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Silver-based Microbial Check Valve for Spacecraft Potable Water Systems

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For my honors thesis I attended the 29th annual Waste-Management Education Research Consortium in Las Cruces, New Mexico. My team's task was to design a "Silver-based Microbial Check Valve for spacecraft potable water systems." This device would improves the waste water purification system in spacecraft such as the International Space Station.

My role on my team was to assist the team and research coordinator. My duties included assigning tasks to team members, analyzing experimental data, collecting technical papers, creating computer simulations, checking work for accuracy and completion.

My team and I started this project in the second week of January, and it had to be presented in early April. In the first weeks, my team spent most of the time collecting information that could help us to evaluate an innovative way to fulfill the task. Past works were reviewed in order to fully understand current spacecraft potable water systems. The main goal of our task was to deliver 300-500 parts per billion of silver ions to a stream of deionized water. Two approaches that have been fully studied were the electrochemical generation of silver ions and the delivery of silver ions by an ion-exchange resin. However, based on our literature review, our team decided that these methods were not practical. Therefore, we decided to develop a new method. The use of membranes for the delivery of silver ions was an option that was never considered before. After some experiments and simulations, we were able to confirm that the delivery of silver ions to a stream of deionized water by a dialysis membrane was possible. Thus, we decided to run long term experiments to collect enough data. I was in charge of running most of the long term experiments with the membranes and the analysis of the results since I was the group member that had the most laboratory research experience. During the data analysis process, I was able to apply my knowledge of Microsoft Excel, MATLAB and COMSOL Multiphysics. Even though COMSOL Multiphysics is not taught nor required in any chemical engineering class, being able to use it allowed me to be a crucial group member, especially for the analysis of the data.

Throughout this project, I was not only able to gain knowledge about spacecraft potable water systems but also I had the opportunity to learn to work alongside my peers. As an international student, I was capable to approach every problem in a different way, and I always felt welcome by my teammates and faculty. Our design was innovative and efficient, therefore;

we were able to patent the technology. I am very proud of the work I did for my Chemical Engineering honors thesis and the Waste-Management Education Research Consortium.

University of Arkansas

Task 1: Silver-based Microbial Check Valve for Spacecraft Potable Water Systems

WERC 2019

WERC 2019

Task #1

March 18th, 2019

Hogs in Space

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EXECUTIVE SUMMARY

As human space exploration increases, the development of a more efficient potable water treatment system suited for spacecraft becomes crucial. This Waste-management Education Research Consortium (WERC) challenge was designed to explore the viability of microbial control through the utilization of silver ions as a biocide for possible integration into the Tranquility Node 3 water purification system aboard the International Space Station (ISS). Current systems using iodine risk causing hyperthyroidism from overexposure; however, silver can be safely ingested without this side effect. After researching silver delivery methods including electrochemical ion production, controlled release, or a combination of the two, our team decided to design a controlled release system capable of meeting the constraints listed in the problem statement. By using a membrane similar to those within dialysis devices a system was designed to deliver silver ions to a stream of water that requires arguably no power and is exceptionally lightweight. While the silver delivery system fulfilled the constraints of the WERC problem statement, our team also examined the use of resins like those contained in the current Microbial Check Valve (MCV). Resin substitutes capable of selective silver sorption are recommended as replacements for those within the current MCV to prevent backwards microbial diffusion through the system. Multiple designs will be presented in this paper. First, our membrane-controlled release silver delivery system (SDS) is presented to specifically address the WERC Task 1 deliverables. Second, a proposed upgrade to the ISS water system is described that replaces the ion exchange resin beds with silver-selective media prevent microbial contamination of water in the potable water system of the spacecraft. Given the extreme lightweight nature of the SDS, nil power requirement, and minor modification to the existing system, *Hogs In Space* has delivered a highly effective method to deliver and control silver based on the WERC Task 1 requirements.

1.0 INTRODUCTION

1.1 BACKGROUND

On the International Space Station (ISS), two primary water filtration systems currently exist: NASA’s water processing system (WPS) located in The Node Three Tranquility module and Russia’s equivalent system on the Zvezda module.[1] Although both possess processing and filtering capabilities for water recycling within the station, a distinct difference in technology exists; the Node Three WPS utilizes iodine for bacterial control, whereas the Zvezda system utilizes silver ions. In contrast, not much is known about the composition or function of the Zvezda system in the United States. However, it is known that the system is based upon the "Mir" three-line collection system with a silver ion biocide, possibly delivered by electrodialysis or electrodeionization.[2] Nevertheless and regardless of mechanism, the hypothesized Russian method of delivery was not considered a viable solution by *Hogs In Space* due to complexity, power requirements, and the possibility of exceeding the weight constraint of the WERC Task 1. Speculation regarding the composition of the system will be addressed in section 1.2.

To adequately address the WERC task, it was necessary to develop an understanding of the WPS in Node 3. Operation of the WPS follows the configuration shown in Figure 1 of the water processing assembly (WPA) in the Environmental Control and Life Support Systems (ECLSS) rack configuration. Specific to WERC Task 1 is a consideration of the Microbial Check Valve (MCV) shown in the schematic, targeted for potential improvements by a new and innovative design. Fluid flows through the MCV intermittently when the rejection line bypass is active, retaining water in the WPA circulation loop until deemed "pure" and sent to the product water tank. Although designated a check valve, the MCV is not a mechanical valve but instead a "check valve" for microbial flow between the incoming waste line and the processed product line. The current WPA utilizes an iodine-based ion exchange bed, which is an effective biocide delivery system, but eventually requires removal of the iodine ions from the water before consumption.[2] Potential utilization of the alternative, a silver biocide system tasked by WERC, may allow for elimination of the iodine delivery and removal steps by providing an acceptable level of silver ions for drinking water whilst continuing to inhibit microbial contamination flowing through the "check valve."

Power for the WPA and ECLSS systems come from the primary bus or secondary bus power systems. The power management and distribution system distributes power from the primary bus system at 160V DC or from the secondary bus system at 120V DC through Buck converter units.[3]

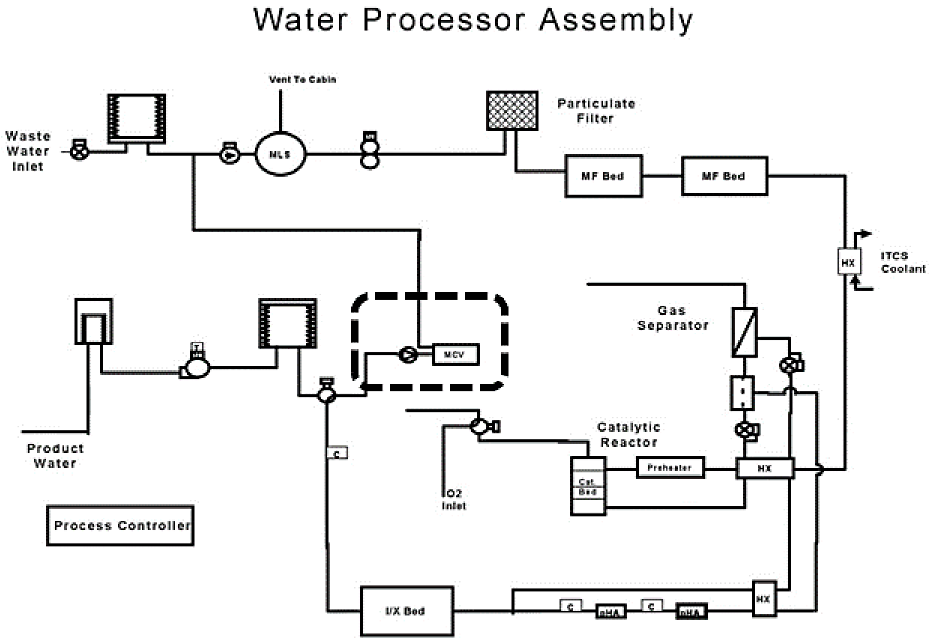


Figure 1: Current WPS rack configuration with the current Microbial Check Valve portion highlighted.[4]

