Membrane and Water Treatment, *Vol. 10, No. 3 (2019) 231-237*
DOI: https://doi.org/10.12989/mwt.2019.10.3.231

Inactivation of *Escherichia coli* and MS2 coliphage by Cu(II)-activated peroxomonosulfate in natural water

Hyung-Eun Kim[1†], Hye-Jin Lee[2†], Min Sik Kim[3], Joon-Young Choi[4] and Changha Lee[*3]

[1]*Center for Water Resource Cycle Research, KIST School, Korea Institute of Science and Technology (KIST), 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea*
[2]*Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada*
[3]*School of Chemical and Biological Engineering, Institute of Engineering Research, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea*
[4]*Hyorim Industries Inc., 96-8, Yatap-ro, Bundang-gu, Seongnam-si, Gyeonggi-do 13517, Republic of Korea*

(Received October 1, 2018, Revised March 28, 2019, Accepted April 1, 2019)

Abstract. Peroxymonosulfate (PMS) in combination with Cu(II) was examined to inactivate *E. coli* and MS2 coliphage in natural water. The combined system (i.e., the Cu(II)/PMS system) caused a synergistic inactivation of *E. coli* and MS2, in contrast with either Cu(II) or PMS alone. Increasing the concentration of PMS enhanced the inactivation of *E. coli* and MS2, but after a certain point, it decreased the efficacy of the microbial inactivation. In the Cu(II)/PMS system, adding reactive oxidant scavengers marginally affected the *E. coli* inactivation, but the inhibitory effects of copper-chelating agents were significant. Fluorescent assays indicated that the Cu(II)/PMS system greatly increased the level of reactive oxidants inside the *E. coli* cells. The sequential addition of Cu(II) and PMS inactivated more *E. coli* than did adding the two simultaneously; in particular, the inactivation efficacy was much higher when Cu(II) was added first. The observations from the study collectively showed that the microbial inactivation by the Cu(II)/PMS system could be attributed to the toxicity of Cu(I) as well as the intracellular oxidative stress induced by Cu(III) or radical species.

Keywords: microbial inactivation; *E. coli*; MS2 coliphage; copper; peroxymonosulfate

1. Introduction

Chemical oxidants (chlorine, ozone, hydrogen peroxide, chlorine dioxide, ferrate, etc.) have been extensively studied as water disinfectants for various microorganisms (Hoff and Geldreich 1981, von Gunten 2003a, Cho *et al*. 2006 and 2010, Huh and Ahn 2017). These oxidants exert oxidative damage on microbial cell components, which inactivates microorganisms. Among these disinfectants, chlorine (free and combined) and ozone are the most effective, and they are widely used in drinking water and wastewater treatment plants (Cho *et al*. 2010, von Gunten 2003b).

Persulfates (i.e., peroxymonosulfate (PMS) and peroxydisulfate (PDS)) are relatively new oxidants that have been intensively studied as alternatives for environmental remediation (mostly for oxidizing organic contaminants in water) for the past decade (Ahmadi *et al*. 2017, Baziar *et al*. 2018, Lee *et al*. 2018). Persulfates are strong oxidants with high standard redox potentials for two-electron reduction $E°[S_2O_8^{2-}/SO_4^{2-}]$ = 1.96 V_{NHE} and $E°[HSO_5^{-}/SO_4^{2-}]$ = 1.75 V_{NHE}), and they are capable of directly oxidizing different organic compounds (Lee *et al*. 2018). However, most researchers on environmental applications of persulfates have worked with the activated persulfate systems to broaden the spectrum of treatable target contaminants. It is known that persulfates can be activated into more reactive oxidants (e.g., sulfate radical anion, $SO_4^{\bullet-}$, $E°[SO_4^{\bullet-}/SO_4^{2-}]$ = 2.5–3.1 V_{NHE}) by different methods via thermal, photolytic, and catalytic reactions (Lee *et al*. 2018). Transition metals such as Co(II), Fe(II), Ru(III), Ti(III), Ce(III), Mn(II), and Ni(II) have been reported to catalyze persulfate decomposition into reactive oxidants (Anipsitakis and Dionysiou 2003, 2004, Gilbert and Stell 1990, Lente *et al*. 2009, Zhang and Edwards 1992). Particularly, the Co(II)/PMS system was highly effective at degrading organic contaminants across a wide range of pH (Anipsitakis and Dionysiou 2003, 2004, Anipsitakis *et al*. 2008).

