한국환경과학회지 제21권(제8호), 901～907, 2012
Journal of the Environmental Sciences
http://dx.doi.org/10.5322/JES.2012.21.8.901

Assessment of Bacteria Removal Using Silver Ion Absorbed Ceramic Filter

Woo-Hang Kim*, James Smith[1)]

Department of Environmental Engineering and Biotechnology, Mokpo National Maritime University, Chonnam 530-729, Korea

[1)]*Civil and Environmental Engineering, University of Virginia, Charlottesville, VA, USA*

(Manuscript received 10 July, 2012; revised 31 July, 2012; accepted 20 August, 2012)

Abstract

The objective of this study was to evaluate bacteria removal ability of the metallic silver which was baked silver ion impregnated ceramic filter at heating condition. Silver leaking from baked ceramic filter was tested to sustain bacteria removal for a long time. Silver impregnated ceramic filter could remove *E. coli* completely at 10^{12} MPN/100ml to 10^{13} MPN/100ml of influent. However, ceramic filter without silver did not remove *E. coli* completely under the same condition. After baking, the silver impregnated ceramic filter almost didn't leak out the silver ion from filter. Photo of TEM (Transmission Electron Microscopy) showed that absorbed silver ions remained in ceramic filter after baking process and most of silver were less than 10 nm. According to the increase in the amount of silver in the ceramic filter, removal efficiencies of *E. coli* were increased but turbidity removal was decreased. It can be accounted that increased removal efficiency of *E. coli* was from disinfection of silver that is in the ceramic filter. Simulated concentrations of bacteria agree well with the observed experimental effluent concentration data. Moreover, first-order decay coefficients increased to 0.0034/min after silver was added in the ceramic filter. Increase of first-order decay coefficient proves that silver-added ceramic filter can remove bacteria easily.

Key Words : Ceramic filter, Drinking water treatment, Bactria, Nano silver, Silver ion, Metallic silver, Silver nanoparticle

1. Introduction

The World Health Organization (WHO, 2000, 2006) and UNICEF (2007) assessed that 1.1 billion people do not have access to improved drinking water sources. Many technologies focus on water treatment at the point of use which is often done within the household. These so-called household drinking water treatment systems contribute to reaching many people in the short-term, even though they demand a certain degree of expertise and commitment by the users. A household water treatment system currently in use by many people worldwide is the ceramic filter.

Ceramic filters (CFs) are known to remove bacteria. However when high concentration of bacteria is applied, people fail to get complete removal. In order to increase bacterial removal ability, many studies are done on ceramic filter impregnated with silver ion(Kim, 2008) or silver nanoparticles(Arnim, 1998; Bell, 1991; Chen and Schluesener, 2008; Lok et al., 2007; Van Halem et al., 2009; Vinka and James, 2008). Both have shown complete removal of bacteria even at high concentrations. However, silver nanoparticles are expensive and silver ion leaks out easily from the ceramic filter due to its high water solubility. It is in

*Corresponding author : Woo-Hang Kim, Department of Environmental Engineering and Biotechnology, Mokpo National Maritime University, Chonnam 530-729, Korea
Phone: +82-61-240-7310
E-mail: whkim@mmu.ac.kr

this manner that, ceramic filter with silver ion is not able to remove bacteria efficiency.

In order to keep disinfection ability with silver ion it has to remain in the ceramic filter. This means that if we somehow prevent the leaking of silver ion for filter, it can keep its disinfection ability for long. One of the easy ways to retain silver in the ceramic filter is baking. However a US patent (1966) on baking method has explained that high temperature convert silver nitrate to metallic silver. Even if baking the silver may allow it to remain in the filter, it will stay in form of metallic silver, instead of silver ion. It is not known if metallic silver also have bacteria removal ability like silver ion and if this ability last for a long time. Therefore there was a needed to test the bacteria removal ability and its sustainability for metallic silver.

The objectives of this study were to evaluate bacteria removal ability of the metallic silver in ceramic filter and leaking of silver from the baked ceramic filter. This research investigated bacteria removal mechanism of ceramic filters. CXTFIT computer model was used to simulate bacteria transport through the filters and to quantify first-order bacterial decay coefficients for filter treated with silver ion.