1.2 CURRENT IODINE-BASED MICROBIAL CHECK VALVE DESIGN

The development of the original iodine-based MCV arose from the need to supply potable water for long-term space missions. The Apollo program was the first attempt to extend the duration of space exploration by astronauts; therefore, the foundation for what would become the MCV began with the introduction of a potable water system in the Apollo spacecraft. The Garrett Airesearch Manufacturing Division (Los Angeles, California) developed an electrolytic water sterilizer that was capable of delivering silver concentrations of 50 to 100 ppb to effectively kill microbes in the Apollo spacecraft water system.[5] Even though this system was used in the Apollo missions, it was later abandoned. It was not present in further exploration programs such as the Space Shuttle Orbiter and the ISS. The available literature is inconsistent about the reasons the electrolytic water sterilizer was discontinued after the Apollo missions. It is noteworthy that the National Aeronautics and Space Administration (NASA) cataloged "*the prime reason for the change was that qualification testing of the silver-ion generator indicated erratic performance and would have required additional expenditures for further development*" according to the creators of the current iodine-based MCV.[6] In contrast, the iodine-based MCV, which was developed by Umpqua Research Company (Myrtle Creek, Oregon) for NASA, is an integral piece of equipment within the circulation loop of the WPA. It prevents microbial back contamination of the potable water that occurs during backflow or stagnant conditions (microorganisms can diffuse in the opposite direction of normal flow). The unit contains a quaternary ammonium anion-exchange resin combined with a triiodide complex, which kills microorganisms with nearly 100% efficiency as contaminated water flows through the unit.[6] However, it has been shown that some components of the reclaimed water streams such as urine, wash water, and humidity condensate can induce excessive stripping of iodine from the resin bed which in turn increases the iodine content in the product water and shortens the life of the resin bed.[7] Therefore, an extra step must be added to remove the iodine before it is consumed by astronauts, not only to improve the taste of water but also to avoid potential adverse effects of iodine on the thyroid. High levels of iodine (<5 mg/L) can increase susceptibility to hyperthyroidism. Hyperthyroidism accelerates the body's metabolism, which can lead to weight loss and irregular heartbeat.[8] The iodine-based MCV that is currently used in the ISS's water processor assembly allows product water to meet the maximum allowable microbe concentration of < 1 CFU/100 mL.[9]

Figure 2 shows the original design for the iodine-based MCV. According to the Umpqua Research Company, the iodine-based MCV features the following characteristics:

1. Small volume and weight.
2. Highly effective in killing bacteria, fungi and viruses.
3. Low pressure drop.
4. Equally effective with flow in either direction.
5. Low iodine residual in product water (at optimum reclaimed water conditions).
6. Low cost.
7. Long operational life (up to 1800 days).
8. Insensitivity to spacecraft operating conditions, i.e., Pressure and temperature).
9. Resin can be replaced easily.
10. Simple interface.
11. No moving parts.
12. Requires no electric power.

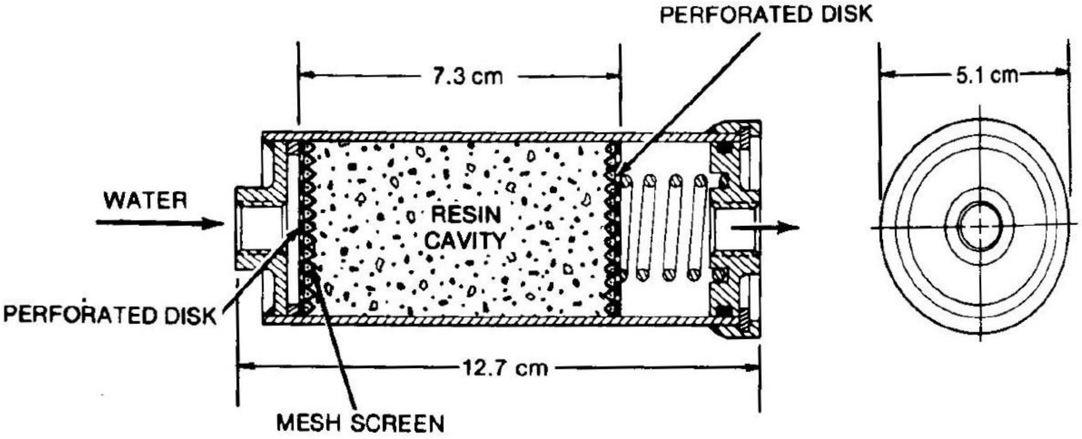


Figure 2: Current Iodine-based Microbial Check valve (retrieved from NASA Tech Briefs).

1.3 POTENTIAL DESIGN OF THE RUSSIAN SYSTEM

Since the Russian system lacks a clear public description of design and capabilities, the details of the system are left to speculation. Based on the MIR base design specifications used for the Zvezda, an electrolytic ally silver salt system may be likely the silver delivery method.[1] However, since a silver salt is mentioned in literature, it can be inferred that the electrolytic portion of the system is not merely an anode and cathode combination that oxidizes Ag^0 to Ag^+. Further examination of the strict constraints of water type and mineral content implies that electrodeionization (EDI) or electrodialysis (ED) likely delivers silver to the system.[1] ED or EDI uses current to drive the migration of ions or charged materials within an electric field, and has been used in a variety of applications in the food and beverage industry. Owing to its complexity, our WERC team chose to forgo this as a potential treatment option.

1.4 ALTERNATIVE WATER STERILIZATION METHODS

Literature on several water sterilization alternatives to the current WPA were explored to provide context for our design: boiling treatment, bleach treatment, and iodine tablets. According to the EPA, boiling water for one minute and allowing it to cool at room temperature provides adequate sterilization of contaminated water. However, boiling water requires a large amount of energy and creates complications for continuous water treatment. Alternatively, adding a small amount of bleach to contaminated water in the range of approximately 80 to 160 parts per million, can kill nearly all harmful organisms when allowed to sit for 30 minutes; however, this treatment process creates an unpleasant taste[10]. Additionally, it is the opinion of *Hogs in Space* that the delivery of caustic material in the form of liquid or powder would be an unacceptable flight risk. Both bleach and heat treatment kill bacteria by denaturing key proteins within the cell.[11] Commercial iodine tablets could be used in principle to sterilize batches of water; however, these tablets are typically used in emergency circumstances.

1.5 POTENTIAL SILVER BASED SOLUTIONS

Electrochemical *in situ* ion generation and controlled ion release were examined by *Hogs In Space*. Silver ion generation through an electrochemical process has an appeal because ions are continuously produced so long as elemental silver is present in the system and a current is applied. Previous studies have shown that electrochemical processes are more complicated, require power, and are prone to electrochemical plating. Controlled release is another option for delivering silver ions. *Hogs In Space* focused on are two methods for controlled release: membrane- or resin- based. These are simplistic options that can run autonomously until they need to be replenished and in fact are similar to the current iodine based MCV. In principle, a combination of the two controlled release methods will not only be helpful in replenishing silver ions but also provide a familiar configuration of the WPA. In the end, because of the task requirements and system reliability, *Hogs In Space* chose the controlled release option over electrochemical methods due to its simplicity.

1.6 SILVER'S DISINFECTING PROPERTIES

The practical antimicrobial attributes of positively charged silver ions were first unknowingly exploited by early civilizations such as Egyptians, Romans, Greeks, and Phoenicians. Before recognizing the harmful effects of microbes, these societies empirically utilized molecular forms of silver mainly to preserve food and water (e.g. silver containers), and to therapeutically treat diseases and injuries (e.g. silver nitrate solutions).[12] Contemporary research has allowed us to understand the antimicrobial mechanisms of silver species and determine when silver needs to be selected over other disinfectant alternatives. Several studies have confirmed silver to be a biocide for some fungi (e.g. *Aspergillus niger, Candida albicans and Saccharomyces cerevisiae*), viruses (e.g. hepatitis B, HIV-1, syncital virus, and norovirus), a spectrum of Gram-positive bacteria (e.g. *Bacillus, Clostridium, Enterococcus, Listeria,* *Staphylococcus and Streptococcus*) and a wide-ranging group of Gram-negative bacteria (e.g. *Acinetobacter, Escherichia, Pseudomonas, Salmonella and Vibrio*).[13] The antibacterial mechanism of silver is exclusively carried out by silver cations after being delivered from silver nanoparticles, oxidation or delivered directly from silver salts. The positively charged ions interact with the cell membrane of microorganisms, causing membrane rupture.[14] The interaction between the silver ions and the negatively charged lipids of microorganisms' cell membrane triggers cell lysis. Within the cell, this manifests as other effects such as the degradation of components of DNA replication and energy-yielding electron transport chains.[15] Not only is silver a versatile agent against microbiological flora, it is also a non-toxic substance to humans at biocidal concentrations. Humans excrete most consumed silver which is different from other metals that are accumulated in the body such as lead and mercury.[16] The United States Environmental Protection Agency (EPA) has imposed drinking water standards limiting concentration up to 0.1ppm.[17] In contrast, other water disinfectant alternatives require high concentrations that are not suitable for long space missions, demand biocidal concentrations that are lethal to humans, and worsen the taste of water. The only other alternative with biocidal activity is copper; however, its efficacy comparatively requires higher concentrations than silver.[18, 19] Thus silver possesses the necessary disinfecting characteristics for an efficient and simple spacecraft potable water system, hence the continued interest by NASA.