Several researchers have attempted to use persulfates (mainly PMS) for water disinfection; for instance, the Co(II)/PMS system was tested for disinfecting swimming pool water (Anipsitakis *et al*. 2008). PMS in the presence of chloride ion has been demonstrated to produce hypochlorite for disinfection (Delcomyn *et al*. 2006, Jang *et al*. 2010). In addition, dioxiranes generated in situ from the oxidation of acetone and pyruvates by PMS have been suggested as disinfectants to inactivate different microbial species (Wallace *et al*. 2005, Wong *et al*. 2006)

In this study, we examined the combination of Cu(II) with PMS for inactivating *E. coli* and MS2 coliphage. Although a few researchers have reported on using copper-activated PMS to oxidize organic contaminants (Ding *et al*.

*Corresponding author, Professor
E-mail: leechangha@snu.ac.kr
† These authors contributed equally to this work.

ISSN: 2005-8624 (Print), 2092-7037 (Online)

2013, Kumar *et al*. 2012), little is known about its feasibility for disinfection, although one group of researchers did apply the Cu(II)/PMS system to inactivate biofilm cells (Wood *et al*. 1996). Our previous studies showed that combining Cu(II) with hydrogen peroxide (H_2O_2) and hydroxylamine generated various microbicidal agents that enhanced the inactivation of bacterial (both planktonic and biofilm) cells and viral particles (Nguyen *et al*. 2013, Kim *et al*. 2015, Lee *et al*. 2017). We anticipated similar multi-microbicidal effects from the Cu(II)/PMS system in this study.

With this study, we aimed to assess the potential of the Cu(II)/PMS system for water disinfection. For this purpose, we conducted a series of experiments using surrogate microorganisms (i.e., *E. coli* and MS2 coliphage) in natural water; we examined the efficacy of microbial inactivation at varying concentrations of PMS as well as the effects of reactive oxidant scavengers and copper-chelating agents on the microbial inactivation. In addition, we monitored the generation of intracellular oxidants in *E. coli* cells in the presence of Cu(II) and PMS.

2. Materials and methods

2.1 Reagents

All chemicals were of reagent grade and were used without further purification. PMS, copper sulfate ($CuSO_4$), ethylenediaminetetraacetic acid (EDTA), 2,9-dimethyl-1,10-phenanthroline (DMP), methanol (MeOH), *tert*-butanol (*t*-BuOH), and sodium sulfite were purchased from Sigma-Aldrich Co. Microbiological reagents including agar, nutrient broth, tryptone, yeast extract for *E. coli* and MS2 coliphage cultivation were purchased from Becton-Dickinson Co. The 3'-(*p*-hydroxyphenyl) fluorescein (HPF) as a fluorescent probe compound to measure cellular oxidants was obtained from Invitrogen Co. All solutions were prepared using deionized water (> 18 MΩ·cm, Millipore Co.). All glassware was washed with deionized water, and sterilized by autoclave at 121°C for 15 min prior to use.

2.2 Natural water characterization

We collected natural water samples from the Hoeya drinking water treatment plant in Ulsan City, Korea. The sampled water was immediately filtered through 0.22 μm nylon filter and stored at 4°C until use. We then measured water quality parameters: pH, conductivity, turbidity, TOC, and UV_{254} (Table 1).