2. Materials and Methods

Ceramic filters (CFs) were made with the following methods. 50% of grog, 40% of clay, 10% of flour were combined and mixed until homogeneous and then added water. The mixture was molded by hand and placed in a 6.2 cm diameter polyvinylchloride cylindrical mold and then compressed for 1 minute at 1000 psi. The filter was air-dried at room temperature for 3days and then fired in a muffle furnace. The temperature was increased at a rate of 150 ℃/h from room temperature to 600 ℃, and increased at a rate of 300 ℃/h to 900 ℃ and then holding this final temperature for 3 hours.

Silver ion was impregnated into the ceramic filters in 3 ways. While making the ceramic filter, grog, clay and flour were mixed with 1.5% of Ag^+ dissolved in deionized water. The same procedure was followed for the other process. This first way was named MCF1. The second technique (MCF2) involved absorbing silver ion from silver ion solution before baking. Dried filter was submerged in the 20,000mg/l of silver nitrate solution for 1 minute. It was then dried at room temperature for 3 days. It was fired in the same conditions after. In the third method, the filter was fired two times. At first, CFs were made through normal process that was described over. Later, at 100 ml of 2% silver nitrate, the solution was passed through CFs. The CF particles were expected to absorb some silver ion from the solution. After this, the filter was dried for 3 days and fired similar with the second method. This third way was named MCF3.

Continuous experiment was conducted using the following method. HPLC pump worked a 0.6 ml/min inflow rate to the chamber. The influent solution was used the 10 mM ion strength of phosphate buffer. After the saturation period, 1 ml syringe was used to inject a 0.6 ml pulse of *E. coli*. The concentration of influent *E. coli* was 10^{12} MPN/100 ml to 10^{13} MPN/100 ml. Flow direction was up flow. A nonpathogenic wild strain of *E. coli* was provided for this test by IDEXX laboratories. The chamber was filled with water and chamber' pressure was regulated to 5 psi. Effluent sample was collected in a flask until 100 minutes. The filter was in the chamber. In order to prevent side flow, the filter was placed in a flexible–wall permeameter with a pressure of 5 psi. The chamber was filled with water. A three-way stopcock was connected to the inflow valve of the permeameter chamber. The ceramic filter was 6.2 cm of diameter and 1.2 cm of tick. Pulse injection volume was 0.6ml. Effluent concentrations

of *E. coli* were detected with an average concentration for 100 minutes using the method of IDEXX laboratories.

Batch test for silver ion leaking was conducted by this method. Silver ion ceramic filter (SICF) was made by submerging, ceramic filter in 10,000 mg/l of silver ion solution for 2 hr and then drying it for 6days. Since filters were not baked, the absorbed silver ions will retain in their original form. Each filter was submerged in 100 ml of deionized water and silver ion was detected by time.

Transport experiments were performed with ceramic filters with and without silver. The ceramic filters were placed in flexible-wall permeameters and a three-way stopcock was connected to the inflow valve of the permeameter chamber. A high-performance liquid chromatography (HPLC) pump and a 1 ml syringe were connected to the three-way stopcock. The HPLC pump maintained a 6 ml/min inflow rate to the chamber. The inflow solution was the phosphate buffer that has 10 mM ion strength. Phosphate buffer solutions were prepared as described by Sherwood et al.(2003). The effluent valve of the permeameter chamber was open to the atmosphere and used to collect effluent water samples for analysis of tracer and bacteria. The ceramic filters were saturated with the phosphate buffer solution through the filter for 6 hours. After the saturation period, a 1 ml syringe was used to inject a 0.6 ml pulse of 4.3 μCi $[^3H]H_2O$ (tritium) into the ceramic filter and effluent samples were collected over time to define the breakthrough of this conservative tracer. Transport of bacteria through each filter was quantified by methods similar to those used for the tracer. A 0.6 ml pulse of concentrated *E. coli* was passed through the filter and effluent samples were collected over time to define the breakthrough of the *E. coli*. These ceramic filters were made with 80% of clay and 20% of sawdust.

"Effluent tracer and bacteria concentrations over time for ceramic filters with and without silver treatments were simulated using the following transient one-dimensional form of the advection-dispersion equation with first-order decay:

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu c$$

Subject to the following initial and boundary conditions;

$c(x,0)=0$

$c(0,t) = c_o$ for $t<t_o$

$c(0,t) = 0$ for $t>t_o$

$$\frac{\partial c(L,t)}{\partial x} = 0$$

Where R is the retardation coefficient, c is the concentration of tritium or *E. coli*, t is time (min), t_o is the tracer and bacteria pulse injection time, D is the dispersion coefficient (cm^2/ min), x is distance (cm), v is the linear velocity (cm/min), μ is the first-order decay coefficient (/min) and L is the thickness of the filter. This model assumes local equilibrium sorption. The computer program CXTFIT (Toride et al., 1995) was used to adjust the relevant model parameters to provide the optimum fit of the model to the experimental data. D and v for each column were determined from the tritium transport experiments (with R=1 and μ=0). R and μ were determined from the *E. coli* transport experiments (Vinka and James, 2008)."

