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Water Impact Statement

Rapid inactivation of *E. coli* was demonstrated in electrochemical disinfection. Residual silver concentration was effectively reduced to the safe level for human consumption in a separate experiment. A bicycle generator or photovoltaic solar panel can provide energy for water disinfection. The findings support that the disinfection method has a potential to provide safe drinking water to people in underprivileged communities.

Electrochemical silver dissolution and recovery as a potential method to disinfect drinking water to underprivileged societies

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Abstract

Limited access to disinfected drinking water is a critical challenge in developing countries. Ionic silver has biocidal capabilities and silver ionization is an established method for cooling water disinfection. However, silver ionization cannot be used in drinking water treatment due to inherent human health risks. In this proof-of-concept study, we developed a lab-scale electrochemical reactor where ionic silver is released via oxidation of metallic silver and subsequently recovered through cathodic reduction. Complete inactivation of *E. coli* was demonstrated in 30 min at 1.2 V application. High silver concentration (>1 mg/L) was achieved in less than 2 min of water residence time within the disinfection reactor. The effluent silver concentration was linearly proportional to the electric current, allowing reliable estimation of silver concentration and corresponding disinfection performance by measuring electric current using an electrical multimeter. The disinfected water was further treated in a separate silver recovery cell. The silver concentration dropped down to safe levels for continued human consumption (0.1 mg/L) via spontaneous cathodic silver reduction coupled with anodic oxidation of metallic aluminum. The estimated energy requirement was 6.1 kJ to treat 1-m^3 water; thus, solar panels or bicycle generators can provide sufficient energy for disinfection. The electrochemical disinfection and subsequent silver recovery methods have a strong potential as a

prospective method to supply safe drinking water in underprivileged and remote societies.

1. Introduction

Limited access to safe drinking water is a serious and insistent challenge in underdeveloped and remote societies.[1-3] Water-related diseases by contaminated drinking water, hygiene, and sanitation have caused an estimated 3.6 million deaths per annum.[4] Water treatment using various disinfection methods, such as chlorination, ozonation, and ultraviolet light radiation, can effectively inactivate microorganisms including human pathogens; however, people in underprivileged societies cannot afford sufficient energy or infrastructure to produce the disinfection chemicals and operate the reactors for drinking water treatment.[5] Thus, the main goal of this study is to develop an affordable disinfection method for people in underprivileged societies.

Silver was used for water disinfection and antimicrobial therapy in ancient civilizations and the biocidal capacity of ionic silver has been demonstrated in a number of modern scientific studies.[6-11] With the strong biocidal capacity, silver ionization has been used to control *Legionella* pathogens in cooling water systems and hosipitals.[12-14] However, silver applications in drinking water treatment have been limited by potential health risks of continued silver consumption and high costs of silver. Silver concentration should be 0.1 mg/L or lower for continued human consumption to avoid potential adverse health risks.[15,16] However, silver concentration at 0.1 mg/L or lower can substantially decrease the disinfection efficiency,[17] indicating that silver concentration should be sufficiently high (e.g., 1 mg/L or higher) for reliable and rapid inactivation of microorganisms. In addition, the high concentration requirement for effective disinfection needs a large amount of silver, making the method expensive and economically infeasible. Applications of nano-sized silver particles have been extensively investigated as an alternative method for water disinfection and treatment .[10,11,18,19] Such nano-sized particles dramatically increase the effective surface area and thus improve the biocidal capacity of silver. However, nano-sized silver particles can cause potential human health risks and they can accumulate in organisms along the food chain if they are released in natural water systems.[20-22] Thus, this study focused on using millimetre-sized silver granules as the source of silver ions for water disinfection.

Here we have suggested and examined an innovative disinfection method where silver ions are released and simultaneously recovered via two electrode reactions (Fig 1A): one discharges silver ions into the solution through the oxidation of metallic silver at the anode (forward reaction of Eq. 1) while the other retrieves the dissolved silver by the reduction reaction at the cathode (reverse reaction of Eq. 1). It should be emphasized that during conventional silver ionization silver ions are dispersed into untreated water with no means of recovery. The cathodic reduction reaction differentiates this system from typical silver ionization techniques.

$$Ag_{(s)} \leftrightarrow Ag^{+} + e^{-} \qquad (1)$$

As silver ions travel from the anode to the cathode, the space between the two electrodes becomes an active disinfection zone where microorganisms are inactivated. Since the silver ions are recovered at the cathode as metallic silver, the disinfected water is expected to have a low silver concentration. In addition, the residual silver ions in the disinfected water can be further recovered by coupling the silver reduction reaction (reverse reaction of Eq. 1) with aluminum oxidation reaction (forward reaction of Eq. 2), allowing safe human consumption of the treated water.

$$Al_{(s)} \leftrightarrow Al^{3+} + 3e^{-} \qquad (2)$$

Aluminum is a commonly used chemical in drinking water treatment for flocculation of suspended particles in water and excessive Al^{3+} will be naturally removed by aluminum hydroxide precipitation.[23] Also, the electric energy requirement is expected to be low since the first redox couple (forward and backward reactions of Eq. 1) is thermodynamically neutral and the second set of the redox reactions (backward reaction of Eq. 1 and forward reaction of Eq. 2) is driven spontaneously.[24] Compared to currently available disinfection methods (e.g., chlorination, ozonation, and ultraviolet radiation), this electrochemical silver disinfection is expected to require an almost negligible amount of electric energy for microbial inactivation. Thus, a large amount of water can be treated using photovoltaic solar panels or bicycle generators, providing safe drinking water to people in underprivileged societies. The specific objectives of this study are to: (1) demonstrate effective microbial inactivation using the electrochemical silver disinfection method; (2) establish a correlation between the electric current and resulting silver concentration for the estimation of disinfection performance; (3) demonstrate further recovery of silver from the treated water using the second set of the electrode reactions; and (4) quantify the energy requirement for this disinfection method.