2.3 Culture and analysis of microorganisms

We chose *E. coli* (ATCC 8739) and MS2 coliphage (ATCC 15597-B1) as indicator microorganisms for bacteria and viruses, respectively. *E. coli* was incubated in 30 mL of nutrient broth at 37°C for 18–24 h. Cells were collected by centrifugation at 3000g for 15 min and washed 3 times with 30 mL of phosphate-buffered saline (PBS, pH 7.2). The cells were resuspended in 20 mL of PBS and kept in the refrigerator at 4°C; the cell stock contains approximately ~10^9 CFU/mL. The population of *E. coli* cells was determined by the spread plate method using nutrient agar plates (Eaton *et al*. 2005). The plates were incubated for 18–24 h at 37°C, and then we counted the numbers of colonies.

Table 1 Water quality parameters of natural water sample

pH	7.23
Conductivity (μS cm^{-1})	178.1
Turbidity (NTU)	0.19
TOC (mg L^{-1})	2.52
UV_{254} (cm^{-1})	0.05

MS2 coliphage was incubated in tryptone broth with *E. coli* C3000 (ATCC 15597) as a host for 18 h at 37°C. The mixture of *E. coli* and MS2 coliphage was centrifuged at 3000 g for 15 min. MS2 particles were collected by filtering the supernatant through a 0.22 μm PTFE syringe filter. We determined the population of MS2 coliphage by plaque assay using 0.5% and 1.5% of agar for the top and bottom layers, respectively (Eaton *et al*. 2005).

2.4 Inactivation experiments

We conducted all inactivation experiments in 60 mL Pyrex reactors using sampled natural water at room temperature (24±0.5°C). *E. coli* cells or MS2 particles were spiked prior to the experiments at an approximate initial concentration of 10^7 CFU/mL or PFU/mL. The inactivation was initiated by adding the microbicidal reagents Cu(II) and PMS. Samples (1 mL) were withdrawn at predetermined times, immediately mixed with quenching reagents (EDTA and sodium thiosulfate), and diluted serially with PBS. We assayed each sample on triplicate agar plates to determine the number of viable cells and viral particles. For some experiments, we used MeOH and *t*-BuOH as oxidant scavengers and used DMP and EDTA as copper-chelating reagents (Cu(I) and Cu(II), respectively). The pH variations were less than 0.1 units during the inactivation experiments under all the tested conditions. In addition, for some of the inactivation experiments, we sequentially added the reagents (Cu(II) and PMS) into the solution with 15 min time interval.

2.5 Measuring the intra-/extracellular oxidants

We measured the levels of reactive oxidants (e.g., hydroxyl radical, •OH and cupryl species, Cu(III)) in the intracellular and extracellular regions using HPF as a fluorescent probe compound; details are described elsewhere (Gomes *et al*. 2005, Kim *et al*. 2015). Briefly, *E. coli* cells were suspended in a solution of HPF (100 μM) for 1 h while stirring at 100 rpm for staining. The stained cells were centrifuged (5000 rpm, 3 min) and washed with PBS; this procedure was repeated three times, and then we measured the intracellular oxidants using the stained *E. coli* cells. We also measured the extracellular oxidants in 10 μM HPF solution without cells. The variations of fluorescence

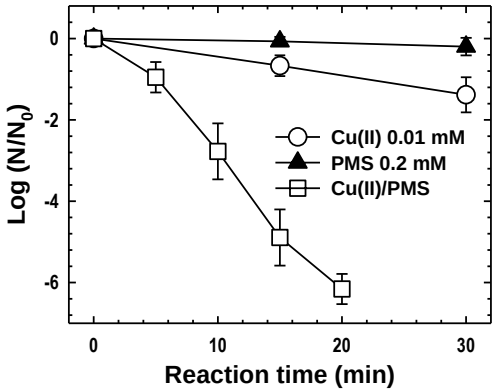

Fig. 1 Inactivation of *E. coli* by Cu(II), PMS, and Cu(II)/PMS in natural water ($[Cu(II)]_0$ = 0.01 mM, $[PMS]_0$ = 0.2 mM)

intensity induced by Cu(II), PMS, and Cu(II)/PMS were recorded on a microplate reader (Infinite M200, Tecan Co.).