2.0 TASK PARAMETERS

2.1 TASK REQUIREMENTS

The apparatus for consideration of silver delivering must be able to process 5 gallons of water that is provided in the bench scale demonstration. The process stream of deionized water must flow at 100 to 150 mL/minute whilst maintaining a concentration of silver within a 300 to 500 ppb range. The apparatus must be able to operate in ambient temperature and under pressure up to 30 psig, while operating within a pH range between 4.5 and 9.0. Due to launch weight considerations, the apparatus must weigh less or equal a total weight of 5 kilograms. The apparatus must also be small, robust, and require little maintenance.

2.2 FLOW RATE DISCREPANCIES

Per WERC task objectives, *Hogs In Space* designed a system for a product treatment water flow of 100 to 150 mL/minute. However, in researching the application requirements for the anti-microbial check valve as well as the maximum rated load of the WPS, a discrepancy arose. In multiple sources, the average daily product water flow rate is given at approximately 28 lbs/day, or 8 mL/minute for the WPS system.[9] This average flow is an order of magnitude lower than the prescribed minimum flow rate of the task. Furthermore, in an examination of the specifications for the design, the maximum demand on the WPS is rated for is a seven-person crew load, totaling to a maximum processing flow of approximately 65 mL/minute.[4] This flowrate is still far lower than the prescribed 100 to 150 mL/minute flow requirement. Flow discrepancies would have an impact on the technological choices. This flow discrepancy was brought to the attention of WERC and ultimately the flow requirement was unchanged.

2.3 PUBLIC INVOLVEMENT

American astronauts residing on the ISS and astronauts on future long-term space missions would be directly affected by the proposed design. The motivation behind changes to the current system should be explained to astronauts with experience using the current system. Recommended training regarding the new system would involve operations, maintenance, and troubleshooting. Feedback from the astronauts directly affected by the system changes would increase the reliability of the new WPS. Procedures regarding the WPS would need to be updated to reflect the needs of the new components.

3.0 RESEARCH

3.1 SILVER SALT ALTERNATIVES

When deciding which silver salt to use, we adhered to the following guidelines: safety for human consumption, medium to high solubility, and compatibility with the materials in the system. Silver nitrate was rejected not only because of its low solubility, it also was rejected because of its toxicity and corrosive nature. The two main options investigated were silver citrate (solubility, 0.0284 g/L) and silver lactate (solubility, 77 g/L). Unlike silver nitrate, both salts are also food grade. When creating solutions ranging from 50 ppb – 1500 ppb it was observed that silver citrate did not easily dissolve into the solute at high concentrations while the silver lactate dissolved at all concentrations. Acid was added to the silver citrate solution to make it dissolve.

3.2 MECHANISMS OF SILVER DELIVERY

Considering the methods of silver delivery, *Hogs In Space* decided to pursue a design that uses controlled release methods. The release of silver by a membrane cartridge allowed for a consistent release of silver ions at the desired concentration range to meet the task requirements. The proposed use of resins capable of efficient silver uptake are also discussed as possible upgrades to the current resin beds within the WPA.

3.3 MEMBRANES AS A CONTROLLED DELIVERY SYSTEM

A controlled delivery system is a process that exploits one or multiple mechanisms to discharge an amount of material at a constant or varying rate from a saturated source to a target domain. Controlled delivery systems have been primarily studied for drug delivery applications in medicine. The main benefit of using a controlled release of a substance is the prolonged duration of action with a simple design. Figure 3 illustrates the controlled delivery of silver ions. Release will proceed at a constant rate if a stable concentration gradient across the membrane is present, and this stable gradient is maintained by providing excess silver ions within the membrane cartridge and selecting a membrane with a proper diffusion rate. Our experimental results with our SDS have shown that it is possible to force a pseudo-constant delivery rate due to the low permeation rate of silver across the test membranes. Furthermore, the concentration of silver in the saturated reservoir remained somewhat constant due to mass balance constraints. While it is true that the delivery rate will drift with time and conditions of the water may change the system can adapt to these circumstances by the equipment configuration of our final designs.

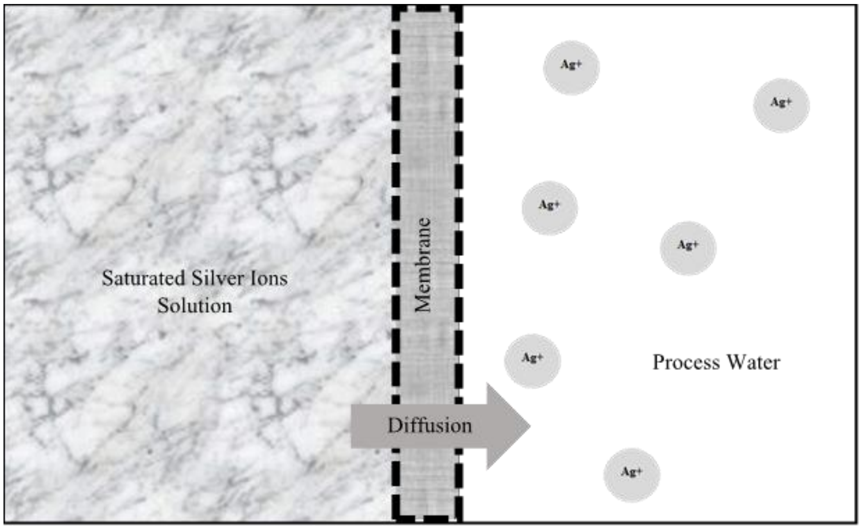


Figure 3: Silver Controlled Delivery Mechanism.

3.4 WATER TREATMENT RESINS

Ion-exchange resins effectively adsorb contaminants that are present in water, exposing them to silver within the resin bed. A consistent concentration of biocidal silver ions is required to prevent bacterial in-line contamination through back flow from a MCV. A triiodinated ion-exchange resin is currently used in the MCV on the ISS. The same principle could be utilized by using a silver-loaded resin. Literature provided information about chelating ion-exchange resins with high affinity for silver. Two ion-exchange resins were obtained: AMBERSEP™ IRC748 and AMBERSEP™ GT74. The IRC748 resin is made up of a styrene-divinylbenzene matrix with an iminodiacetic acid functional group, which is effective at removing metals from water. The GT74 resin has a styrene-divinylbenzene matrix as well but includes a thiol functional group. The GT74 resin effectively removes metals from water but also is advertised to have a higher affinity for silver ions.

3.5 MICROGRAVITY CONSIDERATIONS

Since the design would be implemented in spacecrafts, operation in microgravity must be fully understood. To ensure fully developed flow, positive displacement pumps would be specified for any design. Air pockets within the piping system in space would cause an issue for the flow of water in the system, therefore the smallest diameter tubing should be used. Finally, if any design modifications are needed to account for microgravity, flow fluctuation could be modeled in COMSOL Multiphysics.

4.0 EXPERIMENTAL PROCEDURES

Preliminary experiments were conducted to gather information regarding the biocidal effectiveness of silver lactate solutions, the resin's silver ion release rate, the permeation rate of the membranes, and the biocidal effectiveness of silver-loaded resins.

4.1 BIOCIDAL EFFICACY OF SILVER SOLUTIONS

Hogs In Space first wanted to confirm that the silver ions introduced into the system at the required concentration of 300-500 ppb would effectively inhibit bacterial growth. First experiments exposed *E. coli* to prepared solutions of 50, 250, 500, 750 and 1500 ppb silver lactate and silver citrate in deionized water. Inhibition of microbial growth was determined by using a spectrophotometer. Spectrophotometer readings were measured at an absorbance of 600 nm, a wavelength commonly used to quantify the growth of cells. The 1500 ppb solution of silver lactate and deionized water was made using 500 mL of deionized water and silver salts. Before subsequent dilutions were performed, the concentration of the 1500 ppb solution was checked in the lab using inductively coupled plasma mass spectrometry (ICP-MS) to confirm lack of silver plating on containers. Once all dilutions were performed, the solutions were well mixed and measured out into 50 mL test tubes before introducing *E. coli*.

Approximately 2 mL of *E. coli* in lysogeny broth (LB) was mixed with the silver salt solutions and given approximately three hours to mix before data recordings were taken to determine the effectiveness of silver salts as antimicrobials.

