples in this test were not tested for silver as regularly as done in section 5.5.2. However in terms of the period it took for the silver concentration to drop to below 0.001 mg/L, it was fairly similar. There was a higher concentration of silver in permeate on the first day, although it was still below the WHO guideline level. By the end of 44 days of operation the amount of leaching had decreased to below 0.001 mg/L.

However, it was noted that the disinfection efficacy of the coated filter was good even after the leaching dropped to less than 0.001 mg/L. The filters were able to produce permeate with zero *E.coli* concentration for up to 63 days, however, it is not known what was the silver concentration in permeate when the removal efficiency dropped to less than 100 percent. Therefore, this could mean that even at silver elution concentrations of below 0.001 mg/L, adequate disinfection could be achieved. This was in agreement with Yu et al (2003) who observed significant reduction of silver loading after flushing poly acrylonitrile based hollow fibre with water for 60 days. However it still showed antibacterial activity against *E. coli* and *Staphylococcus aureus*. They attributed the antibacterial activity of the hollow fibre to the silver ion released from the fibre. They proposed that these ions attach to the negatively charged bacteria, thereby prohibiting the growth of bacteria.

It has been reported that leaching of silver from the membranes caused the performance of the membranes to drop over time (Ng *et al.* 2010). A study by Zodrow et al (2009) reported that the silver concentration in the filtrate decreased as more water was filtered. The authors found that after a loss of 10 per cent of the silver loaded on the UF polysulfone membranes, there was a significant reduction in the antimicrobial and antiviral properties of the coated membranes. Therefore leaching reduces the amount of nanosilver on the filter and the disinfection performance of the filter.

The current study proposed, based on the results obtained, that there appeared to be a relationship between the decreases in *E. coli* removal efficiency to less than 100 per cent with the elution of silver from the filters. This further supported the hypothesis that the disinfection may be as a result of the incorporated AgNPs releasing Ag⁺ ions to permeate since the synthetic feed contained no suspended matter that could form a cake layer on the filter and hence aid in separation of *E.coli*. The eluted silver probably acted as a residual disinfectant for the treated water.

5.6 Summary

A major concern over the use of AgNPs in water treatment filters is the possibility of leaching of the nanoparticles and ions into the treated water. This, if occurring at levels above the recommended maximum silver concentration in drinking water, will have detrimental effects on consumers. This study investigated the leaching of silver from the coated filter over a period of 90 days; the dependence of the leaching rate on the flow rate of permeate; the long term disinfection efficacy of the coated filter and the relationship between the leaching of silver and the disinfection efficacy of the filter.

The key findings of this chapter are summarized as follows:

- Silver elution in permeate was less than 0.1 mg/L which meets the recommended specifications for potable water by the WHO.
- The investigation of the effect of permeate flow rate on leaching was not successful, because the flow rate declined with time. This was not expected because deionized water was used as feed. However, it having a turbidity of 0.5 NTU could result in fouling of the membranes over time. It was not investigated further since it is beyond the scope of this study.
- The investigation of silver leaching with time showed that the concentration of silver in permeate generally decreased with time for the three filters due to loss of silver from the filters.
- The long term disinfection test results indicated that the disinfection performance of the coated filters was excellent (100 per cent *E. coli* removal efficiency) for 63

days of continuous filtration after which it dropped. Therefore the system would provide clean and safe water to consumers for at least two months.

- It was noted that despite the decrease of silver concentration in permeate to less than 0.001 mg/L after 44 days of operation, the filters still achieved 100 per cent removal efficiency for 63 days.

Lastly, the slow and continuous release of silver ions in the bacterial environment is an important factor to be considered (Kwaky-Awuah 2008). Therefore the design of membrane filters incorporating nanosilver particles for disinfection should ensure that the particles adhere to the membrane in order to reduce leaching and also to ensure adequate concentration for microbial inactivation.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Overall summary

The challenge of provision of clean and safe drinking water for the world's poorest people requires concerted efforts from different stakeholders in order to address appropriately. One key avenue is the use of POU water treatment systems such as the RRWTS, as an interim solution. The use of POU systems is a widely accepted idea that has demonstrated potential in the reduction of water borne diseases and enhancement of the health of the affected people.