3. Results

3.1 Inactivation of E. coli by the Cu(II)/PMS system

We examined the inactivation of *E. coli* by Cu(II), PMS and Cu(II)/PMS in natural water (Fig. 1). PMS (0.2 mM) caused negligible inactivation of *E. coli*. Cu(II) (0.01 mM) resulted in approximately 1.5 log inactivation of *E. coli* in 30 min. However, the combined use of Cu(II) and PMS exhibited synergistically enhanced bactericidal activity, resulting in more than 6 log inactivation of *E. coli* in 20 min.

For the experiments, we varied the concentrations of PMS from 0.02 mM to 0.8 mM (Fig. 2). We calculated the average inactivation rates from the time-dependent inactivation curves (data not shown) and present them for the different PMS concentrations. With PMS alone, the *E. coli* inactivation rate increased gradually with increasing concentrations (Fig. 2a). In the Cu(II)/PMS system, the inactivation rate increased as the concentration increased from 0.02 mM to 0.4 mM, but it decreased with 0.8 mM PMS (Fig. 2b). Figs. 2a and 2b show clearly that the Cu(II)/PMS system has superior bactericidal activity to PMS alone at all tested PMS concentrations.

3.2 Effects of oxidant scavengers and copper-chelating agents

We next examined the effects of oxidant scavengers (MeOH and *t*-BuOH) and copper-chelating agents (EDTA and DMP) on inactivating *E. coli* in the Cu(II)/PMS system; we present the average inactivation rate for each condition (Fig. 3). Adding oxidant scavengers only marginally decreased the inactivation rate (by 7% and 5% for MeOH and *t*-BuOH, respectively), but *E. coli* inactivation was significantly inhibited by adding copper-chelating agents; the inactivation rate decreased by 95% and 83% in the presence of EDTA and DMP, respectively.

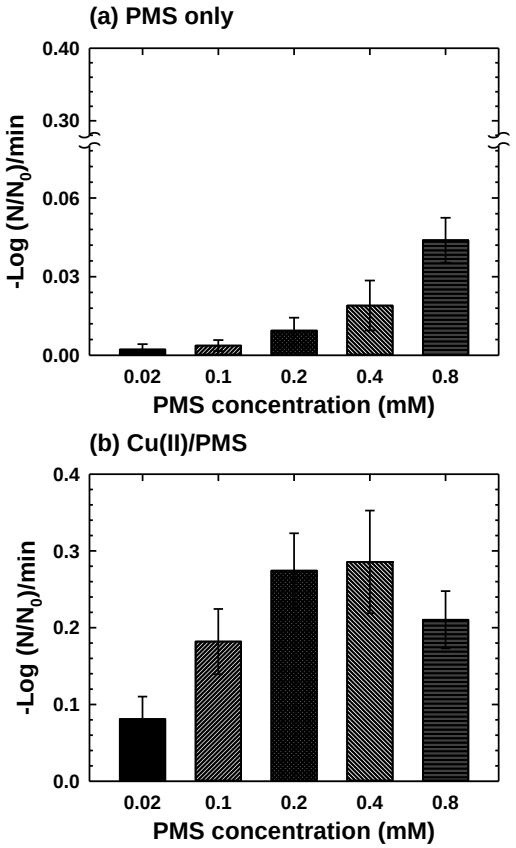

Fig. 2 Inactivation rate of *E. coli* by PMS and Cu(II)/PMS in natural water at different concentrations of PMS ($[Cu(II)]_0$ = 0.01 mM)