4.2 SILVER ION RELEASE RATE FROM RESINS

Two chelating resins, one containing iminodiacetic and the other thiol groups, were loaded with silver. The AMBERSEP™ IRC748 and AMBERSEP™ GT74 resins are macroporous cation-exchange resins with pronounced selectivity for silver cations. The AMBERSEP™ IRC748 resin originally contains sodium cations while the AMBERSEP™ GT74 resin has hydrogen cations. A solution of silver lactate was prepared based on the total exchange capacity of the resins (1.35 eq/L). The silver solution (20 mL) was mixed with 2.25 grams of resin for one hour inside a 40 mL beaker. The resins were then filtered out using a sintered glass funnel and the supernatant solution was collected for ICP-MS. Furthermore, some drops of a concentrated sodium hydroxide solution were added to a small volume of the filtrate to quickly test for the presence of silver by looking for any silver hydroxide precipitate. After the resins were saturated with silver, a silver release rate test was performed. The resin was added to 300 mL of deionized water and the suspension was mixed for three hours in a baffled beaker. Conductivity measurements were obtained using a conductivity probe (SympHony SP70C) to measure the silver ion concentration. Each conductivity reading was repeated at least once, and the silver levels were calculated using a calibration curve.

4.3 MEMBRANE PERMEATION RATES

Three types of membranes were utilized as controlled delivery medium, referred to as Membranes I, II, and III in subsequent sections of this report. Membrane differed by composition of membrane and format. The first experiments were made with Membrane I, a Biotech cellulose ester dialysis membrane (Spectrum™ Spectra/Por™) to prove silver could be successfully released from a high concentration solution at a reasonable permeation rate. The cellulose ester sack dialysis membrane was loaded with a 1 g/L solution of silver ions and it was submerged in 450 mL of deionized water. The increase in silver concentration was determined by measuring the conductivity of the water in which the membrane was immersed over five hours.

Eventually, success with Membrane I led to experiments with two other membrane compositions and formats. Systems II and III are similar in configuration to continuous dialysis systems with a high concentration of silver reservoir used to deliver silver ions at a controlled rate. System II was charged with 20 g/L, whereas System III contained a recirculating solution of 1 g/L silver salt.

4.4 BIOCIDAL EFFICACY OF SILVER-LOADED RESINS

The AMBERSEP™ IRC748 resin that was previously loaded with silver was used for the initial growth inhibition tests. A 20 mL solution of *E. coli* bacteria in LB was combined with 100 mL of deionized water and 2 grams of the resin. The total solution was mixed in a baffled beaker with a magnetic stir bar for 5 hours. By means of a syringe filter, resin was removed from samples and the corresponding resin-free fluid was placed in a spectrophotometer to monitor *E. coli* growth every 15 minutes.

5.0 EXPERIMENTAL RESULTS AND DISCUSSION

5.1 SILVER SOLUTIONS BACTERIAL GROWTH INHIBITION TESTS

Figure 4 shows the *E. coli* kill tests using silver salts at 1500 ppb and 50 ppb. In contrast to merely inoculating an aqueous solution of silver salt, LB was also present to simulate a (worst case) scenario whereby cells are provided a rich medium to grow. At 1500 ppb, silver lactate completely inhibited bacterial growth the bacteria in as little as three hours while it took the silver citrate approximately five hours at the same concentration. At 50 ppb, neither of the salt solutions effectively eliminated *E. coli*, for the bacteria continuously grew during the 8-hour experiment. With the design limit only allowing for 500 ppb of silver in water solutions, further experiments at lower silver concentrations were performed.

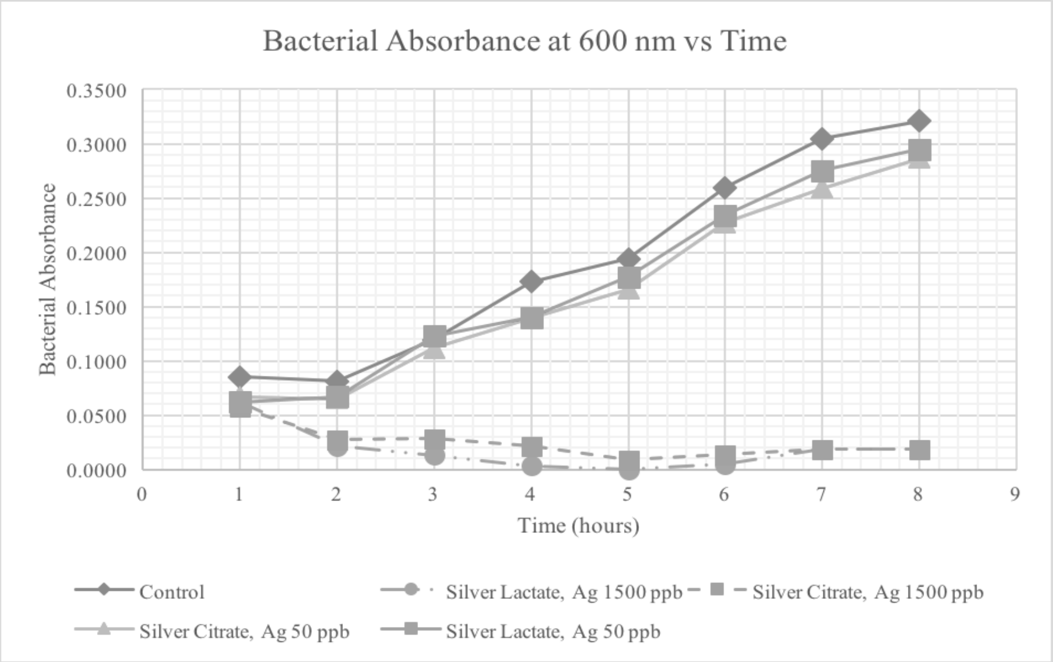


Figure 4: Bacterial absorbance in solution with silver ions at 50 and 1500 ppb from silver lactate or silver citrate.

Table 1 shows the results for the second bacterial kill test using silver lactate and silver citrate at 250, 500 and 750 ppb. This experiment was performed similarly to the first. In total there were six experimental solutions plus a control, with the effectiveness of silver salts compared to the control of zero addition. As seen in Table 1, at any given concentration, silver lactate performed better than silver citrate in microbial growth suppression.

Table 1: Effectiveness of varying solutions of Ag+ in ppb from silver lactate and silver citrate.

	Control	250 ppb Silver Citrate	250 ppb Silver Lactate	500 ppb Silver Citrate	500 ppb Silver Lactate	750 ppb Silver Citrate	750 ppb Silver Lactate
Initial absorbance	0.069	0.031	0.035	0.031	0.022	0.022	0.019
Average absorbance	0.074	0.028	0.011	0.008	0.004	0.012	0.007

5.2 RESIN SILVER RELEASE RATE

Figure 5 contains the results that were obtained from the silver release experiment. The plot shows how much silver was lost from the resin per interval of time. The resins started delivering a relatively high amount of silver reaching concentration up to 7500 ppb during a short period of time, attributed to washout of loosely bound silver. A very low stripping of silver was consistently recorded after 15 minutes. The data reveals that the deionized water does not promote a significant stripping of silver and this result favors the aspects of the proposed silver-based MCV design.

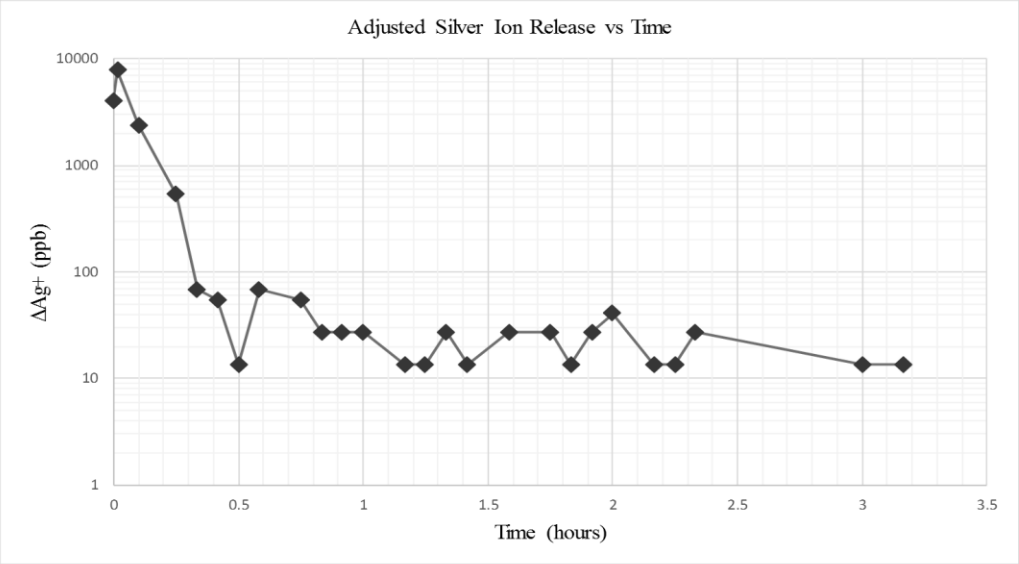


Figure 5: Ambersep IRC748 Ag+ release rate.