This study endeavoured to investigate the use of AgNPs in conjunction with WFMF membranes as an appropriate POU system for water treatment for people living in rural areas of developing nations. These people often fetch water from rivers and use it without treatment or using other costly methods. The aim of this study was to investigate the incorporation of AgNPs on the WFMF membrane in order to increase its disinfection efficacy. These membranes were used to fabricate flat sheet modules for potable water treatment and this study focused mainly on the disinfection aspect.

The coated filter was extensively characterized and used to carry out the investigations. The important aspects that were investigated include: the filtration and disinfection efficacy against *E.coli* bacteria; the leaching of silver with time of filter use and its effect on disinfection performance. Synthetic feed was mainly used although the results obtained were similar to those obtained using river water.

The main investigations carried out and the significant findings obtained are summaries as follows:

6.1.1 Filtration and disinfection effectiveness

The coated membranes achieved 100 per cent *E.coli* removal for a period of 63 days of continuous filtration of synthetic feed (10 000 – 85 000 CFU/100 mL). The LRVs were between four and five for the 63 days, which is acceptable in municipal water treatment.

The separation of suspended matter was also satisfactory with treated water having turbidities less than 1 NTU for influent concentrations of 40– 700 NTU.

6.1.2 Effect of feed *E.coli* concentration on disinfection performance

The range of *E.coli* concentration employed was 2 500– 85 000 CFU/100 mL, which adequately represented the amounts present in river water. It was shown that the coated filter was effective in this range of feed *E.coli* for 63 days of continuous filtration, achieving 100 per cent removal efficiency irrespective of the feed concentration.

6.1.3 Loss of silver from the filters with time of use

A major challenge in the development of water filtration systems incorporating metallic nanoparticles is the control of leaching of related metals to treated water at levels harmful to health. This study developed a system having silver leaching well below the maximum accepted value of 0.1 mg/L. Therefore the system can be used for potable water treatment without risk to human health resulting from high silver concentrations in treated water.

6.1.4 Effect of silver elution on disinfection efficacy

The mechanism of disinfection of the coated filter was proposed to be due to size exclusion coupled with the deactivation of *E.coli* using the AgNPs attached to the membrane. This ideally meant that as silver leached from the filter, there was substantial loss in disinfection efficacy. It was however noted that the removal efficiency remained 100 per cent for 63 days despite the decreasing silver leaching even after the leaching was below 0.001 mg/L after 44 days.

6.1.5 Overall quality of treated water

The results indicated that the filter treated both river water and synthetic feed water to levels that met the internationally accepted standards with regards to physical and microbiological quality aspects. The coated WFMF membranes demonstrated good

filtration and disinfection efficacy, both in one treatment unit, making it a useful alternative small scale water treatment system. The chemicals employed in the synthesis of the AgNPs are readily available and affordable. Moreover, the preparation process adopted is simple to perform and is effective. This filter therefore has the potential for widespread use in water treatment applications for people in rural areas of developing economies. Therefore, the improvement on the RRWTS by incorporation of AgNPs resulted in a unit that can generate a product that is free of suspended solids, and microbiological contamination (*E. coli*) for at least two months.

6.2 Limitations of the study, recommendations and future work

The following limitations were identified and recommendations for future work are proposed.

6.2.1 Silver loading on the membrane

The silver loading adopted for this study was based on literature. The variation of nanosilver loading on the fabric and its effect on the disinfection and silver elution was therefore not investigated. In addition, the ratio of reactants used in the chemical reduction was also selected based on literature. Future work also needs to be conducted in order to optimize the silver loading versus leaching rate.

6.2.2 Use of *E.coli* as an indicator organism

The study employed *E.coli* (Gram- negative bacteria) as the test organism. It was adopted as an indicator of faecal contamination of water. Faecal contamination is common in rural areas where sanitation facilities are still rudimentary, leading to contamination of water sources by human faeces. The results might be different using other microorganisms under different conditions; therefore, the results obtained in this study can be used as a model for other microorganisms. Future work should be done to

investigate the performance of the system using Gram-positive bacteria and other microorganisms.

