Comparison of Four Methods to Assess Silver Release from Nano Impregnated Reverse Osmosis Membranes

by

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ABSTRACT

With the application of reverse osmosis (RO) membranes in the wastewater treatment and seawater desalination, the limitation of flux and fouling problems of RO have gained more attention from researchers. Because of the tunable structure and physicochemical properties of nanomaterials, it is a suitable material that can be used to incorporate with RO to change the membrane performances. Silver is a biocidal, which has been used in a variety of consumer products. Recent studies showed that fabricating silver nanoparticles (AgNPs) on membrane surfaces can mitigate the biofouling problem on the membrane. Studies have shown that Ag released from the membrane in the form of either Ag ions or AgNP will accelerate the antimicrobial activity of the membrane. However, the silver release from the membrane will lower the silver loading on the membrane, which will eventually shorten the antimicrobial activity lifetime of the membrane. Therefore, the silver leaching amount is a crucial parameter that needs to be determined for every type of Ag composite membrane.

This study is attempting to compare four different silver leaching test methods, to study the silver leaching potential of the silver impregnated membranes, conducting the advantages and disadvantages of the leaching methods. An *In-situ* reduction Ag loaded RO membrane was examined in this study. A custom water jet test was established to create a high-velocity water flow to test the silver leaching from the nanocomposite membrane in a relative extreme environment. The batch leaching test was examined as the most common leaching test method for the silver composite membrane. The cross-flow filtration and dead-end test were also examined to compare the silver leaching amounts.

The silver coated membrane used in this experiment has an initial silver loading of 2.0± 0.51 ug/cm^2. The mass balance was conducted for all of the leaching tests. For the batch test, water jet test, and dead-end filtration, the mass balances are all within 100±25%, which is acceptable in this experiment because of the variance of the initial silver loading on the membranes. A bad silver

mass balance was observed at cross-flow filtration. Both of AgNP and Ag ions leached in the solution was examined in this experiment. The concentration of total silver leaching into solutions from the four leaching tests are all below the Secondary Drinking Water Standard for silver which is 100 ppb. The cross-flow test is the most aggressive leaching method, which has more than 80% of silver leached from the membrane after 50 hours of the test. The water jet (54 ± 6.9% of silver remaining) can cause higher silver leaching than batch test (85 ± 1.2% of silver remaining) in one-hour, and it can also cause both AgNP and Ag ions leaching from the membrane, which is closer to the leaching condition in the cross-flow test.

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TABLE OF CONTENTS

CHAPTER

CHAPTER Page

CHAPTER Page

LIST OF TABLES

Table Page

LIST OF FIGURES

ACRONYMS

RO	Reverse Osmosis
AgNP/AgNPs	Silver Nanoparticles
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
FO	Forward Osmosis
TiO_2	Titanium Dioxide
SiO_2	Silicon Dioxide
Au	Gold
LBL	Layer-by-layer (membrane fabrication method)
PDA	Polydopamine
PVA	Polyvinyl Alcohol
TA	Tannic Acid
TFC	Thin-film-composite (membrane)
PEI	Polyethylenimine
SEM	Scanning Electron Microscopy
BSE	Back-scatter Detector
EDX	Energy-dispersive X-ray Spectroscopy
$AgNO_3$	Silver Nitrate
$NaBH_4$	Sodium Hydroborate
NSDWs	Secondary Drinking Water Standards
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Application of Silver in Water Treatment

Water scarcity remains as one of the most challenging problems that humans have faced. In order to solve this problem, some new water treatment technologies have been developed over the last decade. Silver as a biocide, has been immobilized in some water treatment devices to control the transport and growth of microorganisms. For example, silver was added in some point-of-use (POU) water treatment elements to prevent the formation of biofilms as a secondary disinfectant. Table 1.1 shows some of the POU that can be found in the market which contain silver. Recently, loading silver nanoparticles on membranes' surfaces was proved as an effective method to reduce the biofouling on the membrane.

Table 1.1 List of Point-of-use Products with Silver Attached

Name	Function of Products	Silver Function	Link
Katadyn Pocket Water Filter	Filtrating water in outdoor enthusiasts	Against the bacteria and protozoa in the water	https://www.amazon.com/Katadyn-Pocket-Water-Filter/dp/B002IAH85A
Pentek Silvered Carbon Block	Replaced element of potable carbon block water filter; Used to remove fine particles, microorganisms, and a broad array of organics	Reduce microorganisms in the water	https://www.amazon.com/Pentek-PENTEK-SCBC-10-Silvered-Carbon-Block/dp/B003VT3R6Q/ref=sr_1_15?s=home-garden&ie=UTF8&qid=1510534690&sr=1-15&keywords=carbon+block+filter+silver
Doulton Super Sterasyl Ceramic Gravity Filter Candle	Replaced element of potable ceramic water filter; Used to reduce suspended solids, pathogenic bacteria, organic chemicals, and improve taste and odor	Reduce pathogenic bacteria	https://www.amazon.com/Doulton-W9121709-10-Inch-Sterasyl-Ceramic/dp/B009EQNSGE/ref=sr_1_27?s=home-garden&ie=UTF8&qid=1510534579&sr=1-27&keywords=carbon+block+filter+silver

NSF International is an organization that is developing public health standards and certification programs to help protect the world's food, water, consumer products and environment. As the application of the silver attached POU water treatment elements, the potential silver release from the water treatment elements becomes a public health concern. For the further application of silver attached water treatment devices, studying the silver leaching from the silver impregnated products is necessary for NSF International.

1.2 Silver Impregnated Reverse Osmosis Membrane

1.2.1 Introduction of Membrane

Membrane filtration is one of the most useful water treatment technologies, and it has been used for water treatment, wastewater treatment, point of use water treatment, and seawater desalination etc. The most commonly used membranes in water treatment are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Generally, based on physiochemical mechanisms of the membrane being used, NF and RO membranes are characterized under reverse osmosis; MF and UF are characterized under membrane filtration.

MF and UF are used to separate suspended particles from the liquid phase. The predominant removal mechanism for membrane filtration is size exclusion. Reverse osmosis is a process involving water diffusing through a semipermeable membrane under an external pressure to leave dissolved solutes on the feed side. Therefore, nanofiltration and reverse osmosis are used to decrease the solutes concentration of the feed water. Reverse osmosis is commonly used in the desalination of ocean or brackish water, advanced treatment for water reuse, softening, natural organic matter (NOM) removal, and specific contaminant removal[1].

1.2.2 Nano-composite Reverse Osmosis Membrane

Reverse osmosis is a process that using external pressure to overcome the osmosis pressure of a semipermeable membrane, to force the water molecules penetrate through the membrane from rejection side to filtrate side. High pressure is needed in the reverse osmosis process to overcome the water diffusion caused by osmosis pressure, therefore, the membrane properties are critical factors that will determine the performance of the reverse osmosis process. The limited flux, salt rejection, and fouling are the most common challenges the application of reverse osmosis faces[2]. Nanomaterials are defined as materials in nanoscale or materials that are generated by nanotechnologies. Because of the tunable structure and physicochemical properties of nanomaterials, it is a suitable material that can be used to incorporate with RO to change the membrane performances[2, 3]. Different types of nanomaterials are used to be modified in the RO membrane. Generally, metal oxide nanoparticles (e.g. TiO_2, SiO_2), metal particles (e.g. Ag, Au), carbon-based nanomaterials (e.g. graphene oxide, carbon nanotubes), and aluminasilicate-based nanomaterials (e.g. zeolite) are the predominant nanomaterials that have been used in Nano-composite membranes[3]. In addition, graphene, carbon nanotubes, zeolites are generally used to improve the membrane permeability[4-6]; silicon dioxide can improve the hydrophilicity of the membrane surface; Ag nanoparticles, Au nanoparticles, and titanium dioxide have the ability to mitigate the fouling of the membrane[7].

1.2.3 Silver Impregnated Reverse Osmosis Membrane

Silver is known as a material that has high toxic to variety of microorganisms. Variety pathways can be used for silver to kill microbes. Silver ions can react with disulfide or enzymes or DNA to disturb the normal metabolic process of the microorganims[8]. Also, the contacting of Ag nanoparticles (AgNPs) and cells can generate Ag ions which will also contribute to the disinfect reaction[9]. AgNPs in the range of 1 -10 nm can attach to the cells' membranes to disturb the function of cell membranes; it can also penetrate in the microbes to cause further damage[10].

A significant number of studies investigated different methods to loading silver on the polymeric layer of the membrane. Generally, it can be characterized into In-situ reduction coating and layer-by-layer (LBL) self-assembly coating. In-situ reduction is using Ag^+ solutions to rinse the membrane surface attached to Ag^+ and applies a reductant to reduce the Ag^+ to Ag (0) to form a nanoparticle layer on the membrane. Layer-by-layer is based on the electrostatic interactions and van der Waals forces between oppositely charged polyelectrolytes to embed silver into the membrane. Both of the coating methods were verified as effective methods to loading silver on the polymeric membrane. Liu et al. reported that excellent antibacterial properties against both on Gram-positive and Gram-negative bacteria have been shown in the AgNP composite nanofiltration (NF) and forward osmosis (FO) membrane prepared by the LBL assembly method[11]. Yang et al. using polydopamine (PDA) to reduce Ag^+ on the membrane to form AgNP on the RO membrane, showed a 62.7 % reduction of viable *B. subtilis* and 42.4 % for *E. coli* compared to the silver-free control membranes[12].

The silver impregnated RO membrane is remaining a lab-scale study. There are some concerns about the application of silver coated membranes. The silver release from the membrane in the form of both Ag ions and AgNP will accelerate the antimicrobial activity of the membrane, on the other hand, the silver release from the membrane will lower the silver loading on the membrane which will eventually shorten the antimicrobial activity lifetime of the membrane. Moreover, the health concern caused by the silver release is one of the issues that NSF International concerned. Therefore, the silver leaching amount is a crucial parameter that needs to be determined for every type of Ag composite membrane.

1.3 Silver Release Experiment in Recent Studies

Silver leaching was examined in some silver composite membrane studies. Ag leaching tests for Ag composite RO membrane that have been done are summarized in Table 1.1. Batch test is the most common leaching test method for Ag composite membranes, as shown on Table 1.1. Batch test used in leaching test is generally designed to immerge a piece of nanocomposite membrane in certain volumes of water solutions. Soaking the membrane in the states for several days. The method is used by either shaking the membrane on an orbit shaker or keeping it in a static state. As batch test is easy to set-up and a reproducible method, it is regarded as the basic leaching test for nanocomposite membranes. However, the limitations of the batch test are obvious. The batch test can not represent the water treatment process in water treatment systems, which means the leaching results of batch test do not represent the Ag leaching in actuality. Moreover, the batch tests used for nanocomposite membrane leaching test do not have a standard protocol. Membrane area to extraction water volume ratios, shaking states, extraction time, and chemical composition of extraction solutions may vary for each test, as shown in Table 1.2. Therefore, the batch test should not be used as the only nanocomposite membrane leaching test method. More leaching test methods should be examined to compare with the batch test.