2. Experimental Methods

2.1 Electrochemical disinfection reactor

The disinfection reactor was constructed using 3 thin low-density polyethylene (LDPE) blocks covered with polyarcrylic plates (McMaster Carr, USA). Each block was drilled to make a narrow inner chamber (width 0.8 cm, length 12 cm). The middle chamber (0.7 cm thick) was used for water flow and the upper and lower chambers (0.6 cm thick) were filled with silver granules (Silver Casting Grain, 99.9% purity, granule size between 1.6 and 6.4 mm, Alfa Aesar, USA) to be used as the anode and cathode (Fig 1A). Approximately 34.2 g of the silver granules were sandwiched between a polyarcrylic end plate and a piece of stainless steel mesh (SS-306, 200 × 200 mesh, McMaster Carr, USA). The upper layer of the silver granules was used as the anode and the lower layer was the cathode. The silver granules were tightly sandwiched so that the whole layer behaved as an electrical continuum and the stainless steel mesh was used as the current collector. In a separate experiment, corrosion of the stainless steel mesh was not observed (1.2 V application for 24 hr). The effective reactor volume was approximately 11.2 mL while the empty volume was 17.7 mL without the silver granules.

2.2 Escherichia coli preparation

Escherichia coli RS2g was used to examine the disinfection capacity. The microbial strain was enriched in a nutrient broth at 37ºC to an approximate concentration of 10^8 CFU/mL. The nutrient broth was prepared with 10 g HiVeg lysate, 5 g yeast extract, 10 g sodium chloride, 10 mg rifampicin, and 100 mg kanamycin in 1 L of deionized water.[25] The bacterial cells were separated from the nutrient solution in a centrifuge at 8500 rpm for 10 min (Allegra 25R, Beckman Coulter, Germany). The centrifuged cells were then suspended in autoclaved 1 mM phosphate buffer solution (0.15 mM KH_2PO_4; 0.85 mM Na_2HPO_4). These centrifuge and suspension steps were repeated twice for further removal of nutrients. The suspended solution was diluted to ~10^5 CFU/mL using 1 mM phosphate buffer solution before it was used in the silver disinfection experiment.

2.3 Reactor operation for disinfection test

Prior to the disinfection test, 70% (v/v) ethyl alcohol was pumped at 5 mL/min (Masterflex LS, Cole-Parmer Instrument Company, USA) through the reactor for 20 min to control microbial contamination.[26] The ethyl alcohol was replaced by deionized water which was pumped for another 30 min to remove residual ethanol from the reactor. After this cleaning process, the reactor was emptied and the prepared *E. coli* solution (~10^5 CFU/mL) was pumped at 5 mL/min for 15 min and the effluent was discarded. This rinsing step with the *E. coli* solution is necessary to minimize the bacterial loss by adsorption on silver granules and reactor surfaces during the disinfection experiment. The main part of the disinfection experiment was performed for 30 min by circulating 200 mL of the *E.coli* solution between a reservoir and the disinfection reactor at 5 mL/min (Fig 1B). The reservoir was gently stirred using a magnetic stirrer.

During the disinfection experiment, two different voltage conditions (0.6 and 1.2 V) were applied and the resulting electric current was recorded every 30 sec using potentiostat (MGP-2, BioLogic, France). In addition to the two applied voltage conditions, two control experiments were conducted. In one control test, the *E. coli* solution was circulated between the reservoir and reactor without any voltage applications (Open Circuit). In another control experiment, the *E. coli* solution was kept in the reservoir without the circulation (No Silver). All experiments were conducted in an air-conditioned laboratory at 22.1 ± 0.7°C.

2.4 Plate counting

Agar plates were prepared with 15 g agar, 5 g yeast extract, 10 mg rifampicin, 100 mg kanamycin, 10 g HiVeg lysate, and 10 g sodium chloride in 1 L of deionized water.[25] The added antibiotics (rifampicin and kanamycin) are necessary to selectively culture *E. coli* RS2g.

During the silver disinfection experiment, a sample (0.2 mL) was taken from the reservoir at time 0, 10, 20, and 30 min. The sample was serially diluted depending on the expected amount of viable cells. For instance, samples at 0 min were diluted by a factor of 10 and 100 while samples at 30 min with 1.2 V application were not diluted. The diluted or undiluted samples (0.1 mL) were seeded on the agar plates and the seeded plates were incubated at 37ºC for 24 hr.