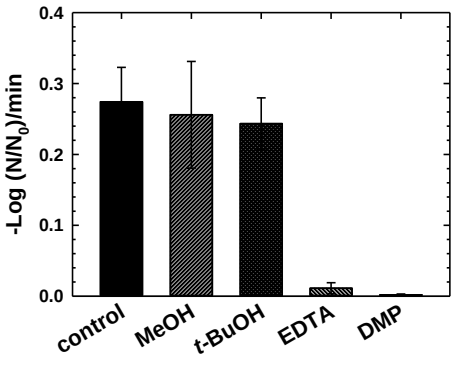

Fig. 3 Effects of copper-chelating agents and oxidant scavengers on the inactivation of *E. coli* by Cu(II)/PMS ($[Cu(II)]_0$ = 0.01 mM, $[PMS]_0$ = 0.2 mM, [MeOH] = [*t*-BuOH] = 200 mM, [EDTA] = [DMP] = 2 mM)

3.3 Sequential addition of Cu(II) and PMS

We also examined sequentially adding Cu(II) and PMS to inactivate *E. coli*, adding either Cu(II) or PMS first for 15 min and then adding the other reagent. We compared the findings for the two sequential treatments (Cu(II)→PMS and PMS→Cu(II)) with those from adding Cu(II) and PMS both alone and simultaneously (Figs. 4a and 4b) and found that both of the sequential treatments inactivated more *E.*

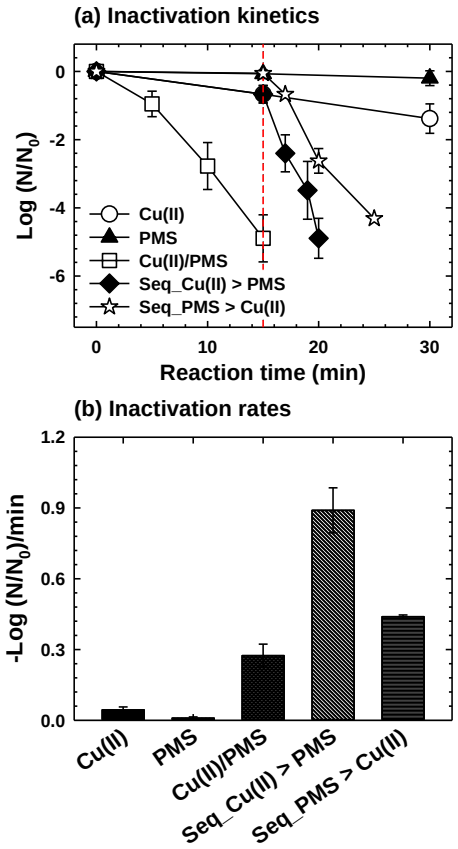

Fig. 4 Inactivation of *E. coli* by Cu(II), PMS, and Cu(II)/PMS (simultaneous and sequential additions); the inactivation rates of sequential additions were calculated from the slopes after the second reagent was added (15 min) ($[Cu(II)]_0$ = 0.01 mM, $[PMS]_0$ = 0.2 mM).

coli than did the combination of Cu(II) and PMS (compare the slope of the inactivation curve for Cu(II)/PMS to those of sequential treatments after the point of the second reagent injection, Fig. 4a). The inactivation rates of *E. coli* for the two sequential treatments (Cu(II)→PMS and PMS→Cu(II), respectively) were 3.5 fold and 1.5 fold higher than that for Cu(II)/PMS (Fig. 4b).

3.4 Generation of intra/extracellular oxidants

We monitored the generation of oxidants by Cu(II), PMS, and Cu(II)/PMS in extracellular (bulk phase) and intracellular (inside the *E. coli* cells) regions (Fig. 5); HPF is known to detect reactive oxidants such as •OH and Cu(III) (Gomes *et al*. 2005, Nguyen *et al*. 2013, Kim *et al*. 2015). The fluorescence intensity ratio (FIR) represents the ratio of the intensity for treatment cases relative to the control intensity (for the solution containing only the probe compound). The FIRs did not significantly change (close to unity) with either Cu(II) or PMS alone in either the extracellular or intracellular regions. However, Cu(II)/PMS increased the FIRs to 1.4 and 10.7 in the extracellular and intracellular regions, respectively. The higher FIR value in the intracellular region indicates that the reactive oxidants are mainly generated inside the cells rather than in the bulk phase.