Table 1.2 Summary of Silver Leaching Tests of the Ag Composite RO Membrane

Coating methods and Membrane type	Type of Leaching Test	Description of Leaching Test	Reference
LBL & RO	Batch Test	Incubated 1 inch coupon in 20 mL DI water on a rotating platform for 14 days, DI water changed every 24 hours	[13]
In-situ reduction coating Ag-zeolite & RO	Batch Test	2.2 cm^2 membrane incubated in 3 mL NaCl solutions (10, 25, 154 mM (0.9% w/w)) on a orbit shaker for 24 hours	[14]
In-situ Reduction & RO	Batch Test	3.8 cm2 membrane coupon incubated at 20 mL DI water and agitated at 200 rpm, DI water changed every 24h	[12]
Ag charged PP	Batch Test	2 cm^2 membrane placed in 500 mL solution which contains 5mM EDTA, 50 mg/L ferrous sulfate, with pH adjusted to 11, shaken for 212 h	[15]
Ag immerged PDA and Ag immerged PVA	Batch Test	2 cm^2 membrane immersed in 1.5 mL 154 mM NaCl solution and shaken at about 90 rpm for 24 hours	[16]
TA-Fe-PEI/Ag-modified membranes	Batch Test	1 cm2 membrane immersed into 40 mL $NaHCO_3$ solution (pH8.2, which is similar to the pH of seawater), static immersed for 6 days	[7]
AgNP coated TFC	Batch Test & Flow-through Test	Batch Test: 1 cm2 membrane incubated at 20 mL DI water and shaken at 100 rpm for 14 days, DI water changed every 24 h Flow-through Test: Driving DI water through the membrane at a constant pressure of 300 psi	[8]
AgNP In-situ Reduction & RO	Batch Test	3.8 cm2 membrane coupon incubated at 10 mL of 5 mM NaHCO3 solution (pH 8.3), shaken for 7 days	[17]

1.4 Scope of Thesis

This study compares different silver leaching test methods for nanocomposite membranes. An In-situ reduction Ag loaded RO membrane was examined in this study. The leaching test methods used in this study include batch test, dead-end filtration test, cross-flow filtration test, and a custom water jet test. Batch test was done by following the NSF/ANSI 61, which was used to reproduce the most common leaching test compared to other leaching tests. Dead-end filtration and cross-flow filtration were chosen because the filtration processes that they had were similar with applying the membrane in water treatment systems. The custom water jet test tried to build a high velocity water flow to create a relative extreme environment to test the silver leaching from the nanocomposite membrane.

The objectives of this study are as follows:

- Develop four membrane leaching methods for silver coated RO membranes
- Apply in-situ silver impregnation method to load RO membrane
- Analyze silver on membranes and released into solution; conduct silver mass balance
- Determine the Ag leaching potential
- Compare the four different leaching methods, and rank based upon
    - percentage of Ag leaching in total Ag loading
    - easiest to replicate the leaching test
    - cost-effectiveness

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials and Chemicals

Four different extraction solutions were used to test silver leaching, as shown in Table 2.1. Nano-pure water (prepared by Barnstead™ GenPure™ xCAD Plus Ultrapure Water Purification System), pH 5 solution without chloride, pH 5 solution with chloride, and pH 10 solution. Nano-pure water was used as the basic extraction solution for all the leaching test methods, which also used as blank experiment to compare with other chemical solutions. The pH 5 with chloride and pH 10 solutions were prepared according to NSF/ANSI 61. As chloride can form colloids with Ag ions, the pH 5 solution without chloride was also prepared to test the Ag leaching.

Table 2.1 Chemical Composition of Extraction Solutions

Chemical Compositions	pH5 (with chloride) *	pH5 (without chloride)	pH10*	Nano-pure Water
#1	2.5mM NaH_2PO_4	2.5mM NaH_2PO_4	5mM NaOH	—
#2	1mM $MgCl_2$	1mM $MgSO_4$	2.5mM $Na_2B_4O_7$	—

The student's T-test was used in the data analysis in this study. The T-test formulas used for this study is for two-samples with assuming different variances. The t statistic is calculated as follow:

$$t = \frac{\overline{x_1} - \overline{x_2}}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

where $\bar{x}$ is the mean of the sample, s is standard deviation of the sample, and n is the sample size. The degree of freedom is calculated as follow:

$$d_f = \frac{(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2})^2}{\frac{(\frac{s_1^2}{n_1})^2}{(n_1 - 1)} + \frac{(\frac{s_{12}^2}{n_2})^2}{(n_2 - 1)}}$$

2.2 Membrane Fabrication

2.2.1 Membrane Coupon Coating (Coating method 1)

This membrane coupon coating procedure was provided by Ben-Sasson et al[17]. A 50 mL dead-end filtration cell (Amicon® Stirred Cell 50 mL, UFSC05001) was used in this coating process. 3mM $AgNO_3$ solution was used as silver source and 3mM $NaBH_4$ was used as reductant in this coating procedure. First, prepared a membrane coupon which diameter is 4.45 cm, and inserted it into the bottom of the dead-end cell; then poured $AgNO_3$ solution into the dead-end house and stirred for 10 minutes; discarded the $AgNO_3$ solution after 10 minutes stirring and only left a thin layer of solution on the membrane; then poured $NaBH_4$ solution into the house and stirred for 5 minutes; discarded all of the $NaBH_4$ solution and rinsed the membrane by Nano-pure water for 10 seconds; carefully removed the membrane from the cell, stored it in the refrigerator and keep it wet.

2.2.2 Spiral Wound Coating (Coating method 2)

The *In-situ* reduction Ag coated membrane used in this expriment was prepared from Spiral Wound Reverse Osmosis membrane (Applied Membrane Inc. M-T1812A24, CA, USA). This coating method was adapted from the membrane coupon coating procedure provided by Ben-Sasson et al.[17] The whole coating procedure was finished in a recirculating membrane filtration system, with the concentrate line half open and filtrate line closed. The feed pressure was maintained at 8 psi, and feed flow rate was around 945 mL/min while the system operating. Before applying the coating solutions to the system, the membrane was rinsed with 1 L Nano-pure water for 10 minutes. After draining all the Nano-pure water out of the system, 1 L 3mM AgNO3 solution was recirculated in the system for 10 minutes. After 10 minutes, AgNO3 solution was also drained from the system, then 1 L 3mM NaBH4 solution was applied, it acted as a reductant in the system and recirculated for 5 minutes. The membrane was flushed for 1 minute by 1 L Nano-pure water after the recirculation of all the solutions were finished. The membrane would be ready after the 1 minute of flushing, and the membrane was sealed to keep it wet and it was stored in refrigerator for further use.

2.3 Membrane Characterization

2.3.1 Membrane Transportation Properties

The membrane transportation properties were measured in dead-end filtration system. The transportation property of the reverse osmosis membrane was measured by a stainless steel dead-end filtration cell (Sterlitech HP4750 Stirred Cell). The pressure was controlled at 90 psi. And the flux was measured every minute along 4 hours. The flux of pristine RO was measured only by using nano-pure water; for *In-situ* Ag coated RO, the flux was measured by using nano-pure water, the pH 5 solution, the pH 5 solution with chloride, and the pH 10 solution (as shown in Table 2.1).

2.3.2 Quantification of Ag Loading on Membrane

Different methods were used to quantify the Ag loading on Ag-composite membrane. Three different digestion methods were used to compare the ability of dissolving the Ag from the membrane. The first method was dipping the membrane coupon in 2% HNO_3 solution in a centrifuge tube and shake it for 24 hours under room temperature. The second one was using the same set-up as the first method but shaking for 48 hours. The third one was using 2% HNO_3 solution to soak the membrane coupon, and sonicated for 24 hours. The membrane area to HNO_3 solution volume ratio was maintained within 30 cm^2/L to 130 cm^2/L.

An X-SERIES II ICP-MS (Thermo Fisher Scientific Inc., Waltham, MA) instrument equipped with a CETAC ASX-520 auto sampler (Teledyne CETAC, Omaha, NE, USA) was operated in normal mode for the detection and quantification of ^{107}Ag in water samples. The method detection limit

(MDL) for ^{107}Ag was determined to be 0.1 µg/L. All water samples were acidified to a final strength of 2% HNO_3 using trace metal grade HNO_3 (OmniTrace, EMD Chemicals, Gibbstown, NJ, USA) prior to analysis. The instrument was tuned prior to each day's run using a tuning solution containing Li, In, Ce and U at 10 µg/L to maximize sensitivity and to minimize oxide levels (CeO/Ce to <2 %). A solution containing ^{45}Sc, ^{72}Ge, ^{115}In and ^{209}Bi at a 200 µg/L was used as the internal standard. A blank (2% HNO_3) was analyzed for every ten samples in a batch to check for carryover. Four-point calibration (minimum) was used, and the calibration standards were freshly prepared prior to each day's run.

Analysis by sp-ICP-MS was performed using a XSeries II ICP-MS (Thermo Fisher Scientific) to characterize the released dissolved silver and nano-scale silver particles. The operating conditions were optimized to produce the maximum ^{107}Ag intensity for each analysis session. A National Institutes of Standards and Technology 60 nm Au NP suspension (NIST SRM 8013) was used at 50 ng/L to determine transport efficiency as described by Pace et al.[18], which varied from 0.023 to 0.028 in this experiment. The instrument calibration utilized a blank and four dissolved Ag standard solutions (100 to 2000 ng/L) in 2% HNO_3 background under sp-ICP-MS mode. Samples from the washing experiments were analyzed within 48 h of collection directly by sp-ICP-MS without dilution or acidification to preserve silver nanoparticles. A data collection time of 120 s was used for all samples at an integration dwell time of 10 ms. To monitor instrumental drift over time, a 200 ng/L Ag dissolved calibration check standard was analyzed in sp-ICP-MS mode after every ten samples. If drift in the standard signal was detected, the particle sizing equation was adjusted accordingly for the decrease in sensitivity.

For sp-ICP-MS, raw intensity data were plotted as pulse intensity versus number of pulses, where any values below the first minimum in the histogram were considered background/dissolved. Background/dissolved counts were substracted from the pulse intensity, and AgNP was sized using a density of 10.49 g/cm^3. The minimum detectable AgNP size was typically 25-30 nm. Contributing factors that tended to increase the minimum size detection limit included decreased

ICP-MS sensitivity, matrix signal suppression, salting of the cones, and increased background Ag(aq). While the differentiation of the background and ENP signals was almost always possible, in some cases, quantification of Ag (aq) accumulation over time was not possible. This was especially evident in complex matrices, where Ag (aq) was either obscured by the background signal due to decreased instrumental sensitivity, or was lost to experimental materials (e.g., sample tubes). Therefore, total Ag components (NP and ionic) were tracked for all samples. To avoid particle coincidence, concentration was used whereby <15% of the measurement were AgNP pulses. The concentration of Ag (aq) and particle mass concentration were summed to provide total Ag. Using the instantaneous average particle diameter, the mass of Ag loss from the plastic container was calculated.

2.3.3 Scanning Electron Microscopy Results

AgNP properties on the membrane surface was measured by scanning electron microscopy (SEM, XL30 ESEM-FEG). The membrane was dried and coated by Au/Pt sputtering or C prior to analysis. The membrane was observed both in normal mode and back scattering mode.

2.4 Ag Leaching Test

2.4.1 Batch Leaching Test

Three different membrane surface area to volume ratios were used to examine the influence of the surface area to volume ratio to the silver leaching. The *In-situ* coating membrane coupons with area of 4.9 cm^2, 2.0 cm^2, and 0.44 cm^2 were soaked in 40 mL nano-pure water, shaking it in an orbit shaker (ORBi-SHAKER, 11101BC198) for 3 days. The nano-pure water was changed every 24 hours.

After study the influence of different surface area to volume ratios, a proper surface area to volume ratio was selected to use for following batch test. In order to study the silver leaching over time in the batch test, the 4.9 cm^2 membrane coupons were incubated in 40 mL nano-pure water on the orbit shaker for 5, 15, 30, 45, and 60 minutes, and then 3, 6, 12, 24, 48, and 72 hours, individually. Each time-period has three duplicate samples.

Four types extraction solutions were applied to study the influence of extraction solutions to the silver leaching. The 4.9 cm^2 membrane coupons were soaked in 40 mL extraction solutions and shaking for 3 days, the extraction solution was changed every 24 hours. Each extraction solution has 5 duplicate samples.

Figure 2.1 Batch Test Set-up

2.4.2 Dead-end Leaching Test

A stainless steel dead-end filtration cell (Sterlitech HP4750 Stirred Cell) was used in this experiment to examine the Ag release. The dead-end cell was fed with 200 mL of extraction solution for each test. Operating pressure of the dead-end test is 90 psi (keeping consistent with cross-flow test), which is given by Nitrogen compressed gas tank. Filtrate was taken at 6 different time periods, the first 10 minutes, then 11 to 30 minutes, 31 to 60 minutes, 61 to 120 minutes, 121 to 180 minutes, and 181 to 240 minutes. Filtrate for each individual time periods was collected to separate centrifuge tubes. The concentrate remaining in the dead-end cell was also collected after 4 hours of filtration.