2.5 Reactor operation for current-silver correlation

The continuous-flow experiment was conducted using 1 mM phosphate buffer solution without the *E. coli* strain to correlate the electric current and concentration of ionic silver present in the effluent from the electrochemical disinfection reactor. The applied voltage increased stepwise every 22 min from open circuit, 0.3, 0.6, 0.9 and 1.2 V while 1 mM phosphate buffer solution was continuously pumped through the electrochemical disinfection reactor at 5 mL/min (no recirculation). At the end of each applied voltage condition, the effluent was taken and acidified using nitric acid (1% v/v) to be analyzed for silver in inductive coupled plasma-optical emission spectrometry (ICP-OES) (Vista Pro, Varian Inc., Australia). The effluent samples were also analyzed for pH and conductivity (Seven Multi, Mettler Toledo Group, Switzerland). There were no discernable changes in pH and conductivity from the influent as pH ranged between 7.2 and 7.4 while the conductivity was also stationary between 222 and 237 μS/cm.

In a separate continuous-flow operation, samples in the water flow chamber of the reactor were taken through predrilled holes located at 3, 6, and 9 cm from the inlet point. Taken samples were acidified and analyzed in ICP-OES to determine the silver concentration in the reactor.

2.6 Silver recovery test using aluminum foil

The silver recovery cell was prepared using a glass beaker with a 5 × 4 cm^2 piece of household aluminum foil as the anode and a 5 × 4 cm^2 piece of stainless steel mesh (SS-306, 200 × 200 mesh, McMaster Carr, USA) as the cathode (Fig 1C). The prepared electrodes were located a few centimeters from each other in the silver recovery cell without mixing conditions. The two electrodes were externally connected through a resistor (1000, 4700, or 9700 Ω). The potential drop across the external resistor was monitored every 30 sec using potentiostat (MGP-2, BioLogic, France) to determine the electric current generated in the silver recovery cell using Ohm's law. The silver recovery cell was filled with 200 mL of silver solution. The silver solution was collected from the electrochemical silver reactor (applied voltage = 1.2 V; flow rate = 5 mL/min) and stored in a glass container for 16 hr prior to the silver recovery experiment. During the silver recovery experiment, a 4-mL sample was taken every 3 hr for the first 12 hr and then another sample was collected at 24 hr. The samples were acidified and analyzed for silver concentration in ICP-OES (Vista Pro, Varian Inc., Australia).

2.7 Silver recovery efficiency

Coulombic efficiency is the charge-based ratio between the amount of silver recovered and total charge transferred via the electrode reactions in the silver recovery cell as:

$$\text{Coulombic efficiency} = \frac{FVz\Delta c}{\int i\,dt} \quad (3)$$

F is the Faraday constant, V is the volume of solution (0.2 L), z is the charge of ionic silver (+1), Δc is the change in ionic silver concentration during the silver recovery test (mol/L), and i is the electric current (A).

3. Results and Discussion

3.1 Disinfection effectiveness

Escherichia coli RS2g was successfully inactivated in the electrochemical system and the disinfection performance was substantially enhanced with an applied voltage. When 1.2 V was applied, viable *E. coli* colonies were not detected after 30 min, indicating complete inactivation of the microorganism (Table 1). When the applied voltage was decreased to 0.6 V, the electrochemical disinfection system showed 99.6% and 99.8% removal after the 30-min treatment (Table 1). For the open circuit condition (no electric current), a partial inactivation of *E. coli* was demonstrated with the observed 60.3% and 79.5% removal in 30 min (Table 1). This partial removal without electric current can be explained by silver ions becoming dissolved via non-electrode reactions because no distinct decreases in CFU (colony forming unit) were observed during the no-silver control experiment (Table 1). It should be noted that the total surface area of the silver granules was substantially large (~63 cm^2), allowing active silver dissolution via non-electrode reactions.

3.2 Ionic silver concentration

Ionic silver (Ag^+) released from the electrode reactions was the active disinfectant in the electrochemical system. In the abiotic experiment under the continuous flow condition, the silver concentration from the reactor increased as the applied voltage increased (Fig 2A). The open circuit condition resulted in 0.15 mg/L of silver in the effluent, indicating that silver is naturally dissolved from the silver granules without electrode reactions, explaining the partial inactivation of the bacteria under open circuit condition (Table 1). There was no statistically significant change in the effluent silver concentration for the increased applied voltage up to 0.6 V (Fig 2A). The relatively low silver concentration (0.2 mg/L) at the 0.6 V application explains the incomplete disinfection capacity (99.6% and 99.8%). It should be noted that the drinking water treatment regulations in developed countries commonly require at least log 3 removal of bacteria (i.e., 99.9% inactivation); therefore, the 0.6 V application does not provide adequate removal of bacteria for drinking water standards.[27] When the applied voltage was increased above 0.6 V to 1.2 V, the silver concentration in the effluent increased sharply to 1.15 mg/L (Fig 2A). As a result, the 1.2 V application achieved the complete inactivation of the *E. coli* strain in 30 min (Table 1). The comparison between the inactivation results (Table 1) and silver concentration (Fig 2A) indicates that the silver concentration should be 1 mg/L or higher for effective disinfection of *E. coli* (i.e. log 3 or higher removal in 30 min). When the silver concentration at 1.2 V application (1.15 mg/L) is normalized by the total surface area of the silver granules, 0.012 mg/L of Ag^+ was produced per cm^2 of the silver granule surface (average silver granule diameter = 4 mm; total mass of silver granules in the reactor = 68.4 g; metallic silver density = 10.49 g/cm^3).