3. Results

Fig. 1 shows that all silver impregnated filters have performed better than ceramic filter (CF) alone, which could not remove *E. coli* completely. Among the impregnated filters, MCF1 and MCF2 have completely removed *E. coli*, but MCF3 did not. This was possibly due to less capacity of baked CF to absorb silver ion. The concentration of influent *E.*

coli was 10^{12} MPN/100ml to 10^{13} MPN/100 ml. At MCF1 is a little high but, influent concentrations of *E. coli* were almost the same. It means that silver in ceramic filter affected to *E. coli* removal. For removal of bacteria, it is more effective to add silver ion before baking.

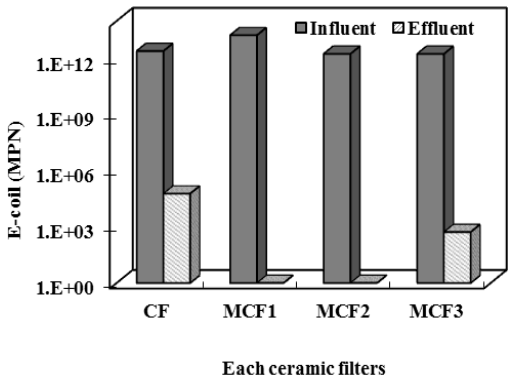

Fig. 1. Comparisons of *E. coli* removal at baked ceramic filters with silver.

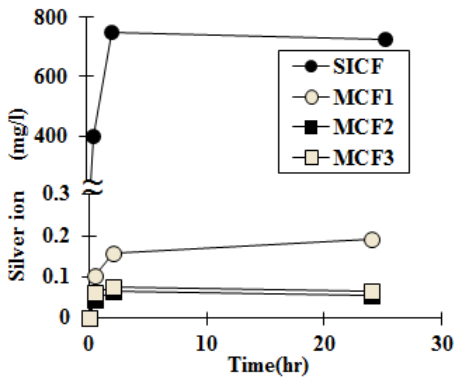

Fig. 2. Leaking of silver ion from baked ceramic filters with silver ion.

Fig. 2 shows the release of silver ion from ceramic filters with metallic silver. The release from MCF1 was a little higher compared to others. This could probably because the amount of silver ion in MCF1 is higher than others, thus higher release of silver ions. However, these concentrations were less than 0.2 mg/l for all 3 filters. Thus, we can conclude that disinfection ability of these filter will last much longer compared to SICF. Silver ions of MCF2 and MCF3 were released lower than that of MCF1. MCF1 and MCF2 were good at bacteria removal and MCF2 and MCF3 were released lower than MCF1. Therefore the making method of MCF2 was chosen in the next experiments. MCF2 was made in order that dried filter was submerged in the 20,000mg/l of silver nitrate solution for 1 minute. It was then dried at room temperature for 3 days and baked.

The above results proved that silver in ceramic filter could increase bacteria removal. However, we don't know yet how are the silvers posited in ceramic filter. In order to show the silvers in ceramic filter, a photograph was taken by TEM. Fig.3 showed silvers size in ceramic filter(0.5g silver/a ceramic filter). Most of silver were less than 10 nm. This photo showed that absorbed silver ions remained in ceramic filter after baking process. While the ceramic filter with silver is baked, the silver can change the pore system in ceramic filters. It is possible that treatment of the ceramic filters by silver and the changed pores both improved bacterial removal efficiency by physically clogging. Also disinfection can improve bacteria removal efficiency. Therefore it is necessary to determine which had the greatest effect on the bacteria.

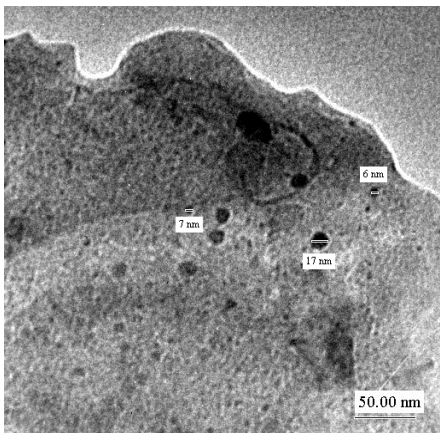

Fig. 3. Silver in ceramic filter after backing process by TEM.