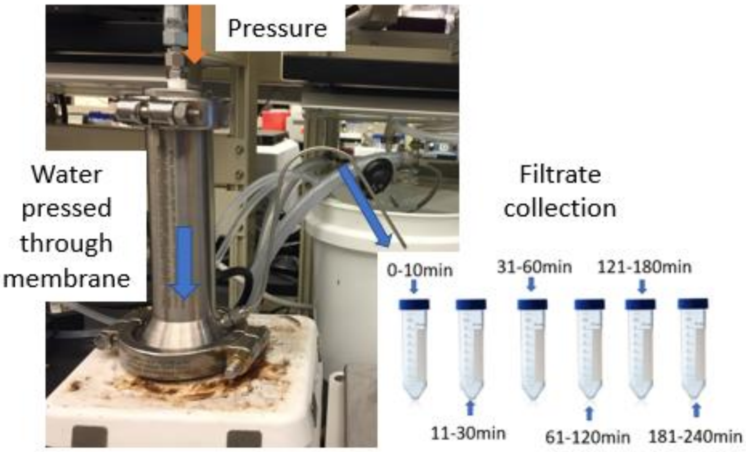


Figure 2.2 Dead-end Test Set-up

2.4.3 Cross-flow Leaching Test

Ag composite membranes were applied in a cross-flow filtration system to test the Ag leaching. The cross-flow system used in this experiment is a membrane cell test system (TOMAR). This set-up is composed of 3 cross-flow filtration cells which connected to each other one by one. Each cross-flow cell has an effective membrane area of 42 cm^2. Each cross-flow leaching test used 23 L (6 gal) water and operated for 50 hours. Both the concentrate and filtrate of the cross-flow test were all recycled to the feed tank during the 50 hours. The system was operating at the pressure of 90 psi. Feed flow rate was controlled around 1.8 GPM. Filtrate samples were taken at certain points in time during the 50 hours. Concentrate was sampled after 50 hours, and the water samples were taken from the feed tank.

Figure 2.3 Cross-flow Test System

2.4.4 Water Jet Spray Test

A water jet leaching test system was designed to study the silver leaching potential under the impact of a high velocity water flow. As shown in Figure 2.4, a peristaltic pump (Cole-Parmer Instrument Company No. 7553-70) was used to deliver water with a high flow rate to a fine needle, creating a high velocity water flow by decreasing the cross-section area of the water flow. A PVC pipe fitting was customized to be used as the water jet cell to fix the water jet and membrane in place and prevent the water splashed out during the water flow hitting the membrane. A membrane coupon can be fixed at the bottom of the water jet cell, and the membrane surface was vertical to the water flow which came out from the water jet. The membrane was placed between two layers of rubber gaskets, as shown in Figure 2.5. The bottom rubber gasket is used to support the membrane, the top one has ¼ inch diameter circle hole in the middle to expose a small area of membrane to have water flow directly impact on the membrane surface. The two layers of rubber gasket and membrane is fixed by a small black PVC pipe fitting at the water jet cell, with the ¼ inch diameter circle hole exposed to the water flow, as shown in Figure 2.5. The feed water was taken from the water jar shown in Figure 2.4, after the water flowed through the water jet cell all the water will flow through the bottom of the water jet cell back to the water jar, which formed a water recycle system.

The highest flow rate delivered by the pump is up to 1.1 L/min, the size of the needle used at the water jet outlet is gauge 16, which has an interior diameter of 1.194 mm. The linear velocity of the water flow right out of the water jet can be controlled up to 16.5 m/s. The water flow coming out of the water jet will vertically impact the membrane surface, and it will cause a pressure on the membrane surface; this pressure can be controlled up to 20 psi. Because the preliminary test results show that the highest flow rate of the system will damage the membrane after one hour of water jet abrasion, the flow rate used in the test should be controlled within a practical range. The flow rate used in the test is 470 mL/min. The corresponding water flow velocity and pressure on the membrane are 7 m/s and 3.6 psi.

1 L solution was recycled in each Jet test, and each test was operated for 1 hour. Water samples were taken from the water jar at 5, 15, 30, 45, and 60 minutes. The total size of the membrane that was used in the water jet system is a circle shape membrane with a diameter of 18 mm. The membrane area that was directly exposed to the water flow is 0.316 cm^2 (D=6.34 mm). Before applied, the 18mm size membrane was cut into three pieces (D=6.34 mm) to measure the Ag Initial loading on the edge of the big membrane coupon (as shown in Figure 2.7). The rest of the membrane was then applied in the double layer rubber gaskets. After 1 hour of water jet abrasion, the exposed area of the membrane was cut off to measure the Ag remaining on the directly impacted area. The rest of the membrane was also digested to measure the Ag remaining on the covered area, to examine the covered efficiency of the set-up.

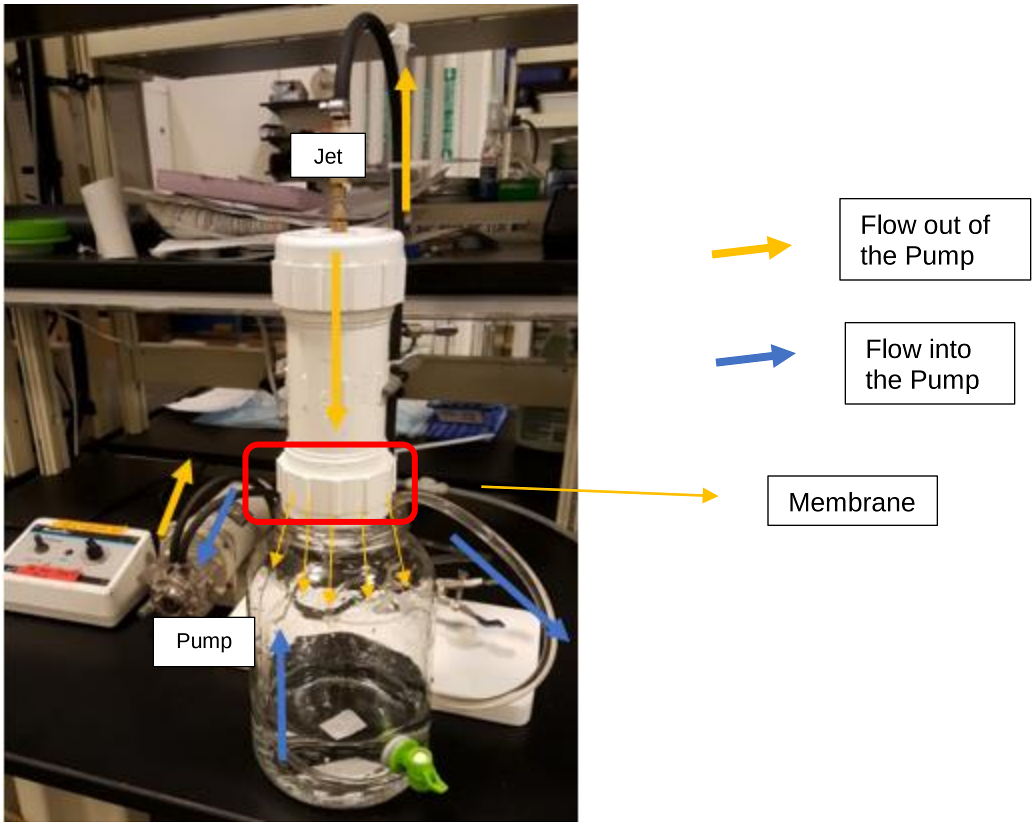


Figure 2.4 Water Jet Set-up

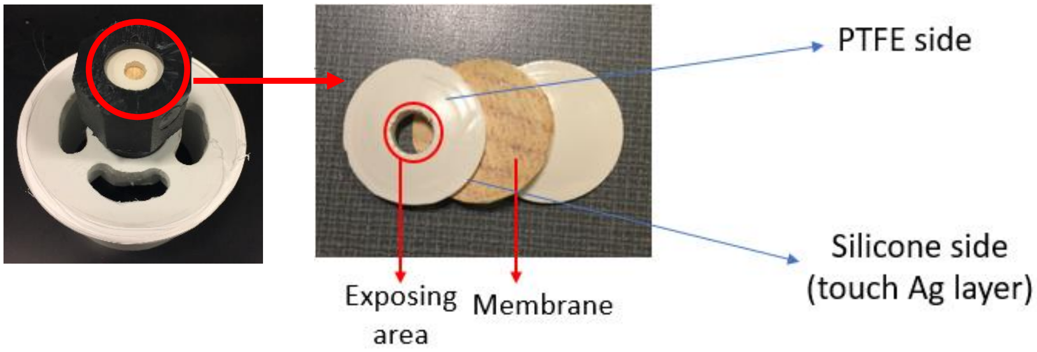


Figure 2.5 Fixation of Membrane in Water Jet Set-up

Figure 2.6 Water Jet

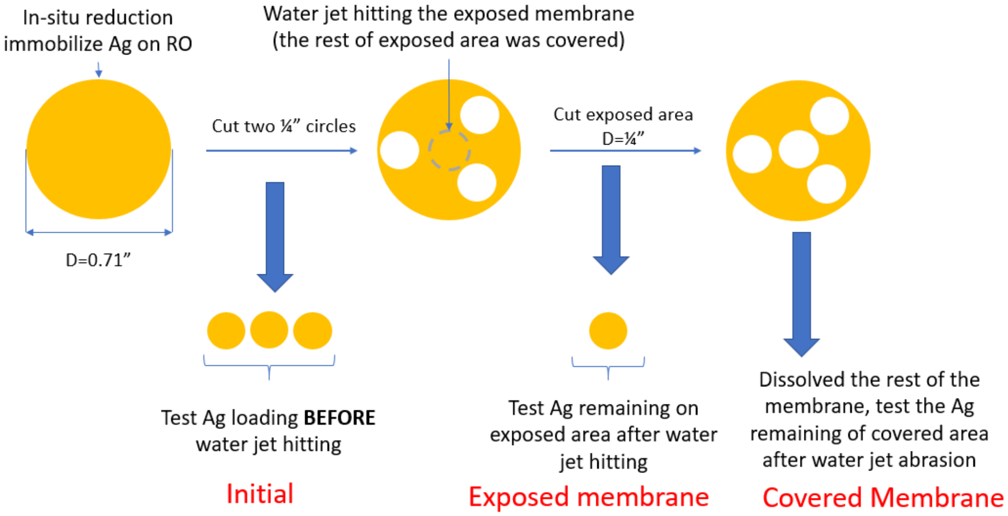


Figure 2.7 Water Jet Leaching Experiment Method

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Membrane Characterization

Three different digestion methods were used to quantify the Ag loading on the membrane, which are stated in 2.3.2. The membrane used in this digestion comparison experiment was coated by the coating method 1 (as described in Chapter 2.2.1). The measured average silver loading concentration by “Shaking-one-day” method was 1.2 ± 0.17 ug/cm^2; for “Shaking-two-day” method was 1.1 ± 0.22 ug/cm^2; for “Sonicating-one-day” method was 1.3 ± 0.10 ug/cm^2. The results are shown in Figure 3.1. The student’s T-tests were conducted to compare the results of the three different digestion methods. The results of the T-tests show that there was no significant difference in the scores for silver concentration measured by “shaking-one-day”, “shanking-two-day”, and “sonicating-one-day” method; $P > 0.05$.

The sonication method shows the highest Ag extraction amount in this experiment and the it was used in additional studies to digest the nano-composite membranes. Therefore, the following experiments are using sonication method to digest silver composite membranes.