The silver concentration in the effluent was linearly proportional to the electric current (Fig 2B). This clear linear trend indicates that the effluent silver concentration can be estimated by measuring electric current in the electrochemical disinfection reactor. Measurement of silver concentration needs expensive analytical instruments (e.g., inductively coupled plasma, atomic adsorption, or photo colorimetry) and various chemicals for sample preparation, making it practically impossible to measure silver concentration in underprivileged communities.[28] However, silver concentration needs to be determined to estimate the disinfection efficiency in the Chick-Watson model:[23]

$$\frac{dX}{dt} = -kc^n \qquad (4)$$

X is the viable microbial population, k is the rate constant for disinfection, c is the disinfectant concentration, and n is the coefficient of dilution. The linear trend between the silver concentration and electric current will allow reliable estimation of the silver concentration and resulting disinfection effectiveness by measuring current using an electric multimeter.

If the applied potential exceeds 1.23 V, the water electrolysis reactions start contributing to the electric current and result in an overestimation of silver concentration as well as disinfection effectiveness. Therefore, we recommend that the electrochemical silver reactor be operated below the threshold voltage for water electrolysis (1.23 V).

3.3 *Energy losses.*

The electric current in the silver reactor showed an exponential increase with the increasing applied voltage (Fig 2C). In an electrolytic cell, the applied voltage is equal to the sum of the equilibrium potential, overpotential loss, and resistive potential loss. For the highest voltage application of 1.2 V, the Ohmic resistance accounted for ~0.17 V of the energy loss (inter electrode distance = 0.7 cm; solution conductivity = 230 µS/cm; I = 0.56 mA; cross sectional area = 9.6 cm^2). This estimation indicates that the majority of the applied voltage was consumed for the electrode overpotential and ohmic losses. The electrode overpotential loss can be reduced by increasing the surface area of the electrode. While relatively coarse silver granules (1.6 - 6.4 mm in diameter) were used in this study, finer granules or other types of silver materials can be used to increase the electrode surface area.

The overall electrode reaction is thermodynamically neutral; that is, metallic silver at the anode is oxidized to ionic silver, which is then reduced to metallic silver at the cathode. Therefore, the equilibrium potential loss was created solely by the difference in ionic silver concentration between the anode and cathode surfaces; thus, this loss can be denoted as the concentration overpotential loss. The local concentration of ionic silver at the anode surface is higher than that at the cathode surface because ionic silver is created at the anode while it is removed at the cathode. This concentration difference can be minimized by inducing sufficient mixing conditions in the reactor. In this proof-of-concept study, the electrode silver granules were separated by a relatively fine stainless steel mesh (200 × 200 mesh) from the 0.7-cm wide inter-electrode space where the water flows easily without any obstacles. The estimated Reynolds number of 0.11 indicates laminar flow regime in the reactor (flow velocity = 0.09 cm/s; water viscosity at 22°C = 0.95 Pa·s), lacking hydrodynamic mixing.[29] Based on this discussion, it is suggested that, in future studies and practical applications, the reactor be designed to induce mixing conditions using lumpy spacers or receive water directly to the anode region and discharge it from the cathode side. These suggested design changes will help reduce the overpotential and equilibrium potential losses in the silver disinfection reactor.

3.4 *Residence time requirement*

In a separate set of the continuous-flow experiment, the silver concentration in the electrochemical silver reactor increased linearly in the water flow direction and reached its maximum value of 1.54 mg/L at 9 cm from the inlet point (Fig 3). The water flow path in the reactor was 12-cm long and the mean hydraulic residence time was 2.2 min during the experiment (effective volume = 11.2 mL; flow rate = 5 mL/min). Thus, less than 1.7 min of hydraulic residence time was actually required to attain the maximum silver concentration. This result indicates that the silver release reaction is achieved rapidly (less than 2 min) and thus the electrochemical silver reactor can be built in a compact size and readily transported to provide safe drinking water to people in remote communities.

3.5 Silver recovery using metallic aluminum

A guideline on drinking water quality by the World Health Organization (WHO) states that silver concentration in drinking water should be 0.1 mg/L or lower for prolonged human consumption without potential adverse health risks.[30] This guideline indicates that the water treated at 1.2 V is unsafe due to its high silver concentration above 1 mg/L. During the silver recovery experiment using the aluminum galvanic cell (Fig 1C), ionic silver concentration dropped to 0.1 mg/L in 12 hr and the rate of silver recovery was not affected by the external resistance between 1000 and 9700 Ω (Fig 4A). It should be noted that the solution used in this recovery experiment was the effluent from the electrochemical silver reactor (applied potential = 1.2 V; flow rate = 5 mL/min) and kept in a glass container for about 16 hr prior to this silver recovery test. The resulting aluminum release does not pose a health concern to humans. Aluminum salts (e.g., aluminum sulfate and poly aluminum chloride) are commonly added in drinking water treatment as a coagulant. In water, Al^{3+} is rapidly converted to $Al(OH)_3$ since it has a very low solubility limit under neutral pH ranges (~10^{-5} M).[16] Thus, the aluminum oxidation reaction in the silver recovery cell does not pose human health risks. It should also be noted that the silver recovery cell was operated without mixing and the inter-electrode distance was approximately 2 cm. The hydrostatic condition and relatively distanced electrodes imply that the slow recovery (requiring ~12 hr) can be accelerated by providing mixing conditions or minimizing the inter-electrode distance.