5.3 SILVER RELEASE IN MEMBRANE SYSTEMS

A preliminary test was completed to examine the feasibility of silver release from a dialysis membrane. Membrane I had a molecular weight cutoff of 100,000. Based on the consistent release of ions from the dialysis membrane shown by the Ag^+ release rate graphed in Figure 6 and the average release values of Table 2, the dialysis membrane acted as an effective delivery vehicle for Ag^+. After obtaining this data with a simple dialysis arrangement, more complex membrane formats, Membrane II and Membrane III, were tested.

Table *2*: Average release, flux, and amount of AG+ released by the membrane I.

Average Release Ag+ concentration (μg/L)
15.19
Surface area (m^2)
0.01
Average Released Ag+ (mol)
6.33E-08
Time interval of Ag+ release (s)
600.00
Ave. Ag + Flux (mol/m^2s)
1.66E-08

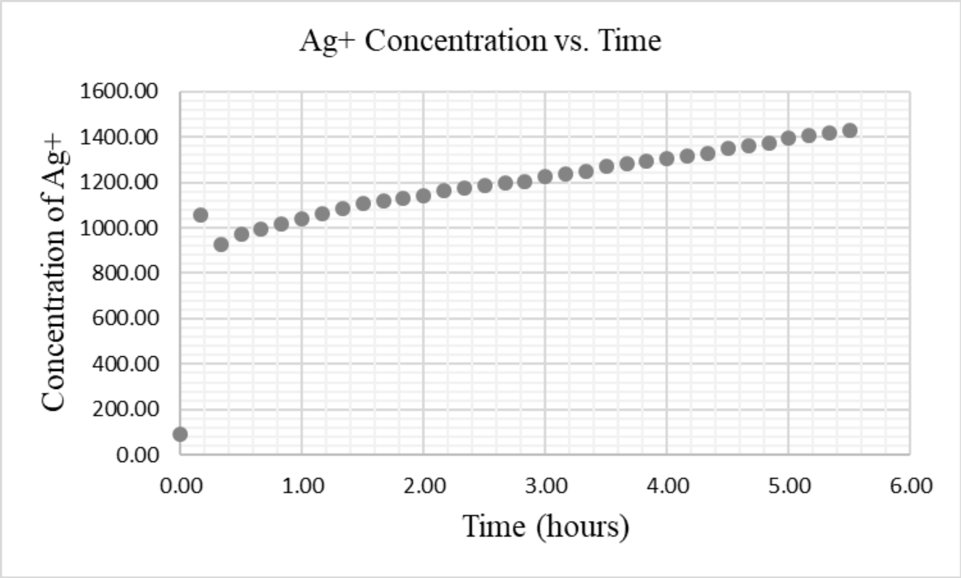


Figure 6: Ag+ release over time from Membrane I.

The system designated as Membrane II yielded the diffusion data shown in Figure 7. It released silver at a fairly consistent rate over time and delivered silver ions within the desired parts per billion limits. Due to the more complex design, silver ion concentrations can be controlled more easily and over a longer period of time.

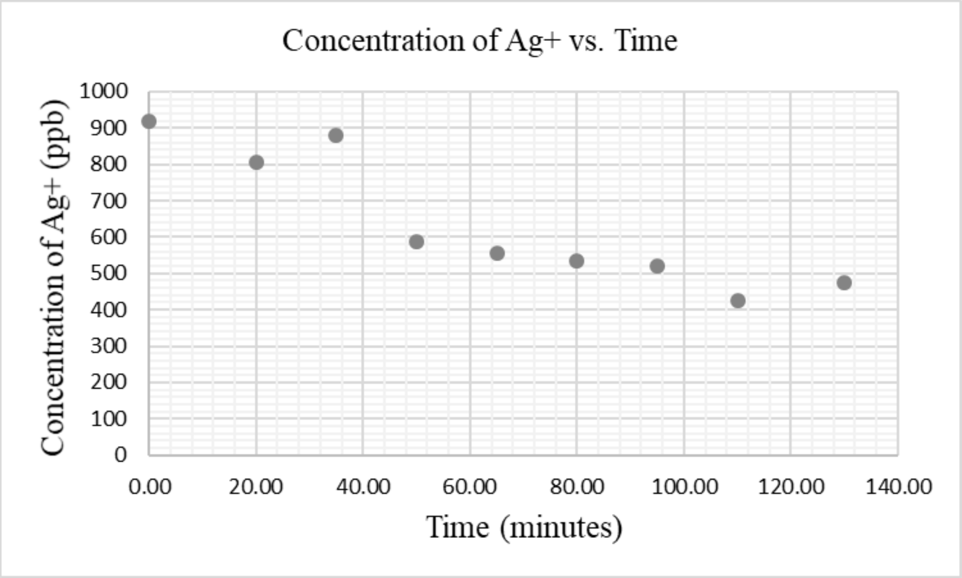


Figure 7: Measured Ag+ release from Membrane II.

Figure 8 shows the results for the system designated as Membrane III. System III was loaded with a 30 mL mixture of silver lactate and deionized water. The silver lactate solution that filled the tube side of the membrane had a concentration of 20 grams per liter. Deionized water was continuously pumped through the shell side and concentration measurements were taken after water passed through the shell. After an initial spike in concentration, there was a consistent release of 1750 ppb of silver ions into the water on the shell side of the dialysis membrane.

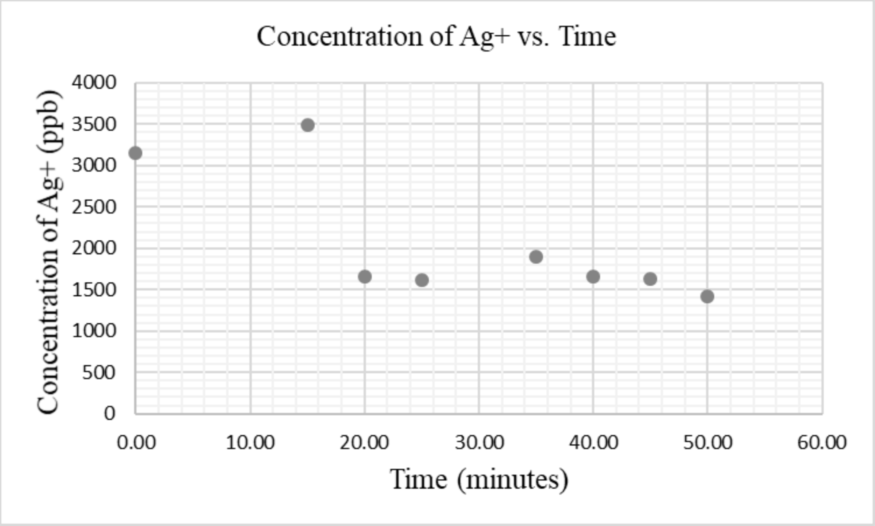


Figure 8: Measured release of Ag+ from Membrane III.

5.4 SILVER-LOADED RESIN BACTERIAL KILL TEST

In Figure 9, the results for bacterial growth inhibition tests are shown. Resin containing silver lactate was well mixed in a solution with *E. coli* and deionized water. This solution was tested against a water blank and a control made up of 19 mL of *E. coli* and 100 mL of deionized water with no silver present. In five hours, the silver containing resin eliminated the *E. coli* completely from the mixed solution.