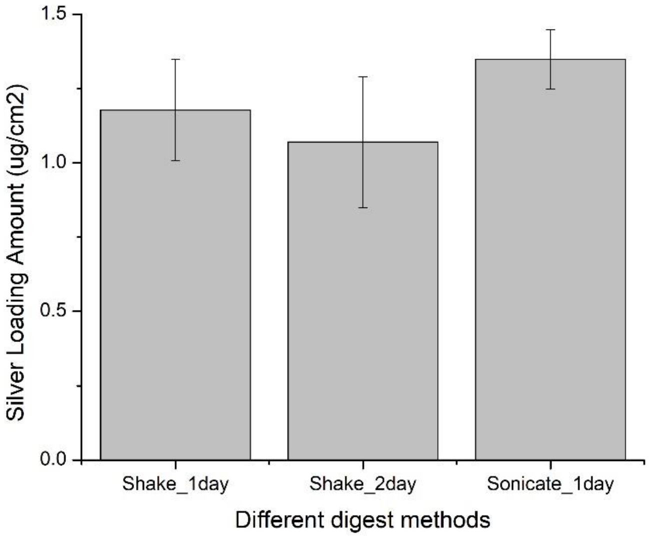


Figure 3.1 Digestion Results of Ag Coated RO in Three Different Methods
(Method A and B are using agitate for 24 hours and 48 hours respectively, Method C is sonicating for 24 hours)

Two types of coating procedures were used in this study. Different coating procedures will result the different silver loading on the membrane. Membrane prepared by Coating method 1 (Chapter 2.2.1) was used in the beginning of the experiment. Ag loading on the membrane for the Coating method 1 varies from 0.5 ug/cm^2 to 1.9 ug/cm^2, which is close to the Ag loading (2 - 4 μg/cm^2) reported by Ben-Sasson et al[17]. For the Coating method 2 (Chapter 2.2.2), the average silver loading on the membrane is 2.04 ± 0.51 ug/cm^2, which shows higher silver loading than the method 1 and silver loading amount more stable.

Scanning electron microscope (SEM) was used to analysis AgNP on the membrane both before and after coating. Figure 3.2(A) shows the pristine RO before coating; B shows the freshly prepared Ag coated RO; C shows the Ag coated RO after 1hour water jet wash. As shown on the SEM images, AgNP was not easy to directly identify in those images. This may be because of a layer of metal (Au/Pt) coated on the membrane.

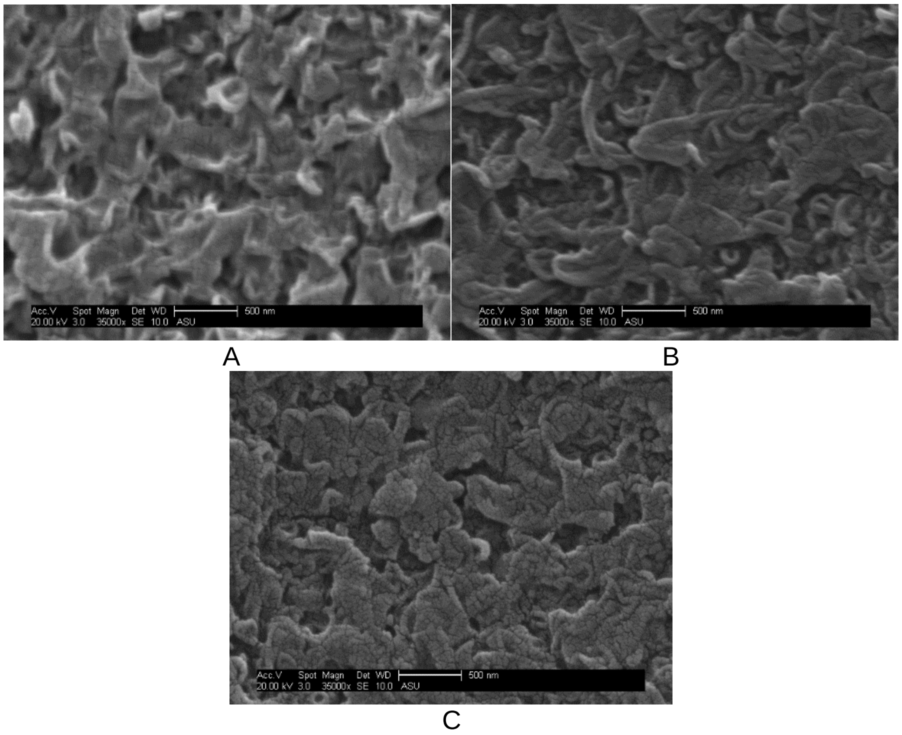
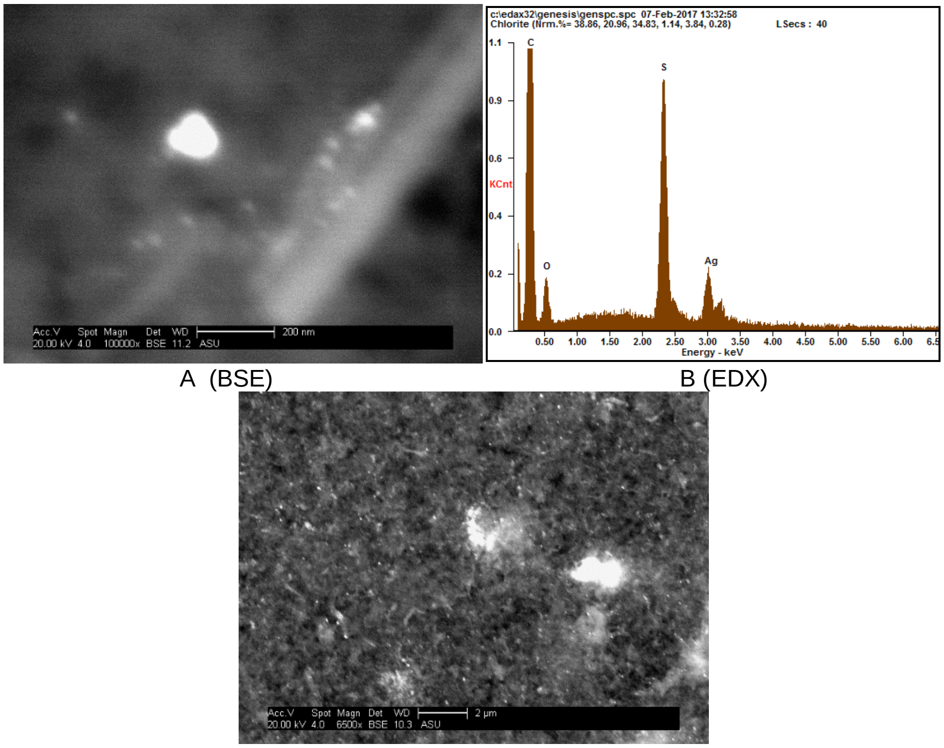


Figure 3.2 SEM Images of Reverse Osmosis Membrane
(A, Pristine RO; B, freshly prepared Ag Coated RO; C, Ag coated RO after I hour water jet wash)

In order to identify the AgNP on the membrane surface, carbon sputtering was used to instead the Au/Pt sputtering. BSE images were shown in Figure 3.3. Some light dots can be observed (shown in Figure 3.3 A) in back scatter mode. The chemical element composition can be identified by Energy-dispersive X-ray spectroscopy, the EDX results are shown in Figure 3.3 (B). Carbon was the highest element in the EDX image, which was coming from the sputter carbon coating and the polymer layer of the membrane. Oxygen and sulfur were also coming from the polymer layer of the membrane. Silver was detected on the membrane surface. As a result, Ag was coated on the membrane surface. As shown in Figure 3.3 (C), the lighting dots on the image are Ag, however, the Ag on the membrane surface was not uniformly coated.



A (BSE) B (EDX)

C (BSE)

Figure 3.3 Back-scatter Detector (BSE) image and Energy-dispersive X-ray Spectroscopy (EDX) results

Membrane flux rates were measured in dead-end filtration. Using 200 mL of solution at 90 psi feed pressure. The flux tested by nano-pure water of pristine RO and Ag coated RO are shown in Figure 3.1.3-1. In order to study the influence of chemical solutions to membrane flux, the flux of Ag-coated RO membrane for different extraction solutions were also examined. The flux of Ag coated RO membrane tested by different chemical solutions are shown in Figure 3.5. The average flux for pristine RO and Ag coated RO are shown in Table 3.1.

Table 3.1 Average Flux of Pristine RO and Silver Coated RO (P = 90 psi)

Solution	Flux of Pristine RO (LMH)	Flux of Silver Coated RO (LMH)
Nano-pure water	21 ± 5.5	20 ± 2.2
pH 5 (with Cl^-)	—	21 ± 5.5
pH 5 (without Cl^-)	—	21 ± 3.6
pH 10	—	18 ± 3.9

A T-test was conducted to compare the flux of pristine RO and Ag coated RO. There was a significant difference in the scores for flux of the pristine RO (21 ± 5.5 LMH) and flux of Ag coated RO (20 ± 2.2 LMH); $P = 3.67 \times 10^{-6}$. These results suggest that coating Ag on the membrane surface do have an influence on the flux of the membrane. The Ag-coated RO membrane has lower flux than the pristine RO membrane. However, the flux of the membrane did not dramatically drop after coating Ag on the top. The average flux of Ag-coated RO is 20.0 LMH which has no significant decrease compared to the pristine RO (average flux is 21.0 LMH). After coating Ag on its top, the RO membrane remained at an acceptable performance level.

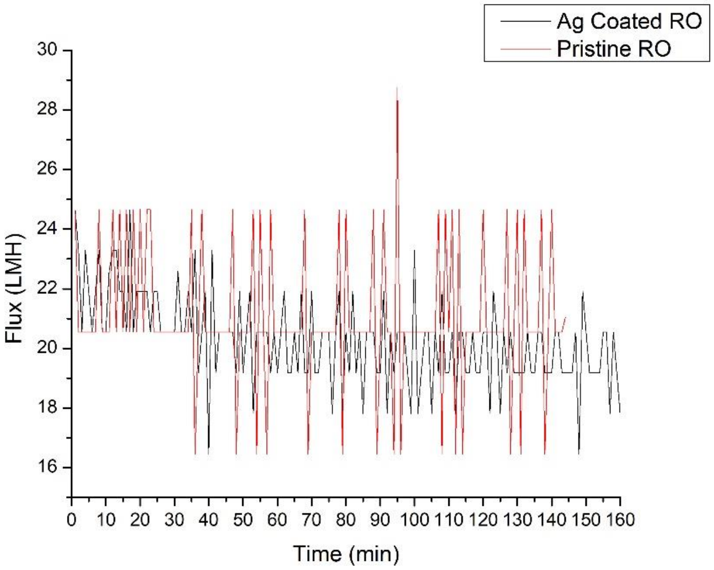


Figure 3.4 Flux of Pristine RO and Ag-coated RO (P = 90 psi)

A series of independent T-tests were conducted to compare the flux of different chemical solutions. As shown in Figure 3.5, the flux decreased after 1 hour. The T-test results are shown in Table 3.2. As shown in the Table 3.2, the flux of pH 5 (with Cl^-) and pH 5 (without Cl^-) have no significant difference. Except pH5 (w Cl^-) and pH5 (w/o Cl^-), the flux of any other two groups of extraction solutions all have significant differences with each other. The results suggest that the pH of the solution has influence of the flux of the membrane. The pH5 solution has relative higher flux compare to pH10 solution. The flux of nano-pure water (pH=6.5) is higher than pH10 solution but lower than pH5 solution, suggests that increase the alkalinity of the test solution will decrease the flux of RO membrane.

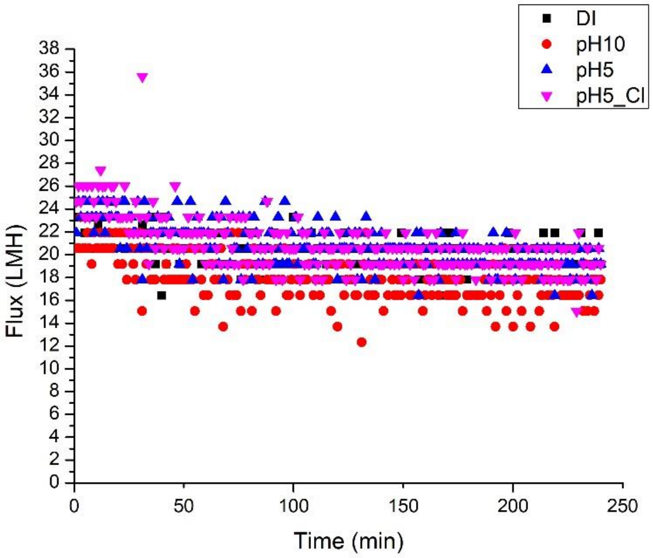


Figure 3.5 Flux of Ag-coated RO by Applied Different Chemical Solutions

Table 3.2 T-test Results for Compare the Flux of Different Chemical Solutions

Significance level ($\alpha = 0.05$)	Nano-pure water (20 ± 2.2 LMH)	pH 5 (without Cl^-) (21 ± 3.6 LMH)	pH 5 (with Cl^-) (21 ± 5.5 LMH)	pH 10 (18 ± 3.9 LMH)
Nano-pure water	—	$P < 0.05$	$P < 0.05$	$P < 0.05$
pH 5 (without Cl^-)	—	—	$P = 0.883$	$P < 0.05$
pH 5 (with Cl^-)	—	—	—	$P < 0.05$
pH 10	—	—	—	—

3.2 Ag leaching Results

3.2.1 Batch Test Results

3.2.1.1 Ag Leaching in Different Surface Area to Volume Ratio

Percentages of silver leaching in different membrane surface area to volume ratios are shown in Figure 3.6. Each column in Figure 3.6 represents different surface area to volume ratios. The y-axis shows the percentage of silver leached in the total measured silver amount. The percentage of silver leached is calculated by

$$Ag\ leached\ \% = \frac{Ag\ leached\ in\ Day\ 1\ (or\ Day\ 2, Day3, Ag\ Remaining)}{Total\ Ag\ leaching\ in\ 3days + Ag\ remaining\ on\ membrane} \times 100$$

where the Ag leached in the equation is the mass of silver leached. The leached silver mass in liquid phase was calculated by the measured Ag concentration multiply by the volume of the extraction solutions. The mass of silver remaining on membrane was directly measured by digest the membrane coupon after the leaching test.