In the silver recovery cell, the theoretical equilibrium potential at the aluminum anode ranges from −1.77 to −1.79 V vs. SHE (standard hydrogen electrode) by the Nernst equation ($\{Al^{3+}\}$ = 0.01-0.1 mg/L; 22°C) while the cathode potential is between 0.45 and 0.52 V vs. SHE ($\{Ag^{+}\}$ =

0.1-1.5 mg/L; 22°C), creating the open circuit potential of 2.22 to 2.31 V. This open circuit potential is large enough to drive the expected electrode reactions (backward reaction of Eq. 1 and forward reaction of Eq. 2) without any expensive catalysts or external power supplies to recover silver.

The electric current gradually decreased with time and the increasing external resistance from 1000 to 9700 Ω (Fig 4B). The Coulombic efficiency values calculated using Eq. 3 were 29% (1000 Ω), 36% (4700 Ω), and 102% (9700 Ω), increasing with the increasing external resistance. This result indicates that the majority of the cathode reaction was driven by the reduction of ionic silver with the large external resistance (9700 Ω); however, the smaller external resistances resulted in other reduction reactions at the stainless steel cathode, such as reduction of dissolved oxygen into water.

3.6 Energy requirement

The energy requirement for the electrochemical disinfection is small enough to be operated by solar panels or bicycle generators. During the experiment, 1.22 J of electric energy was consumed for the treatment of 0.2 L of the *E. coli* solution (1.2 V; 0.56 mA; 30 min), resulting in the energy requirement of 6.1 kJ per treatment of 1-m^3 water. Commercial photovoltaic solar panels can produce electric power between 35 and 103 kJ/h per 1-m^2 solar panel (total solar power assumed to be 411 kJ/h; solar penal efficiency between 8.5 and 25%).[31,32] This calculation indicates that a 1-m^2 photovoltaic solar panel can provide enough energy to disinfect 5.7 to 16.9 m^3 of water in 1 hr. A bicycle generator is known to create electric power up to 1080 kJ/h, which can be used to disinfect 177.2 m^3 of water per hour.[33] Since the reactor in this study was prepared as a proof-of-concept design, there is a room to further reduce energy consumption in practical applications. For instance, the inter-electrode distance (0.6 cm in this study) can be decreased and the electrode surface area can be increased by decreasing the silver granule size (1.6 - 6.4 mm in this study).

4. Conclusions

Limited access to clean and safe drinking water is a global water challenge that millions of people currently face in developing countries. The disinfection system proposed and examined in this proof-of-concept study was targeted to prove that this system has a potential to provide safe drinking water to underprivileged societies without industrial infrastructure for centralized water treatment. In the lab-scale experiments, we demonstrated that the electrochemical reactor achieved complete inactivation of *E. coli* from $>10^5$ CFU/mL to zero viable cells in 30 min when 1.2 V was applied to the system. The rapid inactivation of *E. coli* was achieved by a substantially high residual silver concentration (above 1 mg/L) and the high silver concentration was attained in less than 2 min of water residence within the reactor. A clear linear relationship between the silver concentration and electric current was established. Such a relationship will be useful to estimate disinfection effectiveness by measuring electric current, not silver concentration. Note that silver analyses require expensive analytical instruments and sample preparation chemicals. In the silver recovery cell with aluminum oxidation, the high silver concentration was reduced in the silver recovery cell to the safe level for long-term human consumption (0.1 mg/L). This silver recovery reaction was driven simultaneously without any electric energy demand and the energy requirement for the disinfection was substantially small so that a bicycle pedal generator or photovoltaic solar panel can provide sufficient energy for drinking water treatment. These conclusions support that the demonstrated disinfection and recovery system has the potential to provide safe drinking water to people in underprivileged communities around the world. The examined system can supply clean water for a long time with only a small amount of metallic silver. It should be noted that the disinfection experiment was performed separately from the silver recovery experiment to avoid potential removal of *E. coli* cells by aluminum precipitants. In practical applications, the aluminum electrode can be incorporated in the disinfection reactor so that ionic silver can be recovered directly onto the silver electrodes, allowing an extended use of the silver electrodes for water purification.

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References

1. M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, A. M. Mayes,

Science and technology for water purification in the coming decades. *Nature,* 2008, **452** (7185), 301–310.