6.2.3 Antifouling capability

The results of the Sessile drop contact angle investigation showed that the coating with AgNPs increased the membranes hydrophilicity. This has been suggested by other researchers to decrease the membrane's potential for fouling, however, this was not investigated in this study. Future work should be done to investigate the effect of the coating of the WFMF membranes on fouling mitigation.

6.2.4 Loss of disinfection efficacy

A major shortcoming that was noted during this study was the loss of silver from the filter which compromised the disinfection efficacy after 63 days of continuous filtration. This indicated the lifespan of the filter was limited by the silver elution, which coincidentally was inevitable for disinfection to be achieved. Future work should be done to investigate how the lifespan can be increased and how silver elution can be controlled.

6.2.5 Effect of flow rate on silver leaching

An unusual phenomenon was observed during the investigation of the pure water flux of the coated membranes presented in Chapters Three and Five. The fluxes of the filters decreased with time despite using deionized water as feed (however, it had a turbidity of 0.5 NTU which may cause fouling over time). The flux decline could have been due to the silver coating or membrane fouling. This was repeatable but unexpected; however, it was not investigated further because it is beyond the scope of this study. Future studies should be conducted to investigate this phenomenon.

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APPENDIX A: SILVER CONCENTRATION IN THE FILTERS

Acid digestion of the coated membrane and determination of the silver content

Determination of the silver content in the membrane was done following a method found in literature (Kim, J *et al.* 2009). Qualitative elemental analysis was conducted using ICP-AES. The test was done in triplicate using three different samples of the coated membrane. The weights of media, concentration of silver and total weight of silver in media were measured as follows:

Weight of media

Before beginning the experiments, samples of the coated membrane were dried at 70° C for 1 hour in an oven, and cooled to room temperature. Then, dry weights of the media samples were measured.

Acid digestion

The dried samples were placed in separate beakers each containing a 50: 50 mixture of 55 per cent nitric acid and deionized water. The beakers were heated using a hot plate with continuous magnetic stirring until the mixture boiled and the fabrics were disintegrated. The mixture was thereafter cooled in a water bath at room temperature and filtered through a Millipore membrane filter (0.45 µm). Deionized water was added to the filtrate to a total volume of 50 mL in order to make up for the amount evaporated during heating. The solution was analyzed for silver using ICP-AES (Dankovich and Gray 2011).

Total weight of silver in media

The concentration (mg/L) of silver in solution used for coating was converted to mass (mg) of silver using equation 3-2.

APPENDIX B: PURE WATER FLUX

Statistical determination of the difference in pure water flux between the uncoated and coated membranes

The t-test for independent samples was used with the objective of testing the significance of the difference between their means.

Table B- 1: Data for the pure water fluxes (LMH) of the uncoated and coated filters

TMP (Pa)	2453	2354	2256	2158	2060	1864
Uncoated, average flux (LMH)	140	118	120	112	101	97
Coated, average flux (LMH)	281	238	192	154	126	112

The uncoated is called sample 1 and the coated sample 2

Mean of sample 1 (X_1) = 115, mean of sample 2 (X_2) = 184

Standard deviation of sample 1, S_1 =14, while that of sample 2, S_2 =60

Variance of sample 1, S_1^2 = 196, variance of sample 2, S_2^2 = 3600

Pooled variance is given by the equation (B-1)

$$S_{\text{pooled}}^2 = \frac{S_1^2(n_1-1) + S_2^2(n_2-1)}{n_1+n_2-2} \quad (\text{B-1})$$

Where,

n_1 = number of items in sample 1 (6)

n_2 = number of items in sample 2 (6)

The calculated S_{pooled} =1898

The t value for a one tailed test is calculated using the equation B-2

$$t_{(n_1+n_2-2)} = \frac{X_1 - X_2}{\sqrt{S_{\text{pooled}}^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}} \quad (\text{B-2})$$

The t value (t_{10}) was calculated from equation (B-2) to be -1.94

The level of significance, α , was taken to be 0.05

The t value from the Table B-2, at t_{10} and $\alpha = 0.05$ is -1.812

Since the t calculated is greater than the t value from the tables, therefore there was a significant difference in the means of the fluxes obtained from the uncoated and coated filters.