As the surface area to volume ratio decreased from 122 cm^2/L to 11 cm^2/L, the silver leaching for “Day 1” is increased, the silver leaching for “Day 2” and “Day 3” are decreased. The total silver leaching of the 3 days for different surface area to volume ratios are all kept around 60 %. The results show that lower surface area to volume ratio will cause more silver leaching at the beginning, but silver leaching will keep at the same level for a relative long time test with no influence of the surface area to volume ratio.

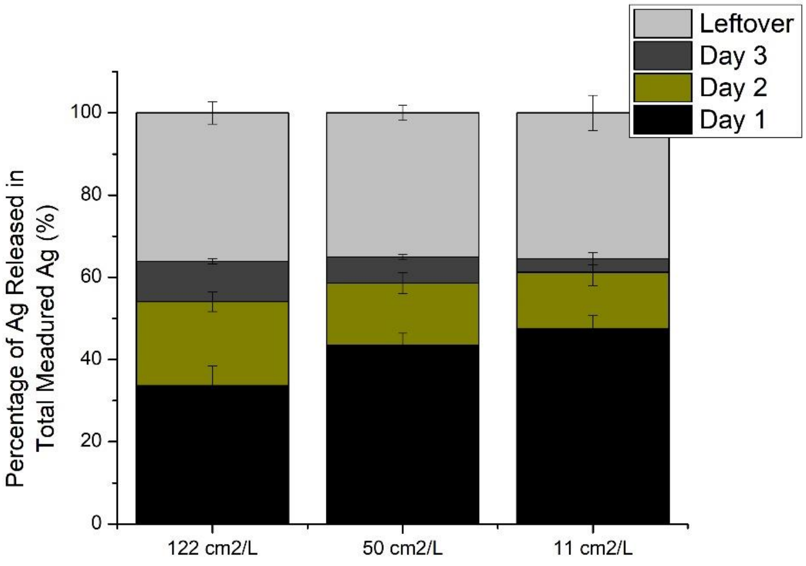


Figure 3.6 Percentage of Ag Leaching in Different Surface Area to Volume Ratio

3.2.1.2 Ag Leaching Trend in Batch Test

Both AgNP and Ag ions leached to the nano-pure water in different soaking times were examined. The AgNP was examined by sp-ICP-MS, and the result shows that there is no silver nanoparticle leached out in the batch test. The Ag ions leaching concentration at different soaking times are shown in Figure 3.7. The silver concentration was continually increased during the three-day batch test. The silver was released very quick at the first hour, the silver concentration in the extraction solution will be close to 100 ppb after the first hour. As the soaking time increased, the silver release rate was decreased. After soaking the membrane for three-day, the silver concentration in the extraction solution was around 180 ppb.

Comparing the leaching results of AgNP and Ag ions in the batch test, most of the silver in the batch test was released as dissolved silver, with almost no silver nanoparticle released in the batch leaching test. The predominant silver leaching mechanism for the batch test is oxidation. The Ag (0) on the membrane is oxidized to Ag^+, then the silver is released in ion form. It may have some silver on the membrane released as AgNP, but it can also be oxidized to Ag ions in the liquid phase.

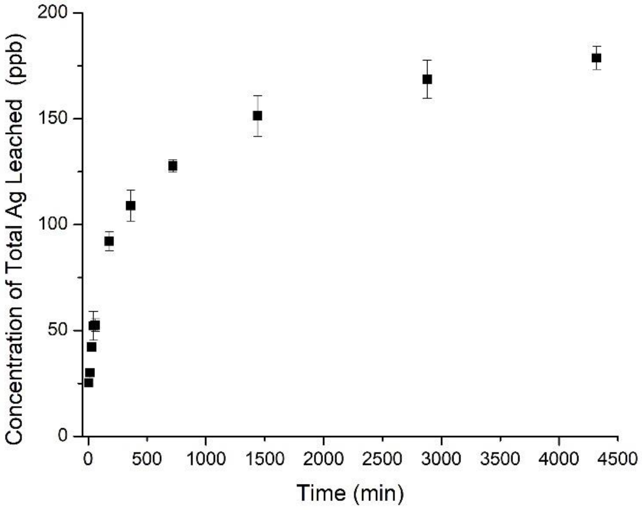


Figure 3.7 Ag Leaching Trend of Batch Test (sa/vol = 122 cm^2/L)

3.2.1.3 Ag Leaching in Different Extraction Solutions

Percentages of Ag leaching during the three-days batch test are shown in Figure 3.8, and numeric results are shown in Table 3.3. Each column in Figure 3.8 represents different chemical extraction solutions. The y-axis shows the percentage of silver leached in the total measured silver amount. The calculation of the silver leaching percentage is same as stated in 3.2.2.1.

The pH 5 without Cl^- group and nano-pure water group have the highest Ag release, both of them have more than 60% of silver release during the three-day leaching test. The pH5 (w/o Cl^-) solution causes more silver release than pH5 (w Cl^-) solution. The pH 10 group causes the lowest Ag release among the four types of extraction solutions.

The relative low leaching amount for pH 5 with Cl^- solution may be caused by the chemical reaction between silver ion and chloride. The Cl^- in the solution can react with Ag^+ in the membrane surface to form AgCl on the membrane to reduce the silver release. Ag (0) at pH10 has a relative high redox potential[19], which may be the main reason of the less silver released for the pH 10 solution group.

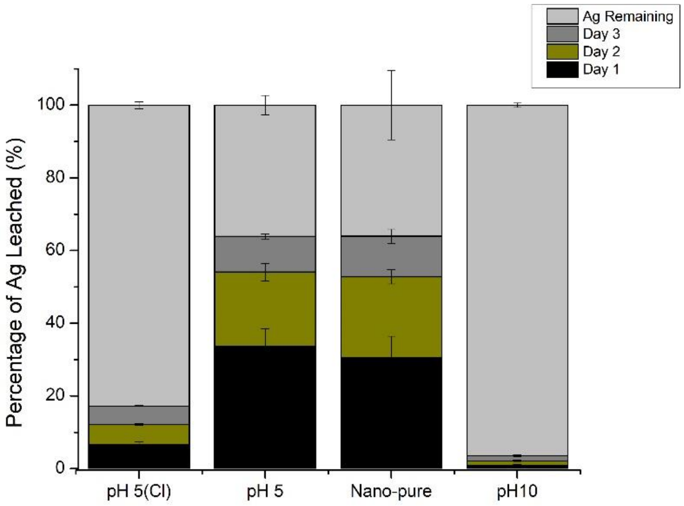


Figure 3.8 Percentage of Ag Leaching for Different Chemical Solutions in Batch Test

Table 3.3 Percentage of Ag Leaching for Different Chemical Solutions in Batch Test

Percentage (%)	pH5 (Cl)	pH5	Nano-pure	pH10
Ag Release in Day 1	6.6 ± 0.72	34 ± 5.0	31 ± 6.00	0.94 ± 0.22
Ag Release in Day 2	5.5 ± 0.23	21 ± 2.4	22 ± 2.0	1.2 ± 0.19
Ag Release in Day 3	5.1 ± 0.15	9.8 ± 0.67	11 ± 2.0	1.4 ± 0.23
Ag Remain on Membrane	83 ± 0.97	36 ± 2.7	36 ± 9.5	96 ± 0.58

3.2.1.4 Comparison of the Silver Leaching Results with Other Batch Leaching Tests

Comparisons of the batch test results with the silver leaching from other studies are summarized in Table 3.4. Because of the silver coating method, surface area to volume ratio, and extraction solution used in those batch tests are different, the silver leaching results shown in Table 3.4 vary greatly from the results of this study.

The last row of Table 3.4 shows the silver leaching results from the same type of Ag coated membrane. The percentage of silver leaching from Ben-Sasson et al.[17] is lower than the leaching percentage of pH5 (w Cl^-), pH5 (w/o Cl^-), and nano-pure water. The difference of surface area to volume ratio and chemical compositions of the extraction solutions may cause the difference of the silver leaching results. However, the results reported by Ben-Sasson et al.[17] is close to the silver leaching percentage caused by the pH10 solution, which may be caused by the high redox potential of Ag (0) in an alkaline environment.

Table 3.4 Summary of Silver Leaching Results from Other Studies

Coating methods and Membrane type	Leaching Test Design	Silver Leaching Results	Reference
LBL & RO	5 cm^2 Membrane + 20 mL DI water + shaking 14 days (water changed every 24h)	Ag Ion leaching concentration: 1st day: about 1.3 ppb 2nd day: about 0.5 ppb After 3rd day: < 0.2 ppb	[13]
AgNP coated TFC	1 cm^2 membrane + 20 mL DI water + 14 days (water changed every 24h)	Initial Ag ion release rate: 0.37 $ug/cm^2/day$ Ag release rate after 7 days: 0.1 $ug/cm^2/day$ 12% of silver leached out (Initial Ag loading 15 ug/cm^2)	[8]
AgNP In-situ Reduction & RO	3.8 cm2 membrane + 10 mL of 5 mM NaHCO3 solution (pH 8.3) + 7 days	After 7 days: residual silver loading roughly 3.5 ug/cm^2 (Initial silver loading 3.7 ± 0.4 ug/cm^2)	[17]

3.2.1.5 Mass Balance

Mass balance of the batch test was done to verify the results of the experiment. Ag total measured is the sum of silver remaining in the membrane and silver leaching during the 3 days. The mass balance calculations for different chemical solutions and different surface area to volume ratios are shown on the last column of Table 3.5 and Table 3.6. The calculated mass balance for all the four different chemical solutions groups (surface area to volume ratio is 122.5 cm^2/L) are within ± 30%, which is an acceptable error for this experiment. For different surface area to volume ratios, the 122 cm^2/L and 50 cm^2/L groups have an acceptable mass balance error. But for 11 cm^2/L group, the mass balance error is relative high. In this experiment, 11 cm^2/L group was using the relative smaller membrane coupons than other two groups. Because of the non-uniformly silver loading of the membrane, the smaller of the membrane have been used, the bigger error will have. Therefore, the high mass balance error may be caused by the non-uniform loading and small membrane size.