2. M. D. Sobsey, C. E. Stauber, L. M. Casanova, J. M. Brown, M. A. Elliot, Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world. *Environ. Sci. Tech.,* 2008, **42** (12), 4261-4267.
3. K. S. Enger, K. L. Nelson, T. Clasen, J. B. Rose, J. N. S. Eisenberg, Linking quantitative microbial risk assessment and epidemiological data: informing safe drinking water trials in developing countries. *Environ. Sci. Tech*., 2012, **46** (9), 5160-5167.
4. A. Prüss-Üstün, R. Bos, F. Gore, J. Bartram, Safer water, better health. WHO, Geneva, 2008.
5. D. L. Sedlak, U. von Gunten, The chlorine dilemma. *Science,* 2011, **331** (6013), 42–43.
6. J. A. Lemire, J. J. Harrison, R. J. Turner, Antimicrobial activity of metals: mechanisms, molecular targets and applications. *Nat. Rev. Microbiol.,* 2013, **11** (6), 371-384.
7. R. B. Thurman, C. P. Gerba, G. Bitton, The molecular mechanisms of copper and silver ion disinfection of bacteria and viruses*. Environ. Sci. Technol.,* 1989, **18** (4), 295-315.
8. J. A. Spadaro, T. J. Berger, S. D. Barranco, S. E. Chapin, R. O. Becker, Antibacterial effects of silver electrodes with weak direct current. *Antimicrob. Agents Chemother.,* 1974, **6** (5), 637-642.
9. A. D. Russel, W. B. Hygo, Antimicrobial activity and action of silver. *Prog. Med. Chem.,* 1994, **31**, 351-370.
10. T. A. Dankovich, J. S. Levine, N. Potgeiter, E Dillingham, J. A. Smith, Inactivation of bacteria from contaminated streams in Limpopo, South Africa by silver- or copper-nanoparticle paper filters, *Environ. Sci.: Water Res. Technol.,* 2015, DOI: 10.1039/c5ew00188a
11. O. Choi, K. K. Deng, N.J. Kim, L. Ross Jr., R. Y. Surampalli, Z. Hu, The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth. *Water Res.,* 2008, **42** (12), 3066-3074.
12. J. E. Stout, V. L. Yu, Experiences of the first 16 hospitals using copper-silver ionization for *Legionella* control: implications for the evaluation of other disinfection modalities. *Infect. Control Hosp. Epidemiol.,* 2003, **24** (8), 562-568.
13. J. E. Stout, Y. E. Lin, A. M. Goetz, R. R. Muder, Controlling *Legionella* in hospital water systems: experience with the superheat-and-flush method and copper-silver ionization. *Infect. Control Hosp. Epidemiol.,* 1998, **19** (12), 911-914.
14. Z. Liu, J. E. Stout, L. Tedesco, M. Boldin, C. Hwang, W. F. Diven, V. L. Yu, Controlled evaluation of copper-silver ionization in eradicating *Legionella pneumophila* from a hospital water distribution system. *J. Infect. Dis.,* 1994, **169** (4), 919-922.
15. P. Gleick, Dirty Water: Estimated deaths from water-related diseases 2000-2020. *Pacific Institute Research Report.,* 2002.
16. United States Environmental Protection Agency. Secondary drinking water regulations: guidance for nuisance chemicals, http://water.epa.gov/drink/contaminants/secondarystandards.cfm#tabletop Date of Access: August 18, 2015
17. N. Silvestry-Rodriguez, K. R. Bright, D. C. Slack, D. R. Uhlmann, C. P. Gerba, Silver as a residual disinfectant to prevent biofilm formation in water distribution systems. *Appl. Environ. Microbiol.,* 2008, **74** (5), 1639-1641.

18. S. L. Loo, W. B. Krantz, A. G. Fane, Y. Gao, T. T. Lim, X. Hu, Bactericidal mechanisms revealed for rapid water disinfection by superabsorbent cryogels decorated with silver nanoparticles. *Environ. Sci. Tech.,* 2015, **49** (4), 2310-2318.
19. D. T. Schoen, A. P. Schoen, L. Hu, H. S. Kim, S. C. Heilshorn, Y. Cui, High speed water sterilization using one-dimensional nanostructures. *Nano Lett.*, 2010, **10** (9), 3628–3632.
20. J. Tang, L. Xiong, S. Wang, J. Wang, L. Liu, J. Li, F. Yuan, T. Xi, Distribution, translocation and accumulation of silver nanoparticles in rats. *J. Nanosci. Nanotechnol.,* 2009, **9** (8), 4924-4932.
21. W.-Y. Kim, J. Kim, J. D. Park, H. Y. Ryu, I. J. Yu, Histological study of gender differences in accumulation of silver nanoparticles in kidneys of Fischer 344 rats. *J. Toxicology Environ. Health A,* 2009, **72** (21-22), 1279-1284.
22. F. R. Khan, K. B. Paul, A. D. Dybowska, E. Valsami-Jones, J. R. Lead, V. Stone, T. F. Fernandes. Accumulation dynamics and acute toxicity of silver nanoparticles to Daphnia magna and Lumbriculus variegatus: implications for metal modeling approaches. *Environ. Sci. Technol.,* 2015, **49** (7), 4389-4397.
23. M. M. Benjamin, D. F. Lawler, *Water quality engineering: physical / chemical treatment processes*. John Wiley & Sons, Hoboken, NJ, 2013. pp. 488-502, pp. 532-535.
24. A. J. Bard, L. R. Faulkner, *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, Hoboken, NJ, 2001. pp. 44-86.
25. J. M. Passmore, D. L. Rudolph, M. M. F. Mesquita, E. E. Cey, M. B. Emelko, The utility of microspheres as surrogates for the transport of E. coli RS2g in partially saturated agricultural soil. *Water Res.,* 2010, **44** (4), 1235-1245
26. W. A. Rutala, D. J. Weber, Guideline for disinfection and sterilization in healthcare facilities. http://www.cdc.gov/hicpac/pdf/guidelines/Disinfection_Nov_2008.pdf pp. 39 Date of Access: August 19 2015.
27. Government of Ontario. Procedure for disinfection of drinking water in Ontario. https://dr6j45jk9xcmk.cloudfront.net/documents/1182/99-disinfection-of-drinking-water-en.pdf pp. 4 Date of Access: August 19 2015.
28. A. D. Eaton, M. A. H. Franson, *Standard methods for the examination of water & wastewater. 18th edition*. American Public Health Association, Washington, DC, 2005. pp. 3:13-3:93.
29. E. J. Finnemore, J. B. Franzini, *Fluid mechanics with engineering applications*. *10th edition.* McGraw Hill, New York, NY, 2006. pp. 234-241.
30. World Health Organization. Guidelines for drinking-water quality. 3rd edition. 2008. http://www.who.int/water_sanitation_health/dwq/fulltext.pdf pp. 434 Date of Access: August 19 2015.
31. Q. Schiermeier, H. Tollefson, T. Scully, A. Witze, O. Morton, Energy alternatives: electricity without carbon. *Nature,* 2008, **454**, 816-823.
32. M. A. Green, K. Emery, Y. Hishikawa, W. Warta, Solar cell efficiency tables (version 35). *Prog. Photovoltaics,* 2010, **18**, 144-150.
33. MNS Power Generating Systems. Roller style bicycle generator. http://pedalpowergenerator.com/shop-pedal-power/roller-style-bicycle-generator/ Date of Access: August 19 2015.