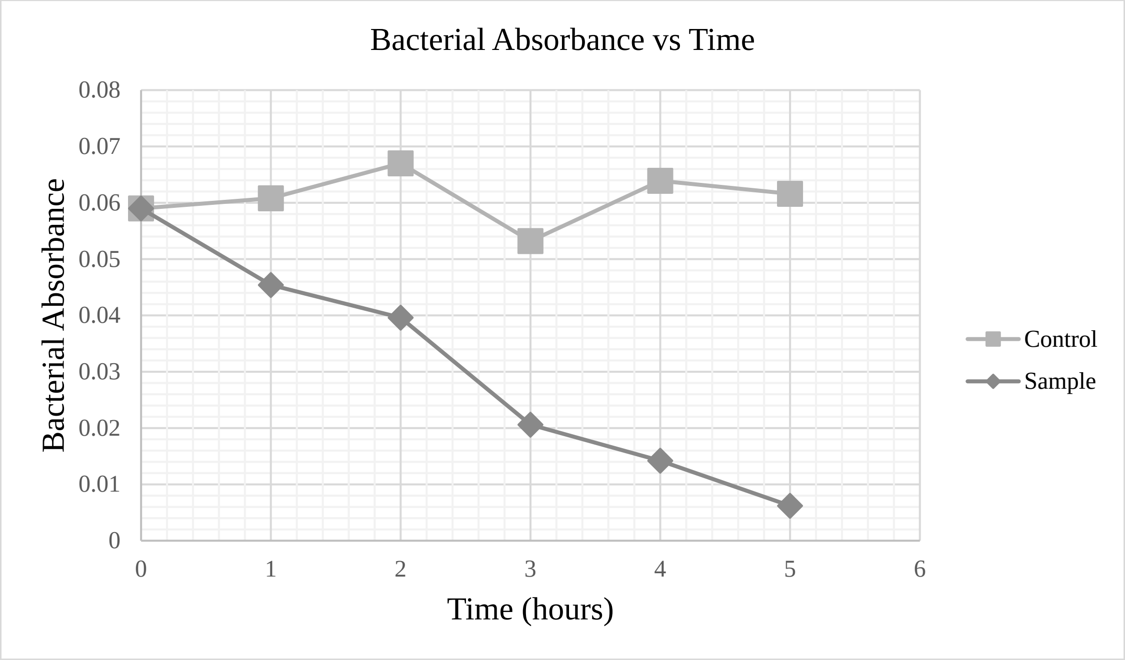
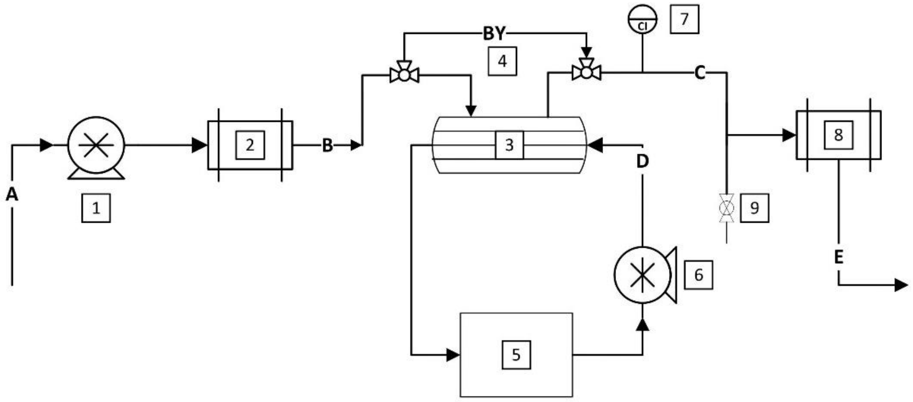


Figure 9: Bacterial absorbance versus time for silver ions.

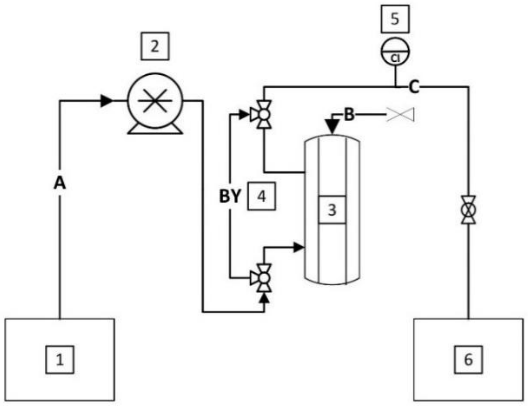
6.0 APPARATUS DESIGN

6.1 APPARATUS PIPING AND INSTRUMENTATION DIAGRAMS



Number	Equipment	Stream Letter	Material
1	Positive Displacement Pump	A	De-Ionized Water
2	Resin Bed	B	De-Ionized Water and Trace Silver Ions
3	Silver Lactate Delivery System	C	De-Ionized Water and 300-500 PPB Silver Ions
4	Silver Lactate Delivery Bypass	D	Aqueous Silver Lactate Solution
5	Silver Lactate Circulation Tank	E	De-Ionized Water and <500 PPB Silver Ions
6	Positive Displacement Pump	BY	De-Ionized Water and Trace Silver Ions
7	Conductivity Meter		
8	Resin Bed		
9	Sample Port		

Figure 10: Proposed Inline Replacement Within the WPS with Membrane II/III (if II, equipment 5 and 6 will be omitted)



Number	Equipment	Stream Letter	Material
1	Feed Tank	A	De-Ionized Water
2	Positive Displacement Pump	B	Concentrated Silver Solution
3	Membrane Apparatus II	C	De-Ionized Water and 300-500 PPB Silver Ions
4	Deionized Water Bypass	BY	De-Ionized Water
5	Conductivity Meter		
6	Product Tank		

Figure 11: Process & Instrumentation Diagram of the Membrane II. Membrane II contains a concentrated solution of silver lactate on the tube side of the membrane.

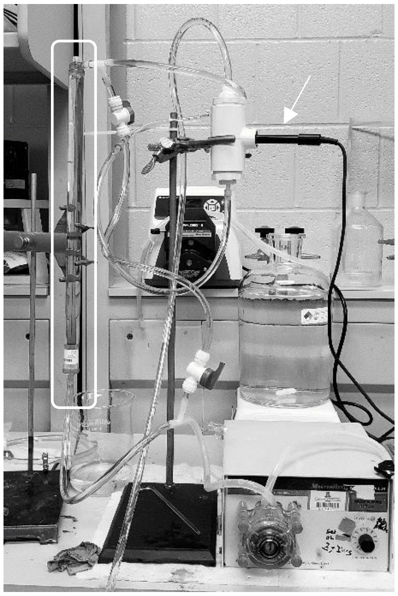
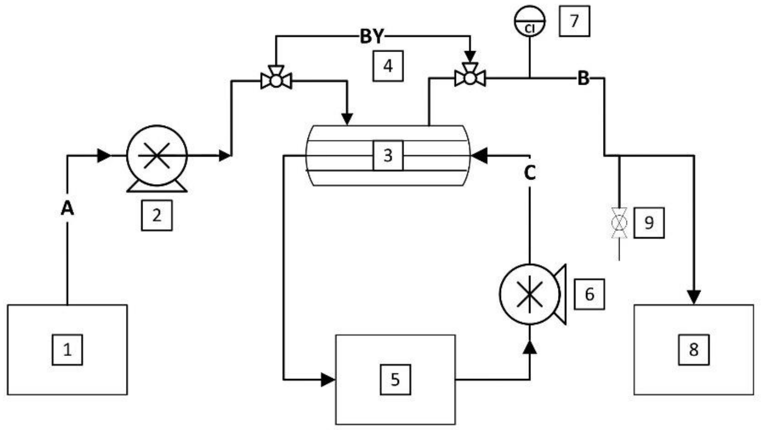


Figure 12: Equipment configuration for Membrane II. Membrane cartridge containing silver concentrate is circled. Downstream silver concentration measured with online conductivity probe (arrow).



Number	Equipment	Stream Letter	Material
1	Feed Tank	A	De-Ionized Water
2	Positive Displacement Pump	B	De-Ionized Water and 300-500 PPB Silver Ions
3	Membrane III	C	Aqueous Silver Lactate Solution
4	Silver Lactate Delivery Bypass	BY	De-Ionized Water
5	Silver Lactate Circulation Tank		
6	Positive Displacement Pump		
7	Conductivity Meter		
8	Product Tank		
9	Sample Port		

Figure 13: Process and Instrumentation Diagram of the Membrane III apparatus

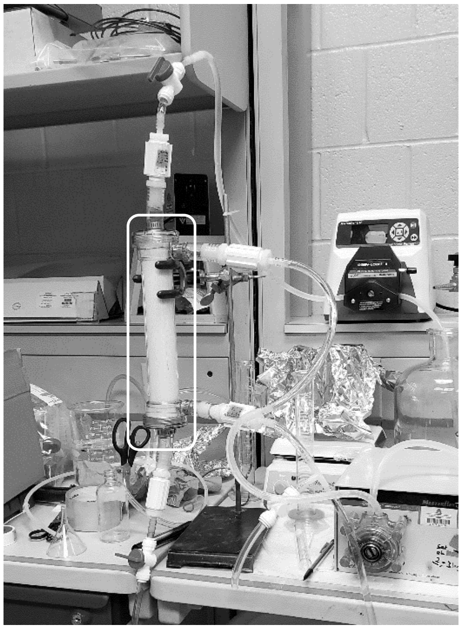


Figure 14: Equipment configuration for Membrane III. Membrane cartridge containing silver concentrate is circled.