Table 3.5 Mass balance of Batch Test for Different chemical solution groups

Chemical solutions	Ag Mass (ug)						Mass Balance (%)
	Day 1	Day 2	Day 3	Ag remain	Total Measured Ag	Initial Loading	
pH 5_Cl	0.86 ± 0.07	0.72 ± 0.04	0.66 ± 0.06	11 ± 1.0	13 ± 1.1	13 ± 1.2	100 ± 8.5
pH 5	4.5 ± 0.86	2.7 ± 0.41	1.3 ± 0.23	4.8 ± 0.46	13 ± 1.5		100 ± 11
DI	3.7 ± 0.30	2.8 ± 0.44	1.4 ± 0.14	4.8 ± 1.8	13 ± 2.6		96 ± 20
pH10	0.10 ± 0.01	0.14 ± 0.02	0.16 ± 0.01	11 ± 2.1	11 ± 2.1		86 ± 16

Table 3.6 Mass Balance of different Surface Area to Volume Ratio Groups

	Ag Mass (ug)						Mass Balance (%)
	Day 1	Day 2	Day 3	Ag remain	Total Measured Ag	Initial Loading	
Group 1	4.5 ± 0.86	2.7 ± 0.41	1.3 ± 0.23	4.8 ± 0.46	13 ± 1. 5	13 ± 1.2	100 ± 11
Group 2	1.9 ± 0.11	0.66 ± 0.16	0.28 ± 0.04	1.5 ± 0.10	4.3 ± 0.29	5.3 ± 0.50	81 ± 5.4
Group 3	0.30 ± 0.05	0.09 ± 0.01	0.02 ± 0.01	0.23 ± 0.06	0.67 ± 0.10	1.2 ± 0.11	53 ± 8.3

3.2.2 Dead-end Results

3.2.2.1 Silver Leaching Results

The average silver concentrations of the filtrate and the silver concentration in retentate for different chemical solutions are shown in Table 3.7. The silver concentrations are lower than the Secondary Drinking Water Standard for silver which is 100 ppb both for filtrate and retentate. The silver concentration of the filtrate for each type of extraction solutions shows big variance among their duplicate experiments, which may be caused by the inconsistency silver loading on the membrane.

Table 3.7 Silver Concentration in Filtrate and Retentate of the Cross-flow Test

Silver Concentration (ug/L)	Nano-pure Water	pH 5 (without Cl^-)	pH 5 (with Cl^-)	pH 10
Average of Filtrate	1.6 ± 0.83	0.47 ± 0.28	0.42 ± 0.51	0.46 ± 0.47
Retentate	5.4 ± 0.89	0.74 ± 0.49	5.3 ± 1.5	5.6 ± 0.58

The cumulative leached dissolved silver and silver nanoparticle amount in the filtrate over the 4 hours dead-end filtration (for nano-pure water) are shown in Figure 3.9. The fraction of AgNP in total leached silver is also plot in the Figure 3.9. The cumulative silver amount for both Ag ions and AgNP are increase in relation of the time, which represents that the dissolved silver and AgNP were keeping releasing during the 4 hours filtration process. But the percentage of the AgNP are decreased in relation of the time, represents that the releasing rate of Ag ions are relative higher than AgNP.

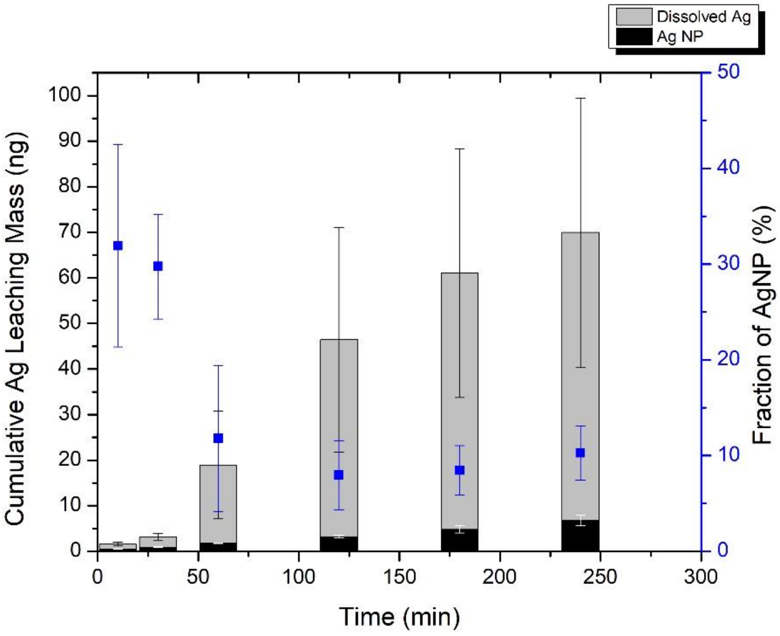


Figure 3.9 Ag Ions and Ag NP in Dead-end Filtrate (Nano-pure water)

The cumulative silver leaching amount in the dead-end filtrate were shown in Figure 3.10. Different marks represent different chemical solutions that had applied. For nano-pure water group, the silver was keeping releasing during the dead-end filtration process (same results as shown in Figure 3.9). For other three chemical solutions, the silver leaching rate decreased dramatically after the first hour operation. Nano-pure water caused the highest silver leaching to filtrate among the four different solutions in Dead-end filtration.

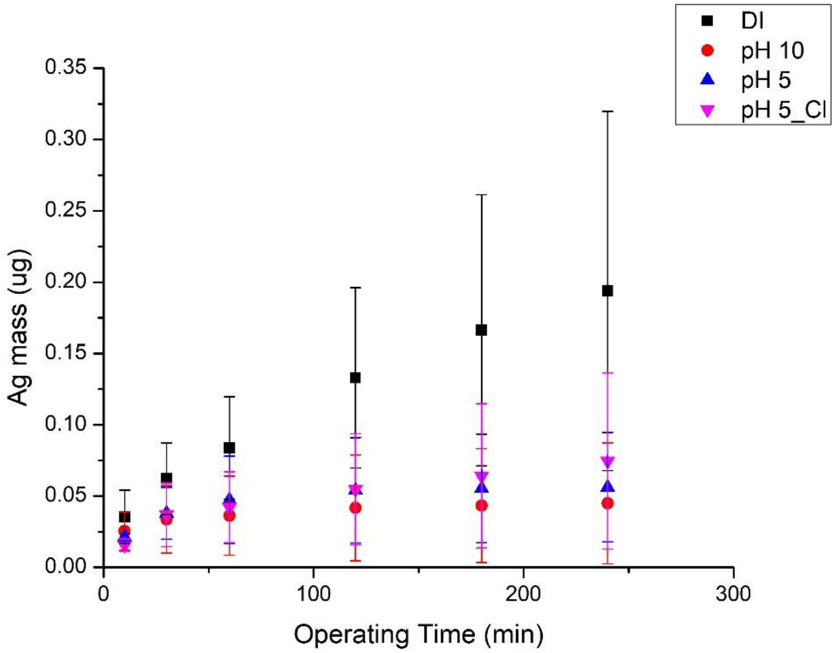


Figure 3.10 Cumulative Ag leaching in Dead-end Filtration

3.2.2.2 Silver Remaining on Membrane

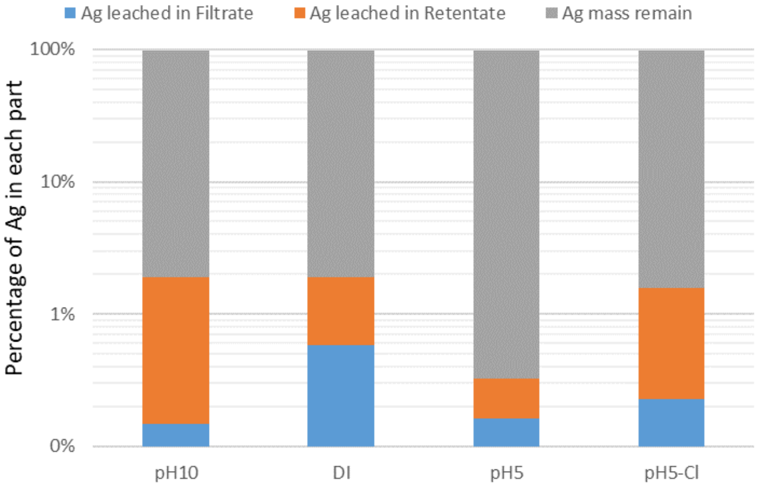


Figure 3.11 Leaching Percentage of Different Chemical Solutions in Dead-end Filtration

The percentage of silver released to filtrate, concentrate, and remained at membrane for different chemical solutions are plotted in log scale in Figure 3.11. The percentage of silver in Figure 3.11 was calculated by the silver in each part divided by the total silver amount of the three parts. More than 98% of silver remaining in the membrane after 4 hours filtration for all four chemical solutions. Less than 1% of silver leached to the filtrate for all four chemical solutions.

3.2.2.3 Mass Balance

Mass balance of the dead-end test was done to verify the results of the experiment. Ag total measured is the sum of Ag remaining in the membrane, Ag leaching to the filtrate, and Ag leaching to the concentrate. The mass balance calculations are shown on the last column of Table 3.8. The calculated mass balance for all four groups are within ± 70%, which is an acceptable error for this experiment.

Table 3.8 Mass Balance of Batch Test

Chemical solutions	Ag leached in Filtrate	Ag leached in Retentate	Ag mass remain	Total Measured Ag	Initial Loading	Mass Balance
	(ug)	(ug)	(ug)	(ug)	(ug)	(%)
pH10	0.05 ± 0.04	0.54 ± 0.12	30 ± 4.3	31 ± 4.3	37 ± 5.4	83 ± 12
DI	0.19 ± 0.13	0.44 ± 0.10	33 ± 0.60	33 ± 0.61		90 ± 1.7
pH5	0.06 ± 0.04	0.06 ± 0.03	35 ± 2.9	35 ± 2.9		95 ± 7.8
pH5-Cl	0.08 ± 0.06	0.44 ± 0.24	32 ± 1. 7	33 ± 1.5		88 ± 3.9

3.2.3 Cross-flow Results

3.2.3.1 Silver Ion & Silver Particles in Concentrate

The silver ion and nanoparticle leaching concentrations trend over 50 hours in cross-flow system by applying nano-pure water and pH5 (without Cl$^-$) solution are shown in Figure 3.12 and Figure 3.13, respectively. The percentages of AgNP in total silver released (include Ag ion and AgNP) are also plot in Figure 3.12 and Figure 3.13.

The total silver amount in both nano-pure water and pH5 (without Cl^-) shows a decreasing trend in relation to the time. And pH5 (without Cl^-) solution has lower silver decreasing during 50 hour operation compare to nano-pure water. The concentration of AgNP increased during the 50 hours in relation to the operation time (as shown in Table 3.9), and the AgNP concentration in the concentrate during the 50 hours are all below 50 ng/L which is lower than the dissolved silver concentration. The AgNP takes less than 5% of total silver in the first 24 hours. With the increase of the operation time, the percentage of AgNP increased because of the decrease of the dissolved silver amount.

Both the concentrate and permeate of this cross-flow test were recirculated in the cross-flow system. Some of the silver ions may not be reduced to Ag (0) during the coating procedure but still attached at the membrane, which may cause the dramatically release of silver ions at the beginning. The decrease of the dissolved silver amount may be caused by the silver reattached to the membrane because of the filtration process, or the silver attached to the filtration system set-up (tubes, filtration cells, and water tank etc.). The slightly increase of the AgNP shows that the AgNP was keeping detached from the membrane during the cross-flow filtration process. The silver ions will be more stable at acid solutions which made the pH5 solution causes less decrease of silver ion concentration.