Tables

Table 1. Amount of viable *E.coli* cells (mean ± standard deviation in CFU/mL) during electrochemical disinfection. (Water volume = 200 mL; recirculation flow rate = 5 mL/min; 22°C; duplicated experiments performed independently; n = 2)

	1.2 V Application	0.6 V Application	Open Circuit	No Silver
0 min	441500 ± 330219	149000 ± 41012	253100 ± 247346	344000 ± 5657
10 min	6685 ± 1393	16780 ± 4455	323050 ± 419951	386500 ± 251023
20 min	170 ± 226	13295 ± 9355	303200 ± 309430	302000 ± 65054
30 min	0^*	390 ± 127	93000 ± 108894	505500 ± 65761

* No detection of viable colonies

Figures

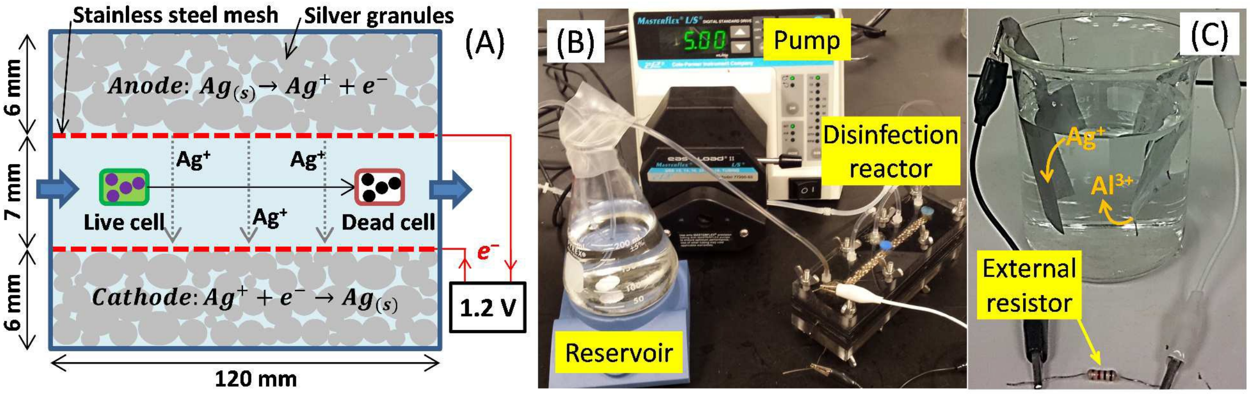

Figure 1. (A) Reactions expected in the electrochemical disinfection reactor. (B) Experimental setup for the disinfection experiment. (C) Silver recovery cell using aluminum foil.