6.2 DESIGN SPECIFICATIONS

Pictured in the Figures 10 – 14 are two designs for the SDS per Task 1 requirements, accompanied by Figure 10 which describes the proposed upgrade to the WPA. First, SDS designs (Figures 10 - 14) are described. Each contain a membrane cartridge, a bypass to tune the final concentration of silver, and depending on the design either a silver reservoir within the cartridge (Membrane II) or a silver charging loop / reservoir (Membrane III). Both systems will be transported to the WERC competition, but *Hogs In Space* reserves the right to demonstrate the system which consistently satisfies the task objectives. During the competition feed and product tanks will be used to provide and collect water and low weight positive displacement pump(s) will move fluid in the system. It is assumed that the power supplies for pumping will not be counted against the weight requirement of the *Hogs In Space* design.

While the benchtop design addresses the SDS, a full WPA upgrade must also be considered. The SDS could be integrated into the existing WPA and would be accompanied by changing the resin in Beds 3 and 9 from a quaternary ammonium anion exchange resin to an AMBERSEP resin. This arrangement is illustrated in Figure 14. However, it is feasible that a simple media replacement in the resin beds may be sufficient to satisfy flight requirements. Any final design would be challenged with raw water of composition similar to that fed to the WPA to determine the most effective arrangement. Regardless of the final arrangement, the proposed area for upgrade is illustrated in Figure 15.

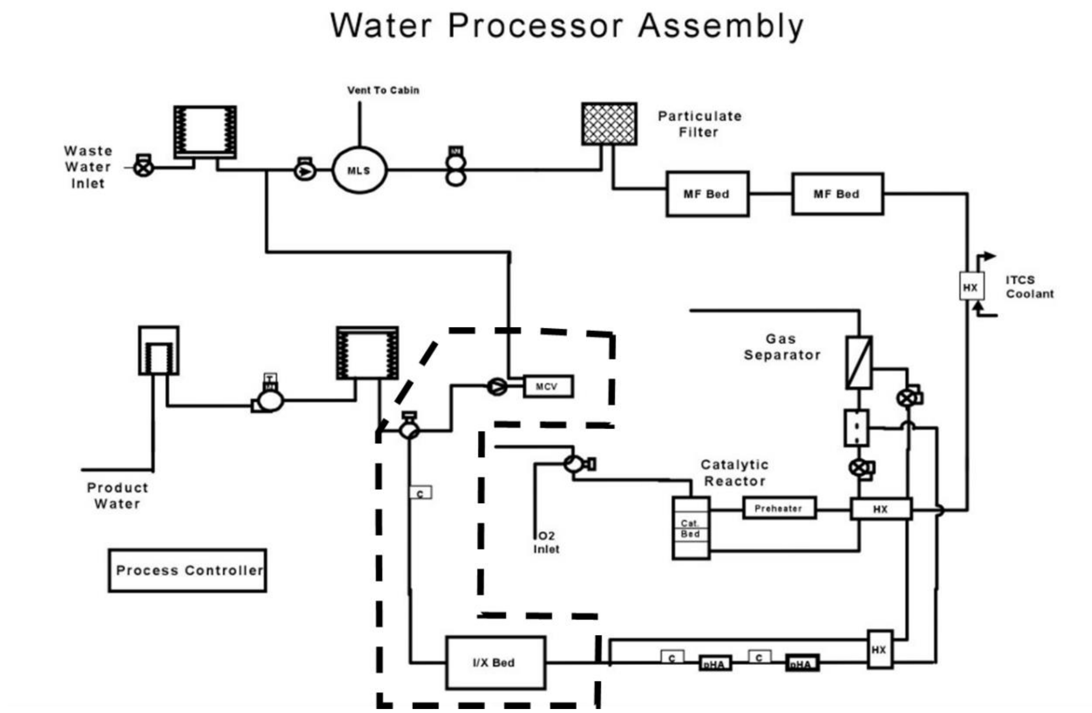


Figure 15: Proposed area for option 3 implementation within the WPS system.

6.3 COST ANALYSIS

A traditional cost analysis is not amenable for the uniqueness of the Task 1. However, the required parts to construct the experimental apparatus did not exceed more than $500. Furthermore, the preliminary results suggested that approximately 3 grams of silver lactate must be added to the membrane system every month to maintain proper delivery of silver within the target concentration (further research is being conducted to confirm this parameter). In total, the final cost of the design will ultimately be a function of its weight, as the apparatus is intended for spacecraft.

7.0 CONCLUSION

Completion of this precursory study allowed our team to confirm the effectiveness of the proposed apparatus. It was reaffirmed that silver ions at a concentration between 300 and 500 parts per billion prepared using silver lactate effectively kill bacteria. Silver and iodine have similar biocidal efficacy, but silver at biocidal levels is much safer for human consumption. It was concluded that silver lactate is an excellent candidate for implementation into a water sterilization apparatus because it is readily soluble in water and a noncorrosive silver ion source. Furthermore, both AMBERSEP™ IRC 748 and AMBERSEP™ GT 74 resins were loaded with silver and possessed the capability to kill bacteria without losing a considerable amount of silver. Moreover, controlled release systems were used to release silver ions into process water at an optimal delivering rate. The suggested design will potentially serve as an adequate MCV replacement. The designed apparatus operates at a flow rate between 100-150 mL/min, provide the required silver ion concentration of 300 to 500 parts per billion, and is well under the 5 kg limit. Exploratory research collected, along with potential design characteristics investigated, allows for a groundwork into the utilization of smaller, more lightweight, silver ion microbial spacecraft systems.

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Comments on University of Arkansas Silver-based Microbial Check Valve for Potable Water Systems

Reference WERC 2019 Task: Hogs in Space

Michael Wood

Director/Consultant, Gateway Projects Office

Retired Chief Engineer, Space Launch System, Boeing

Overall the project description demonstrates excellent knowledge of the biology and chemistry surrounding the use of silver as a water treatment biocide. The paper outlines good logic and data on the selection of silver lactate and the paper contains good experimental results demonstrating the efficacy and viability of a silver based antibacterial approach for ISS. The paper also points toward a promising design solution that would be light weight, simple and robust with minimal to no power demands. The Hogs in Space team also addressed the microgravity environment which is important to understand for this application and addressed other key factors such as materials compatibility.

The paper is somewhat confusing on whether the optimal solution would use only a membrane release method, a silver based resin bed or both. This will be discussed further in the comments that follow.

Executive Summary

The executive summary is a succinct statement of the WERC problem statement of assessing the viability of using silver ions as a biocide on the ISS. The summary alludes to a set of constraints and task requirements in the problem statement, but they are not listed or described in the summary. Perhaps it would be useful to reference the task parameters given in section 2.1 or summarize them here. If there are any additional constraints given in the WERC problem statement, then it would be good to summarize those as well.

1.0 Introduction

1.1 Background
Overall this section demonstrates a good understanding of the heritage bacterial control approaches used in the Russian and US segments of the ISS. Good rationale is given for ruling out a complex Russian-like approach which is further explained in section 1.3.

1.2 In the executive summary, hypothyroidism is listed as a concern with iodine based approaches. However, in this section, the concern is stated to be hyperthyroidism. It was helpful to list the key characteristics of the Umpqua MCV. Many of those were addressed with the Hogs in Space MCV. It might be useful to review this list to see if others might need to be addressed in the project.

1.3 Good reasoning and rationale for moving away from an expected complex design solution.

1.4 No comment

1.5 The language in this section is a bit confusing. The author mentions that the silver ions can be "released via a membrane or resin bed". The next paragraph says the team chose the "latter owing to its simplicity assuming a membrane and/or a resin could be identified…". It's not clear what is meant by latter and what is the former? Is the author recommending a membrane or resin bed or both? Are there design discriminators between those configurations? Also, the discussion on silver regeneration seems possibly out of place in this section and might fit better in a section that discusses initial silver charging or replenishing silver, perhaps in the context of component or system operation or logistics.

1.6 This section demonstrates the biological understanding of how silver functions as an antibacterial agent.

2.0 **Task Parameters**

2.1 Task Requirements

Good summary of the performance requirements for the silver biocide apparatus.

2.2 Flow Rate Discrepancies. A likely explanation for the flow rate discrepancy is that the WPA operates in a batch processing mode. As I recall, it processes ~ 10 lbm/hr. The duration of the batch process varies based on the fill level of the waste water tank, storage tank, Oxygen Generator production rate and related crew activities. It generally processes a few hours every 2-3 days and so the average flow rate can create the apparent discrepancy.