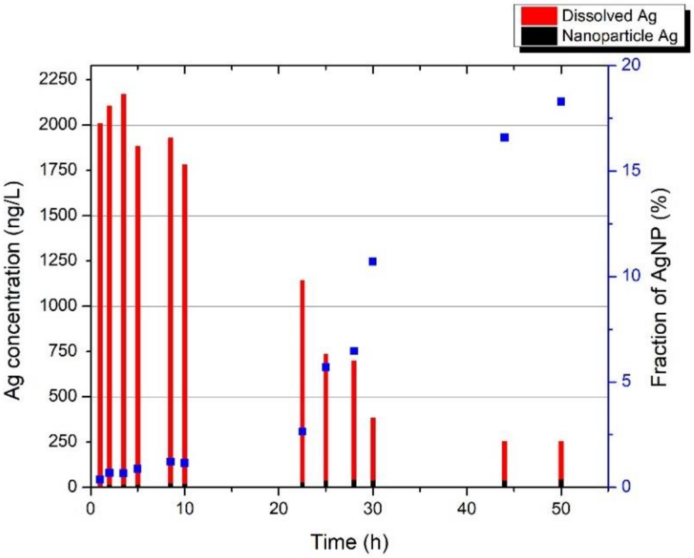


Figure 3.12 Ag Ions and Ag NP of Nano-pure Water Group
(Cross-flow Concentrate)

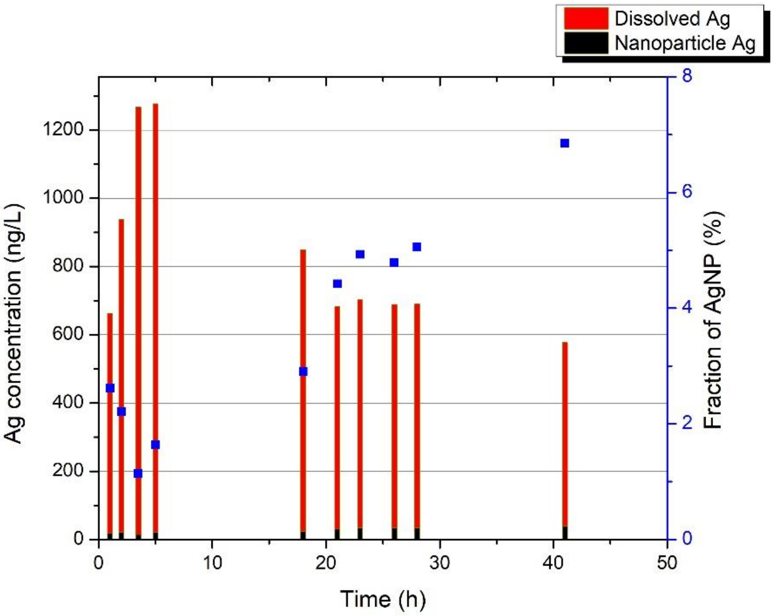


Figure 3.13 Ag Ions and Ag NP of pH5 (without Cl-) Group
(Cross-flow Concentrate)

Table 3.9 AgNP Concentration in the Concentrate of Cross-flow Leaching Test

Time (h)	AgNP Concentration of Nano-pure Water Group (ng/L)	AgNP Concentration of pH5 (without Cl^-) Group (ng/L)
1	7.5	17
2	14	21
3.5	15	14
5	17	21
8.5	24	25
10	21	30
22.5	30	35
25	42	33
28	45	35
30	41	40
44	42	—
50	46	—

3.2.3.2 Mass Balance

The mass balance results of the cross-flow test are shown in Table 3.10. The total measured silver was calculated by the sum of the silver remained at the membrane after leaching test and the silver detected at the recycled water at the end of the leaching test. Bad silver mass were observed. The results show that only less than 20% of silver can be detected after the leaching test. The undetectable silver may be attached at the cross-flow set-up. Or it may be caused by water leaking out from the recirculated water flow during the 50 hours operation.

Table 3.10 Mass Balance for Cross-flow Leaching Test

Extraction Solutions	Ag Mass (ug)				Mass Balance
	Remain on Membrane	Measured at Liquid Phase	Total Ag Measured	Initial Ag Loading	%
Nano-pure Water	11	6.3	17	340	5.0
pH 5 (without Cl^-)	42	9.9	52	340	15

3.2.4 Water Jet Results

1 L of water sample was recycled in the water jet system for 1 hour. The flow rate was adjusted to around 500 mL/min. Water samples were taken at 5, 15, 30, 45, and 60 minutes to measure the both AgNP and Ag ions that had been leached out.

3.2.4.1 Ag Remaining After Jet Wash

Four types of chemical solutions were applied in the water jet system to test the Ag leaching. Before the membrane was applied to the system, three pieces of membrane coupons (D=1/4 inch) were cut off to measure the Ag initial loading, which is shown as the "Initial" in Figure 3.14. After 1 hour of water jet wash, the membrane area (D=1/4 inch) which directly exposed to the water flow was cut off to measure the Ag remaining, shown as "Exposure" in Figure 3.6. Additionally, the rest of the membrane coupon which was covered by the rubber gasket was also digested to measure the Ag remaining on it, shown as "Cover" in Figure 3.14.

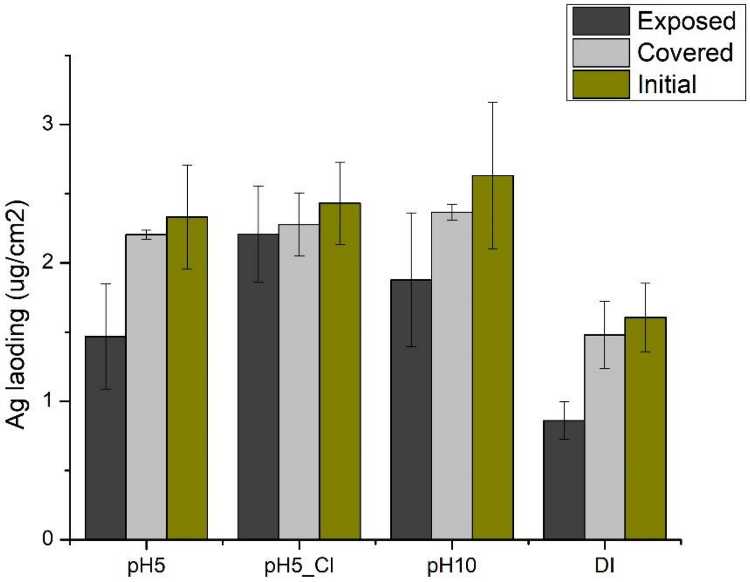


Figure 3.14 Ag Remaining on Different Part of Membranes after 1hour Water Jet Test

The purpose of using a rubber gasket to cover part of the membrane in this water jet set-up was to try to control the Ag lost on the "non-impact" area. As shown in Figure 3.14, most of the Ag on the covered area stayed on the membrane after the water jet wash. The percentage of the Ag remaining on the covered area was shown in the last column of Table 3.11, showing that the lost Ag on the covered area was controlled within 20%. The student's T-tests were conducted to compare the residual silver loading on the covered area with initial silver loading, and residual silver loading on the exposed area. There was a significant difference in the scores for residual silver loading of the covered area (2.0 ± 0.18 ug/cm^2) and residual silver loading of the exposed area (1.5 ± 0.38 LMH); $P < 0.05$. There was no statistical difference for residual silver loading of the covered area (2.0 ± 0.18 ug/cm^2) and initial silver loading (2.2 ± 0.28 ug/cm^2); $P > 0.05$. The T-test results indicate that there was no silver released from the covered membrane area. Moreover, the exposed area did have silver released during the water jet wash.

The Ag remaining on the "directly impacted area" varies from different solutions. As shown in Table 3.11, the pH5 with Cl^- group has the highest Ag remaining, 90.9% of Ag remained at the membrane after sprayed by water jet by 1hour. The pH5 without Cl^-, pH10, and nano-pure water have relative higher Ag releasing within 1hour water jet abrasion. Almost half of the Ag was leached out after sprayed by water jet for 1 hour, showing nano-pure water has the highest Ag leaching.

Table 3.11 Percentage Ag Remaining After 1hour Water Jet Wash

Percent of Ag Remaining		
%	Exposed	Covered
pH5	62.9 ± 6.88	94.5 ± 15.5
pH5_Cl	90.9 ± 8.33	93.7 ± 9.20
pH10	71.3 ± 8.62	89.9 ± 15.0
DI	53.5 ± 6.90	92.2 ± 7.58

3.2.4.2 Ag Leaching Trend of Water Jet Test Method

Water samples were taken at 5, 15, 30, 45, and 60 minutes when applied nano-pure water, pH5 (w/o Cl-) and pH10 solutions to spray the Ag-coated membrane. Both Ag nanoparticles (AgNPs) and Ag ions were examined by ICP-MS. Figure 3.15, 3.16 and 3.17 show the AgNP and Ag ions concentration changes over time for nano-pure water, pH10 solution and pH5 (w/o Cl-) solution, individually.

Comparing the concentration of AgNP in different extraction solutions, shows that AgNP in nano-pure water group was keeping in a constant centration, in pH 5 (w/o Cl^-) solution it increased after 30 minutes, and in pH 10 solution it was decreased over time. For total silver concentration, it was increased in relation of the time in both nano-pure water and pH 10 solution. The increase of total silver means that the silver was continues releasing from the membrane. The oxidation of Ag (0) and physical abrasion can be assumed as the two main mechanisms for silver leaching from RO membranes. The oxidation process can make the silver released in the form of Ag+. The physical abrasion may cause more silver nanoparticles released to water, however, the released AgNP in liquid phase may also be oxidized to Ag^+. Because of the Ag+ is hard to be reduced to Ag (0) without a reductant, the increase of AgNP in pH5 group indicates that the AgNP was continues leaching from the membrane during the one-hour water jet wash. Moreover, the release of the AgNP was caused by the physical abrasion of the high velocity water flow. The decrease of the AgNP concentration in pH10 solution and consistency of the AgNP concentration in nano-pure water because of the oxidation of AgNP in liquid phase.

The total silver concentration in pH5 (w/o Cl^-) solution decreased after 30 minutes, which may because of the silver ions attached at the water jet set-up. The results of pH10 and pH5 (w/o Cl^-) groups need more replicated experiments to improve its’ reliability.

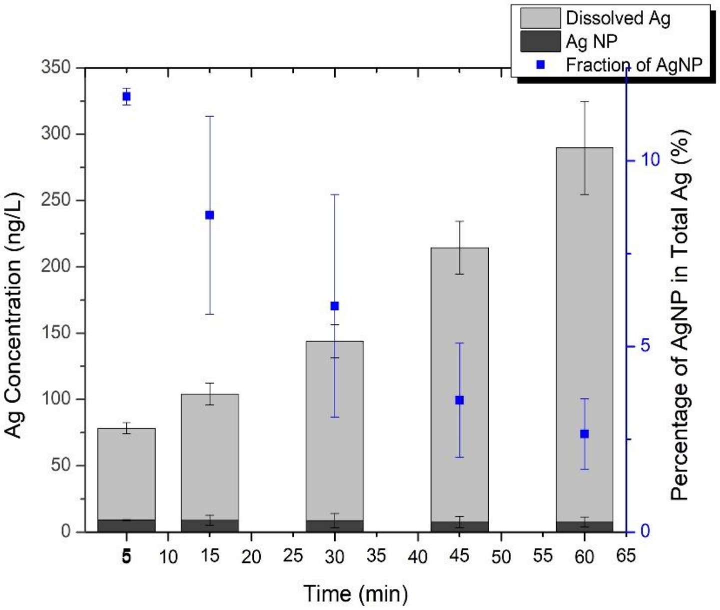


Figure 3.15 Ag Leaching Trend of Water Jet Test (Nano-pure water)
(Exposed membrane area 0.32 cm^2)

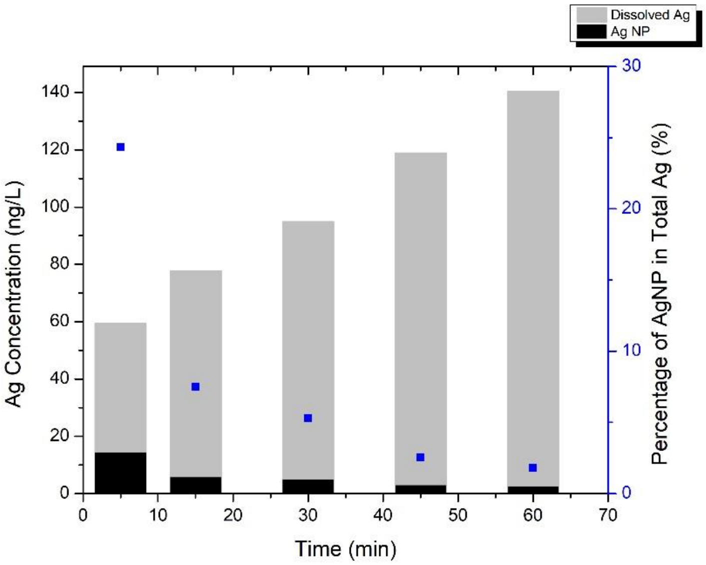


Figure 3.16 Ag Leaching Trend of Water Jet Test (pH10)
(Exposed membrane area 0.32 cm^2)