Table B-2: A table of one-tailed t -values for specified levels of significance and degrees of freedom (Remenyi *et al.* 2009)

$\backslash \alpha$	0.1	0.05	0.025	0.01	0.005	0.0025	0.001	$\backslash \alpha$
1	3.077685	6.313749	12.70615	31.82096	63.6559	127.3211	318.2888	1
2	1.885619	2.919987	4.302656	6.964547	9.924988	14.08916	22.32846	2
3	1.637745	2.353363	3.182449	4.540707	5.840848	7.4532	10.21428	3
4	1.533206	2.131846	2.776451	3.746936	4.60408	5.59754	7.17293	4
5	1.475885	2.015049	2.570578	3.36493	4.032117	4.773319	5.893526	5
6	1.439755	1.943181	2.446914	3.142668	3.707428	4.316826	5.207548	6
7	1.414924	1.894578	2.364623	2.997949	3.499481	4.029353	4.785252	7
8	1.396816	1.859548	2.306006	2.896468	3.355381	3.832538	4.500762	8
9	1.383029	1.833114	2.262159	2.821434	3.249843	3.689638	4.29689	9
10	1.372184	1.812462	2.228139	2.763772	3.169262	3.581372	4.143658	10
11	1.36343	1.795884	2.200986	2.718079	3.105815	3.496607	4.024769	11
12	1.356218	1.782287	2.178813	2.68099	3.054538	3.428451	3.929599	12
13	1.350172	1.770932	2.160368	2.650304	3.012283	3.372479	3.852037	13
14	1.345031	1.761309	2.144789	2.624492	2.976849	3.325695	3.787427	14
15	1.340605	1.753051	2.131451	2.602483	2.946726	3.286041	3.732857	15
16	1.336757	1.745884	2.119905	2.583492	2.920788	3.251989	3.686146	16
17	1.333379	1.739606	2.109819	2.56694	2.898232	3.222449	3.645764	17
18	1.330391	1.734063	2.100924	2.552379	2.878442	3.196583	3.610476	18
19	1.327728	1.729131	2.093025	2.539482	2.860943	3.1737	3.579335	19
20	1.325341	1.724718	2.085962	2.527977	2.845336	3.1534	3.551831	20
21	1.323187	1.720744	2.079614	2.517645	2.831366	3.13521	3.527093	21
22	1.321237	1.717144	2.073875	2.508323	2.818761	3.118839	3.504974	22

APPENDIX C: RAW DATA

a. Filtration performance of the uncoated and coated filters

Table C- 1: Results from filtration of feed with a turbidity of 700 NTU

Time (min)	<i>Uncoated filters</i>	<i>Coated filters</i>
0	20	4.5
10	10	1.23
20	7.52	1.53
30	2.24	1.67
40	2.73	1.52
50	2.44	0.87

Table C- 2: Results from filtration of feed with a turbidity of 100 NTU

Time (min)	<i>Uncoated filters</i>	<i>Coated filters</i>
0	4.52	5.53
30	1.92	1.2
60	0.73	0.57
90	0.48	0.56
120	0.65	0.64
150	0.52	0.44

Table C- 3: Results from filtration of feed with a turbidity of 40 NTU

Time (min)	<i>Uncoated filters</i>	<i>Coated filters</i>
0	1.38	0.69
10	0.67	0.92
20	0.61	0.75
30	0.52	0.81
40	0.74	0.53
50	0.69	0.48

b. Silver elution from filters

The mass of silver (mg) eluted from the filters was calculated using the integral of time (h) with the silver concentration (mg/L) and the permeate flow rate (L/h) over the period of study (equation 5-2). The numerical integration was used because the permeate flow rate was not constant over time. Average permeate flow rate for given periods of time was used.