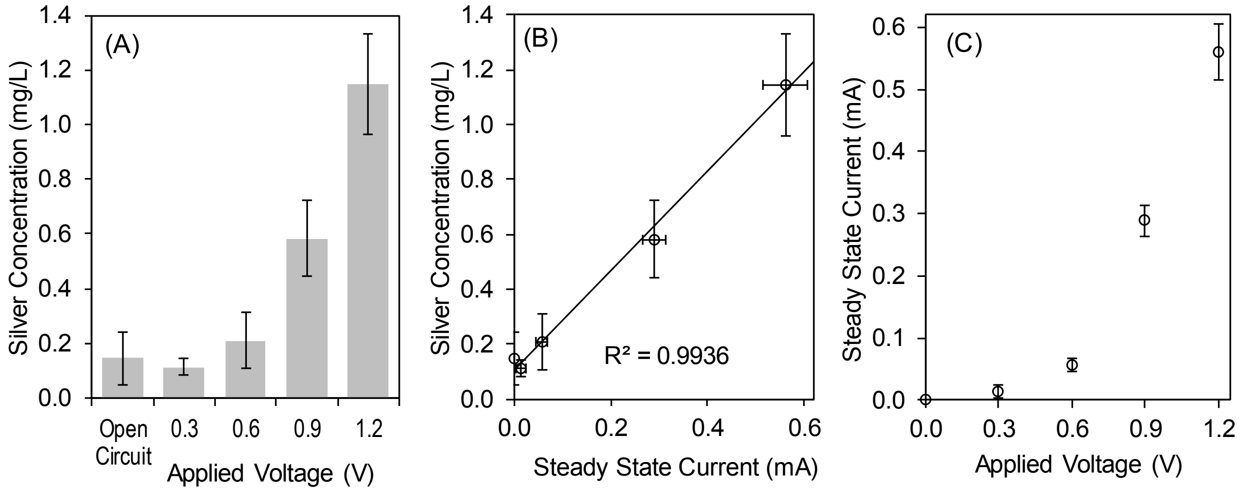

Figure 2. (A) Effluent silver concentration from the electrochemical disinfection reactor. (B) Linear correlation between the electric current and silver concentration. (C) Correlation between the electric current and applied voltage. (The steady-state current was obtained by averaging measured current values over the last 10 min of 22 min continuous-flow operation.) (Error bar = 2 × SD; N = 3)

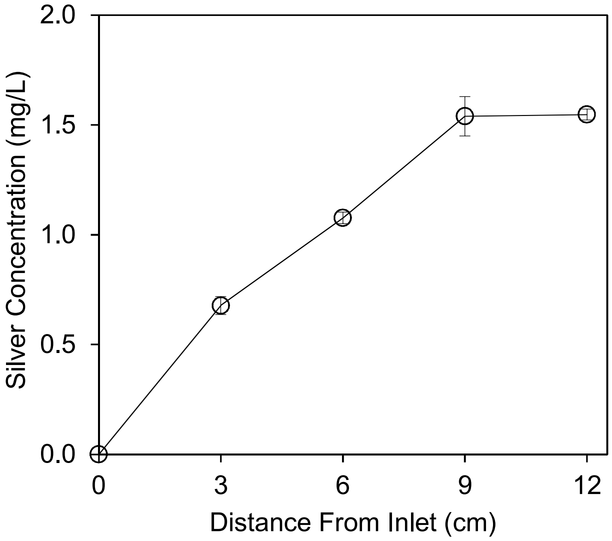

Figure 3. Silver concentration in the electrochemical disinfection reactor during continuous flow operation. (Applied voltage = 1.2 V; flow rate = 5 mL/min; length of the flow path in the reactor = 12 cm; error bar = 2 × SD; N = 3)

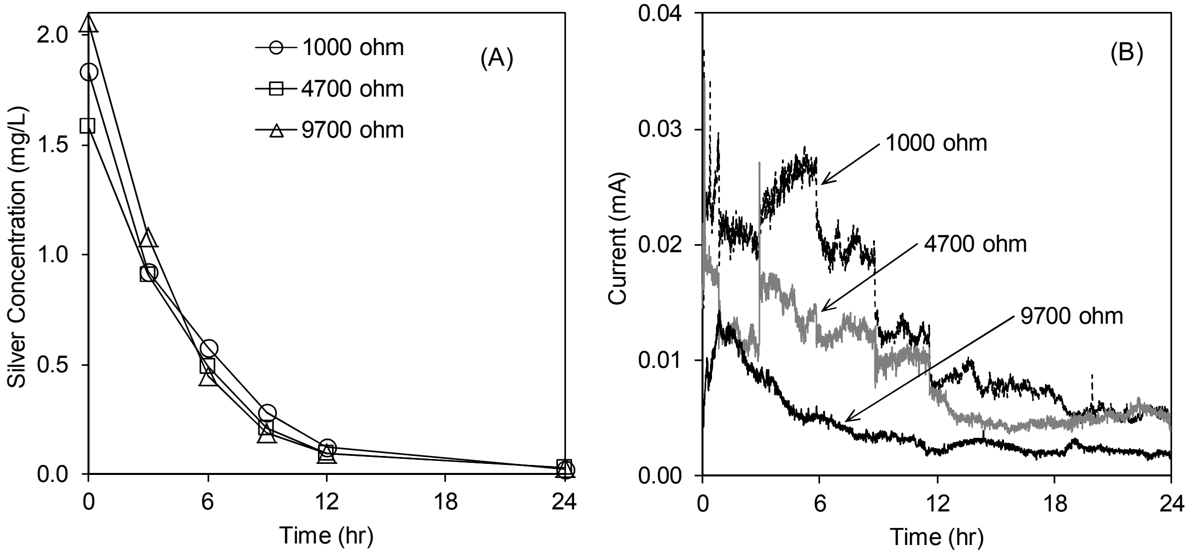

Figure 4. Silver recovery from 200 mL silver solution using aluminum foil with various external resistors. (A) Silver concentration in the silver recovery cell. (B) Electric current during the silver recovery experiment. (The initial silver solution was the effluent from the electrochemical disinfection reactor at 1.2 V and 5 mL/min.)