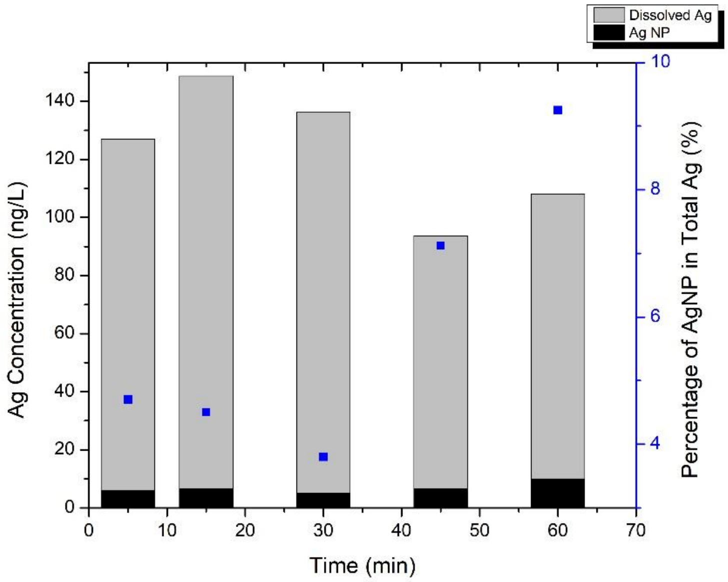


Figure 3.17 Ag Leaching Trend of Water Jet Test (pH5 without Cl^-)
(Exposed membrane area 0.32 cm^2)

3.2.4.3 Comparison of Batch Test and Water Jet

Plotted the total silver released of the batch test only for the first hour is shown in Figure 3.18. Comparing the silver leaching concentration of the batch test and the water jet test, shows that the silver concentration leached out from batch test (25 ppb to 55 ppb) is much bigger than water jet (0.07 ppb to 0.3 ppb). The variances of the impacting membrane area and the volume of extraction solutions of the two leaching methods made the two methods difficult to be compared directly with their silver leaching concentration. Therefore, the percentage of silver remaining on the membrane after one hour leaching test was compared for batch test and water jet. For batch test, there are 85 ± 1.2 % of silver was remained at the membrane after soaking the membrane for one hour. For water jet, 54 ± 6.9 % of silver was remained at the exposed area after one-hour water jet wash. The water jet can cause more percentage of silver leached out than batch test in a one hour leaching test.

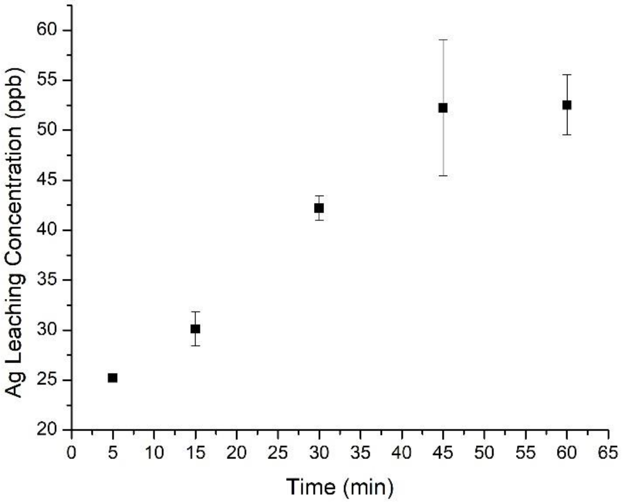


Figure 3.18 Ag Leaching Trend of Batch Test for One Hour (sa/vol = 122 cm^2/L)

3.2.4.4 Mass Balance

Mass balance of the water jet test was done to verify the results of the experiment. Ag total measured is the sum of Ag remaining in the exposed area, Ag remaining in the covered area, and Ag released to water. The mass balance calculations are shown on the last column of Table 3.12. The calculated mass balance for all four groups are within ± 75%. As consider the silver was not perfectly uniformed loaded on the membrane, the 25% losses can be regarded as an acceptable error for this experiment. The directly contact of rubber gasket and covered membrane surface, silver attached in the water tubing, and silver attached on the Water Jet Cell may cause the silver loss in the mass balance calculation.

Table 3.12 Mass Balance of Water Jet

	Silver Mass (ug)					Mass Balance (%)
	Remain in Exposed Area	Remain in Covered Area	Leached to Water solution	Ag Total measured	Initial Loading	
pH5	0.46 ± 0.12	4.9 ± 0.07	0.05 ± 0.03	5.4 ± 0.22	6.0 ± 0.93	93 ± 13
pH5_Cl	0.70 ± 0.11	5.1 ± 0.50	0.08 ± 0.04	5.9 ± 0.64	6.2 ± 0.76	95 ± 1.0
pH10	0.59 ± 0.15	5.3 ± 0.12	0.11 ± 0.08	6.0 ± 0.22	6.7 ± 1.4	91 ± 14
DI	0.27 ± 0.04	3.3 ± 0.54	0.08 ± 0.03	3.7 ± 0.58	4.1 ± 0.70	89 ± 6.0

3.3 Comparison of Four Leaching Test

The choice of a leaching test method is not single-element-dependent. The performance of each leaching method, the cost of the method, the equipment needed for the test, and the time you can spend on the experiment etc. can all influence the choice of leaching test method. The comparison of the four leaching test methods is shown in Table 3.13.

3.3.1 Comparison of Silver Leaching Results

The silver loading amount that remained on the membrane, silver concentration leached to water, percentage of the silver remaining on the membrane, and the error range of mass balance are compared to determine the performance of each leaching test methods.

The cross-flow test has the lowest silver remaining among the four types of leaching test, which is 0.22 ± 0.15 ug/cm^2, as shown in Table 3.13. Because of the initial loading of the membrane that had been used in each test are inconsistent, the percentage of the silver remaining on the membrane are also examined, which shows that the cross-flow test still has the lowest silver remaining percentage. The cross-flow filtration process is designed to simulate the operating process of spiral wound filtration cell (the most commonly reverse osmosis membrane application), therefore, the silver leaching in realistic scenarios may be closer to the leaching results of the cross-flow test. The water jet test and batch test have a similar percentage of silver leached out during the leaching test, which have 40 to 60 percent of silver released. The dead-end test has the lowest silver leaching in the four tests, which only causes less than 2% of silver releasing.

The silver concentration of the water samples that collected from the four leaching tests varies a lot. For the water jet test, the silver concentration in the recirculated extraction water are all below 1 ppb. The highest silver concentration measured in the batch test is around 100 ppb which is close to the NSDWs for silver. However, the surface area to volume ratio of the batch test has an influence on the leached silver concentration, which may cause the variance of silver leached concentration. For the dead-end test and cross-flow test, the silver concentration of both concentrate and permeate for both tests are extreme low compare to the NSDWs.

The release of AgNP was also examined for all four leaching test methods. The AgNP can not be detected in the batch leaching test. Except batch test, the AgNP was detected in other three leaching methods. The dead-end test has the highest AgNP leaching concentration, which may because of the high effective membrane area to extraction solution ratio of the dead-end test. Also, because of the dead-end test set-up is an air-tight equipment which may influence the oxidation process of the Ag (0), the AgNP concentration may also be influenced by this.

The errors of mass balance of the water jet test, batch test, and dead-end test are all in the acceptable range. Because the scalability of the cross-flow test, the silver loss from the initial condition is relative higher than the other three tests.

3.3.2 Comparison of the Operation Parameters of Each Leaching Tests

The operation time for each leaching test, water required for the test, size of the nano-composite membrane needed for leaching test, and the capital costs of the leaching test' set-up are compared as the operation status.

The water jet test has the shortest operation time than other three test methods, which only consumes 1 hour to operating the leaching test. The batch test was following the NSF/ANSI 61 which indicated the extraction time should be 3 days at least. The operation time for the RO dead-end test had been reported was generally from 1 hour to 8 hours[20]. The operation time for high pressure membrane cross-flow test is generally counted by day.

The cross-flow set-up needs the highest volume of water solutions to operating the leaching test. Other three test methods only need less than 1 L water to do the leaching test. The membrane consumed for the leaching test need to be considered because of the time-consuming of the fabrication process of nano-composite membrane. The water jet shows the most economy membrane usage in the four test methods.

Generally, a dead-end filtration cell for high pressure membrane costs more than 2000 dollars. A cross-flow filtration cell needs more than 10000 dollars. To build up a water jet set-up, about 350 dollars is needed including the pump. For a batch test, a shaker is needed which may cost 200 to 400 dollars. After comparing the set-up costs of each leaching test methods, the batch test set-up and water jet set-up need less budget than dead-end filtration and cross-flow filtration. However, dead-end filtration cell and cross-flow filtration cell are more useful than other two set-ups which may be more worth to spend the money on it. Therefore, the choice of the leaching test method is depending on what is needed for your experiment, which set-up is easier to be built in your laboratory.

Table 3.13 Comparison of the Performance of the Four Methods

	Categories	Unit	Water Jet Test	Batch Test	Dead-end Test	Cross-flow Test
Ag Leaching Results (Nano-pure water)	Ag remaining on membrane	ug/cm^2	0.86 ± 0.14	1.1 ± 0.09	2.1 ± 0.04	0.22 ± 0.15
	Ag concentration leached in water	ppb	< 1	0.3 ~ 100	0.3 ~ 10	2 ~ 15
	AgNP concentration	ng/L	~ 10	0	30 ~ 100	10 ~ 40
	Percentage of Ag Remaining	%	53 ± 6.4	36 ± 9.5	98 ± 0.32	13 ± 2.6
	Error Range of Mass Balance	%	± 25	± 30	± 30	± 95
Operation Parameters	Operation Time	hour	1	72	4	50
	Water Assumed	L	1	0.12	0.2	23
	Membrane Assumed	cm^2	2.5	4.9	15.5	42
	Cost of the set-up	$	~ 350	200 ~ 400	> 2000	> 10000

CHAPTER 4

SUMMARY AND CONCLUSION

The major conclusions of this study include:

- Four membrane leaching methods which include batch test, dead-end filtration, cross-flow filtration, and water jet test were all developed and finished the leaching tests
- Silver nanoparticle was impregnated in RO flat sheet membrane, the silver loading on the RO flat sheet membrane varies from 0.5 ug/cm^2 to 1.9 ug/cm^2; the same in-situ coating method was also adapted to impregnate the silver directly in the spiral wound RO element, the silver loading of the spiral wound coating method is 2.0 ± 0.51 ug/cm^2
- For all the leaching tests, the silver remaining on the membrane and silver released into the solutions were examined, and conducted the mass balance for each leaching test. The mass balance for the batch test, water jet test, and dead-end filtration are all within 100 ± 25 %, which is acceptable in this experiment; bad silver mass balance was observed at cross-flow filtration which may because of the attachment of silver ions in the cross-flow set-up and a large amount of water samples were taken out during the cross-flow operation
- The cross-flow test causes the highest percentage of silver released, more than 80% of silver released, and both Ag ions and AgNP can be released due to the hydraulic abrasion and oxidation reactions; the batch test can cause 60% of silver leaching in three-day, but the silver was only exist as the form of ions in the extraction solutions which means the oxidation is the major silver release mechanism in batch test; the water jet test caused nearly 50% of silver released in the one-hour leaching test, the silver released was exist as both AgNP and Ag ions; the dead-end filtration also caused both AgNP and Ag ions released, but there are only less than 2% of silver released after the four-hour leaching test
- The pH of the extraction solution will influence the silver release from the RO membrane, according to the results of the batch test, silver release can be restrained in the alkalinity

environment, which is probably because of the high redox potential of the Ag (0) in high pH

- The percentage of silver leaching from the membrane of the four leaching methods can be ranked as: cross-flow > batch test > water jet > dead-end
- The batch test is the easiest to be replicated leaching test among the four leaching methods
- The water jet test is the most cost-effective leaching method that can be used in the membrane leaching test. As both cross-flow and dead-end tests need heavier workload and more consumption of resource, the batch test and water jet test can be used to replace the cross-flow and dead-end to do the leaching test. Moreover, the water jet can cause higher silver leaching than batch test in one-hour, and it can also cause both AgNP and Ag ions leaching from the membrane, which is closer to the leaching condition in cross-flow test
- The silver releasing concentration from all the four leaching tests are all below the Secondary Drinking Water Standard for silver which is 100 ppb

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