Table C- 4: Spreadsheet for calculating the mass of silver eluted

t(h)	Q(L/h)	Ag(mg/L)	Δt	Average Q	Average Ag	Mass (mg)
24	1.25	0.017				
24	1.26	0.016				
24	1.27	0.019				
48	1.05	0.012	24	1.15	0.0145	0.4002
48	1.08	0.012	24	1.14	0.014	0.38304
48	1.075	0.016	24	1.17	0.0175	0.4914
72	0.89	0.013	24	0.97	0.0125	0.291
72	0.9375	0.014	24	1	0.013	0.312
72	0.925	0.015	24	1	0.0155	0.372
108	0.758	0.011	36	0.824	0.012	0.355968
108	0.8125	0.016	36	0.87	0.015	0.4698
108	0.795	0.017	36	0.86	0.016	0.49536
120	0.646	0.014	12	0.7	0.0125	0.105
120	0.704	0.013	12	0.76	0.0145	0.13224
120	0.688	0.012	12	0.74	0.0145	0.12876
240	0.279	0.011	120	0.46	0.0125	0.69
240	0.345	0.011	120	0.525	0.0115	0.7245
240	0.325	0.011	120	0.506	0.0115	0.69828
336	0.145	0.004	96	0.212	0.0075	0.15264
336	0.195	0.004	96	0.27	0.0075	0.1944
336	0.179	0.002	96	0.25	0.0065	0.156
432	0.075	0.004	96	0.11	0.004	0.04224
432	0.108	0.005	96	0.152	0.0045	0.065664
432	0.096	0.004	96	0.1375	0.003	0.0396
504	0.0625	0.005	72	0.06875	0.0045	0.022275
504	0.0938	0.004	72	0.1	0.0045	0.0324
504	0.108	0.003	72	0.102	0.0035	0.025704
600	0.069	0.005	96	0.0658	0.005	0.031584
600	0.075	0.005	96	0.0844	0.0045	0.036461
600	0.106	0.004	96	0.107	0.0035	0.035952
672	0.067	0.006	72	0.068	0.0055	0.026928
672	0.0645	0.005	72	0.071	0.005	0.02556
672	0.1	0.004	72	0.103	0.004	0.029664
1152	0.042	0.001	480	0.0545	0.0035	0.09156
1152	0.039	0.001	480	0.052	0.003	0.07488
1152	0.072	0.007	480	0.086	0.0055	0.22704

The results are shown in Tables C-5 and C-6.

Table C- 5: Concentration of silver (mg/L) eluted from filters with time

Days	1	2	3	4	5	10	14	18	21	25	28	48
Filter 1	0.017	0.012	0.013	0.011	0.014	0.011	0.004	0.004	0.005	0.005	0.006	0.001
Filter 2	0.016	0.012	0.014	0.016	0.013	0.011	0.004	0.005	0.004	0.005	0.005	0.001
Filter 3	0.019	0.016	0.015	0.017	0.012	0.011	0.002	0.004	0.003	0.004	0.004	0.007

Table C- 6: Mass of silver eluted and cumulative mass of silver (mg) eluted from the three filters with time

Days	2	4	5	8	10	16	20	23	26.5	38
Filter 1	0.4	0.291	0.356	0.105	0.69	0.15	0.042	0.022	0.031	0.027
Filter 2	0.38	0.312	0.47	0.132	0.725	0.19	0.066	0.032	0.036	0.025
Filter 3	0.49	0.372	0.49	0.129	0.7	0.16	0.04	0.0257	0.035	0.03
Cum Filter 1	0.4	0.691	1.047	1.152	1.842	1.992	2.034	2.056	2.087	2.114
Cum Filter 2	0.38	0.692	1.162	1.294	2.019	2.209	2.275	2.307	2.343	2.368
Cum Filter 3	0.49	0.862	1.352	1.481	2.181	2.341	2.381	2.4067	2.4417	2.4717

c. Long term disinfection performance

Table C- 7: *E.coli* concentration (CFU/ 100 mL) in feed and permeate with time

Days	1	8	12	26	41	49	56	63	70	77	90
Feed	10 000	10 000	85 000	85 000	10 000	10 000	30 000	12 000	60 000	36 400	57 300
Permeate	0	0	0	0	0	0	0	0	6 000	3 100	6 300