3.0 Research

3.1 Silver Salt Alternatives. Good rationale. No comments.

3.2 Mechanisms of Delivery. A controlled release mechanism is good. The authors again uses "membrane cartridge or resin bed" so it's still not clear if there are any discriminators between these methods.

3.3 Water Treatment Resins. No comments.

3.4 Microgravity Considerations. This is good to acknowledge this space environment and address how your device will address the concern. Membranes can be susceptible to two-phase solutions in microgravity environments.

4.0 **Experimental Procedures.** No comments to this section or its subsections. The experimental approach seems to be well thought out.

5.0 **Experimental Results and Discussion.** Generally, this section seems to be well substantiated with data.

5.1 No comments

5.2 The early silver washout might point to a need for a "break-in" flush prior to on orbit application.

5.3 At the bottom of page 14, it says that "Due to the more complex design, silver ions can be….". It's not clear what is being referred to as the more complex design.

5.4 No comments.

6.0 Apparatus Design

6.1 Apparatus P&ID. Spell out acronym for first use.

I struggled to understand Figure 3 on page 17. Additional text providing a functional description or a discussion of the diagram would be helpful. I believe I came to understand that the diagram represents both the WERC project silver biocide apparatus in terms of the membrane (items 4-7) as well as enhancements to the existing ISS WPA (resin beds 3 and 9). It's difficult to get that information from the figures and accompanying text in section 6.2. It would be useful to either add a better description of the figure or break it into smaller constituents and then show the integrated, enhanced WPA. A fundamental question that may need to be addressed is: given that the current ISS MCV is an iodine resin bed, why not replace it with just a silver resin bed? In other words, what are the benefits or a combined resin bed and membrane? When and how are they both used and why are they needed in combination? How is the system charged and replenished in either configuration?

7.0 Conclusion. Good summary and solid recommendation for silver lactate.

24 March 2019

To: University of Arkansas “Hogs in Space” Team

From: Mary Cheung

Subject: Review of University of Arkansas “Hogs in Space” Team Concept Paper for WERC 2019
Task 1: Silver-based Microbial Check Valve for Spacecraft Potable Water Systems, WERC 2019

Thank you for the opportunity to review you proposal. Just to provide a little information about my background in water, I exclusively deal with industrial water, wastewater, and product recovery from wastes at Veolia Water America. I am by no means a drinking water expert. Our operations do at times include drinking water systems for the local plant, and some of my counter parts in the municipal business are experts in drinking water, so I know just enough to know when to call an expert. I have read through this a few times, but I am no where close to understanding the problem and solution as well as you all do. However, I am used to working with and optimizing water treatment systems. Here goes on my comments and questions....

1.) In the executive summary, I would like to see a little more explanation of your two options for the overall solution. A block flow diagram of today’s system vs your proposed solution, just high level highlights on the advantages & simplifications, would have been helpful for me.
2.) Glad to see the check for “food grade” available chemicals. I know in the US on earth everything has to be NSF/ANSI 60: Drinking Water Treatment Chemicals – Health Effects approved. This includes resin and membranes and any chemical feeds to the system, such as sodium hypochlorite. If you can, I’d make a point of stating that all the components of you system can comply.
3.) The silver disinfection treatment: At the 300-500 mg/l concentration the silver is non-toxic and does not accumulate “much” in human bodies.
    a. So where does the silver consumed in the drinking water go? I assume it comes back in the wastewater. I’m sure at concentrations to low to be useful.
    b. Does it need to be purged from the closed water loop from time to time?
4.) Page 16 figure 4 – the initial release rate from a resin is common for all “regenerated” resins. How is that initial spike of 7500 mg/l handled to meet the 300-500 mg/l concentration target? I think the final resin bed catches it in the resin case and/or there is some blending?
5.) P&ID - I’d visually present the resin option and membrane options separately so it’s clear.
6.) You’ve kind of explained normal operation. What’s maintenance look like? In a conventional IX resin system you monitor for breakthrough and have regeneration waste to dispose of. In a conventional membrane system you also monitor for leakage and fouling. You have to periodically clean the membranes and dispose of that cleaning waste. Maybe on the space shuttle you just send up new cartridges and slap them in?
    a. Do you regenerate the 3 and 9 resin beds? Or swap them?
    b. What about the membrane system? What’s expected life for the membrane? How would it be changed out?
    c. Is there any other daily, weekly or monthly attention that the system would need? Validation of conductivity? Or testing for bio? I assume the astronauts have to do similar testing on the existing iodine system. Or maybe it’s all instrumented.

I believe you’ve come up with a viable solution based on confirmation of the original premise that silver works, and experimentation to understand what’s needed to safely and reliably deliver clean drinking water on the Space Station. Good luck!

Dear Hogs in space,

It was a pleasure to review your work. This is a very interesting approach with high technical merit. I hope my comments will help make this project even better. Please let me know if I can provide additional clarification and assistance.

Comments:

1. Your experiment and result discussion will be easier to follow if you can introduce your design concept and establish objectives ahead of your experiment.
2. Most syringe filters contain microfiltration membrane and microfiltration is known to reject bacterial. Please justify that your cell growth result obtained using samples that had been filtered using syringe filter is accurate.
3. Please justify that using spectrophotometer to determine design parameters (such as residence time and concentration) is sufficiently accurate to meet safety and disinfection requirements. Please note that CFU measurement is the standard method for water disinfection research.
4. In Section 4.2, supernatant were measured using ICP-MS at the end of silver loading. This value was not reported and the total exchange capacity of 1.35 eq/L was not confirmed. How long do you expect a single load of silver to last? You will need this for economic analysis and waste calculation.
5. It makes more sense for Y-axis in Figure 4 to be concentration change (dC) instead of concentration (C). If it is actually concentration please explain why the concentration of silver in solution dropped over time in your batch experiment.
6. It is not described in the report and is assumed here that the calibration equation for conductivity is merely a relationship of concentration versus conductivity. In the ion-exchange process, ions are exchanged but the overall concentration of positive and negative charge groups in the solution may remain unchanged depending on the valance of the ions. With the above understanding (please correct me if I am wrong), please justify why your use of conductivity measurement is appropriate to elucidate the transfer of silver ions.
7. Is the leaching of silver ion from resin a zero order kinetics? How do you prevent the initial high dose of silver into water starting from dormancy/idle? I just want to make sure that the first sip of water by the astronaut from the “fountain” is safe.
8. In the membrane permeation graphs, please indicate what concentration you are plotting – source phase or receiving phase?
9. Since the Resin beds #3 and #9 and the membrane unit are all capable of functioning as MCV, why do you need all the 3 units? It make sense to include a detail equipment description table to clearly describe the main function of each unit to help explain the design concept. Please also provide explanation and calculation on how you plan to achieve the delivery target. Note that all three units are delivering at the same time.
10. You will need a balancing chamber to make sure that the inlet and outlet of the receiving phase are equal. Using ultrafiltration membrane (hemodialysis membrane) as a counter current aqueous-aqueous based contactor, the first half of the dialyzer will be operating in a forward-filtration mode and the second half of the dialyzer in a back-filtration mode. It is very difficult to maintain equal inlet/out if you do not have a balancing chamber. One suggestion is to stack two tubing pumps (peristaltic pump) on one drive and have the pumps connected to the inlet and outlet of the dialyzer.

11. The benefits of using a dialyzer should be highlighted:
    a. Dialyzer packed with very fine hollow fiber resembles a pack Bed of ion exchange resin
    b. Dialyzer is better than packed bed because the pressure drop is very low
    c. Packed bed needs to be reloaded upon exhaustion, whereas dialyzer can operate continuously as long as silver ion is continuously added to the circulating source phase
    d. Just like a packed bed, dialyzer is about 1ft long and is capable of providing about 1ft of disinfection zone for bacterial to migrate during system dormancy. Dialyzer could be an effective microbial check valve by itself.
12. Addition factors to be considered when using hemo-dialyzers:
    a. Most dialyzer has an area of 1.5-2.5 m2. It is designed to transfer >70% of ions at a counter current flowrate of 300ml/min (source phase) and 500ml/min (receiving phase) in a single pass contact.
    b. Pediatric dialyzer with area of 0.3 m2 and a design flowrate of 50-200 ml/min is available (this is exactly what you need to treat 150ml/min of water).
    c. The tube and shell side concentration will equilibrate almost immediately upon stopping the flow.
    d. What concentration of silver do you want to have in the dialyzer when the system is idle?
    e. The required silver concentration is so low in comparison with the saturation concentration of the silver salts evaluated. Is there any benefit to look for another silver ion source that has a significantly lower solubility? How about supersaturated colloidal silver or silver nanoparticle. Supersaturation is an easy way to prepare and control concentration without fancy equipment.

Regards,
Jiunn

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