Fig. 4 shows removal efficiency of *E. coli* and turbidity. Ceramic filter without silver ion had 85.4% of removal efficiency. Removal efficiency of *E. coli* was increased with increase of silver content in ceramic filters. At 0.05g, 0.05g and 0.5g silver ion added to the ceramic filter, removal efficiency of *E. coli* were 98.34% 99.0 and 99.8%. Bacteria can be removed by two mechanisms: physical clogging and disinfection. In order to clarify this removal mechanism, physical filtration was conducted using kaolin because it can be removed the physical clogging only. If removal efficiency of kaolin will be increased, increasing bacteria removal may also be improved by physical clogging. If it will not be increased, increasing bacteria removal is from disinfection only. In this figure removal efficiency of kaolin was decreased with increasing silver concentration. It means increased bacteria removal due to disinfection. Decreasing of kaolin removal could be that ceramic filter also physically changed while it was baked with silver ion. However the physical changing did not improved bacteria removal.

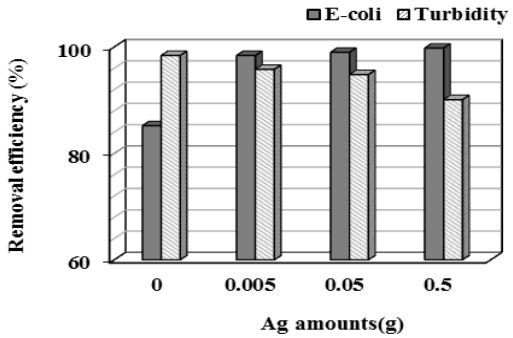

Fig. 4. Removal efficiency of *E. coli* and turbidity according to silver ion concentration.

This figure also shows removal efficiency of *E. coli* increased a lot with even small amounts of silver ion (0.005 g). This test used a little different ceramic filters that is made with 80% of clay and 20% of sawdust. Because 50% of grog, 40% of clay, 10% of flour contained ceramic filter removed *E. coli* completely at small amounts of silver contained in the ceramic filter.

Fig. 5 shows effluent tritium concentrations normalized to the influent pulse concentration as a function of time. Simulated concentrations of tritium agree well with experimentally observed effluent concentration data. The tritium was a conservative tracer in all ceramic filters. Therefore greater than 90% of all influent tritium was recovered during effluent sample collection for both tests. The fitted values of the linear velocity (v) and dispersion coefficient (D) were determined for the ceramic filter based on analysis of the tracer experiments. Linear velocities were 0.044 cm/min and 0.049 cm/min and dispersion coefficients were 0.0079 cm^2/min and 0.0106 cm^2/min at without Ag and with Ag 5 mg. This figure shows linear velocity and dispersion coefficient became a little bigger at Ag addition. It means tracer flow out fast in the Ag added ceramic filter. It can be explained that decrease of turbidity removal using silver in ceramic filter is due to this higher concentration.

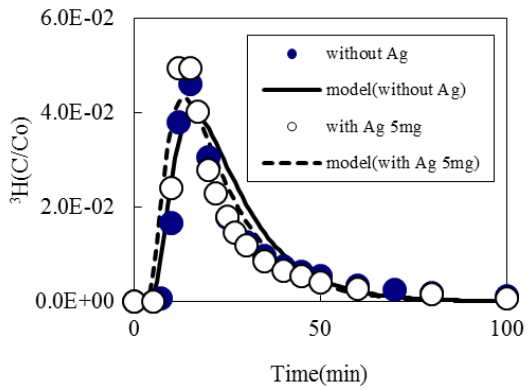

Fig. 5. Tritium effluent nomalized to the influent pulse concentration at with and without silver.

Simulated concentrations of bacteria agree well with the observed experimental effluent concentration

data (Fig.6). This simulation was used to get other factor: retardation factor (R) and first-order decay coefficient (μ). The values of retardation factor were 0.97 and 0.74 at with and without silver added ceramic filters. This means that *E. coli* flow out later in the silver added ceramic filters. First-order decay coefficients were 0.0034/min with silver added. For bacteria transport experiments through ceramic filters untreated with silver ion, first-order decay coefficient was assumed to equal zero. Since this coefficient is related with bacteria removal, large value means decay rate of bacteria is high.

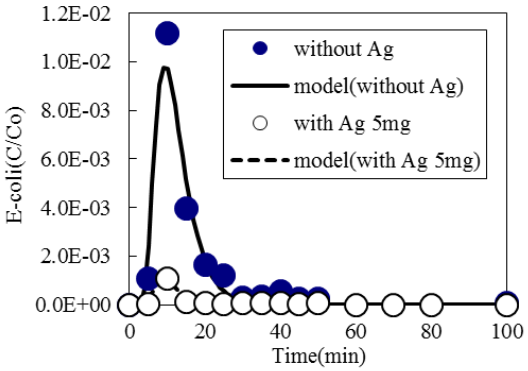

Fig. 6. *E. coli* effluent nomalized to the influent pulse concentration with and without silver.

4. Conclusions

Silver impregnated ceramic filter could remove *E. coli* completely at 10^{12} MPN/100ml to 10^{13} MPN/100ml of influent. However, ceramic filter without silver did not remove *E. coli* completely under the same condition. After baking of silver impregnated ceramic filter, almost all of the silver ion didn't leak out from filter. Photo of TEM showed that absorbed silver ions remained in ceramic filter after baking process and most of silver were less than 10 nm. According to the increase in the amount of silver in the ceramic filter, removal efficiencies of *E. coli* were increased but turbidity removal was decreased. Therefore increased removal efficiency of *E. coli* was from silver disinfection in the ceramic filter. Simulated concentrations of bacteria agree well with the observed experimental effluent concentration data. First-order decay coefficients increased 0.0034/min after silver was added in the ceramic filter. Increase of first-order decay coefficient proves that silver-added ceramic filter can remove bacteria efficiently.

Reference

Arnim, H., 1998, Colloidal Silver Nanoparticles: Photochemical Preparation and Interaction with O_2, CCl_4, and Some Metal Ions, Chem. Mater, 10, 444-450.

Bell, F. A. Jr., 1991, Review of effects of Silver-Impregnated Carbon Filters on Microbial Water Quality, J. AWWA Research and Technology, 83(8), 74-76.

Chen, X., Schluesener, H. J., 2008, Nanosilver: A nanoproduct in medical application, Toxicology Letters, 176, 1-12.

Kim, J. Y., Lee, C. H., Cho, M., Yoon, J. Y., 2008, Enhanced inactivation of E.coli and MS-2 phage by silver ions combined with UV-A and visible light irreadiation, Water Research, 42, 356-362.

Lok, C. N., Ho, C. M., Chen, R., He, Q. Y., Yu, W. Y., Sun, H., Tam, P. K., Chiu, J. F., Che, C. M., 2007, Silver nanoparticles: partial oxidation and antibacterial activities, J. Biol. Inorg. Chem., 12, 527-534.

Sherwood, J. L., Sung, J. C., Ford, R. M., Fernandez, E. J., Maneval, J. E., Smith, J. A., 2003, Analysis of bacterial random motility in a porous medium using magnetic resonance imaging and immunomagnetic labeling, Enciron. Sci. Technol., 37(4), 781-785.

Toride, N., Leij, F. J., Genuchten, M. T. V., 1995, CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.0, Research report 137, U.S. Salinity Laberatory, USDA: Riverside, CA.

UNICEF/WSP, 2007, Improving Household Drinking

Water Quality; Use of Ceramic Water Filters in Cambodia. Water and Sanitation Program (WSP).

United States Patent Office, 1966, Impregnation of carbon with silver, (3,294,572), Dec. 27.

Van Halem, D., Van der Laan, H., Heijman, S. G. J., van Dijk, J. C., Amy, G. L., 2009, Assessing the sustainability of the silver-impregnated ceramic pot filter for low-cost household drinking water treatment, Physics and Chemistry of the Earth, 34, 36-42.

Vinka, A. O., James, A. S., 2008, Sustainable Colloidal-Silver-Impregnated Ceramic Filter for Point-of-Use Water treatment, Environ. Sci. Techol., 42(3), 927-933.

World Health Organization/UNICEF, 2000. Global Water Supply and Sanitation Assessment Report, Geneva.

World Health Organization/UNICEF, 2006. Guidelines for Drinking-Water Quality, First Addendum to Third Edition, Volume 1 Recommendations, Geneva.