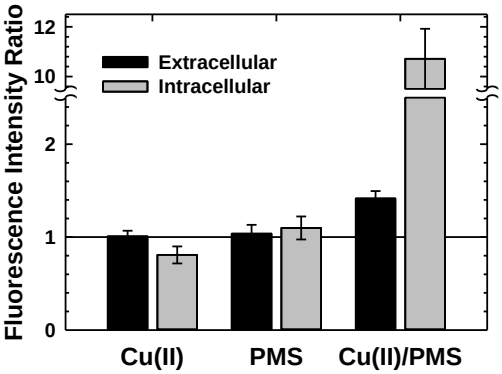

Fig. 5 Generation of intracellular/extracellular oxidants by Cu(II), PMS, and Cu(II)/PMS ($[Cu(II)]_0$ = 0.01 mM, $[PMS]_0$ = 0.2 mM).

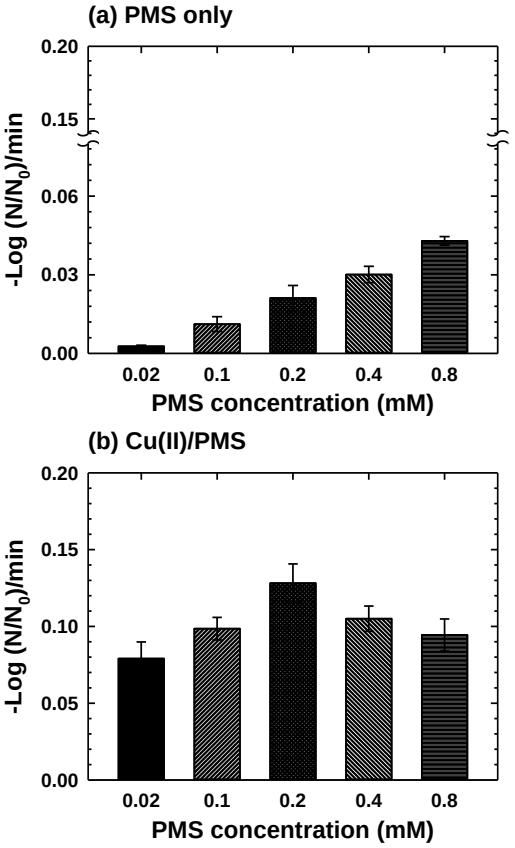

Fig. 6 Inactivation rate of MS2 coliphage by PMS and Cu(II)/PMS in natural water at different concentrations of PMS ($[Cu(II)]_0$ = 0.01 mM).

3.5 Inactivation of MS2 coliphage

The inactivation of MS2 coliphage by PMS and Cu(II)/PMS was examined by varying the concentration of PMS; the average inactivation rates were presented at different PMS concentrations (Figs. 6a and 6b). The inactivation rate of MS2 gradually increased with increasing the PMS concentration (Fig. 6a). On the other hand, the inactivation of MS2 by Cu(II)/PMS was optimized at 0.2 mM PMS (Fig. 6b). The overall trends of

MS2 inactivation by PMS and Cu(II)/PMS were similar to those of *E. coli* inactivation (Figs. 2a and 2b). However, the inactivation rates of MS2 by Cu(II)/PMS were generally lower than those of *E. coli* (compare the values of Fig. 2b and Fig. 6b).

4. Discussion

4.1 Generation of biocides by the Cu(II)/PMS system

Multiple biocides can be generated in the Cu(II)/PMS system. PMS is catalytically decomposed by Cu(II) to produce reactive oxidants such as $SO_4^{\bullet-}$, $^{\bullet}OH$, and Cu(III) (Anipsitakis and Dionysiou 2004, Ding *et al*. 2013, Ji *et al*. 2011, Rastogi *et al*. 2009). First, Cu(II) can be reduced to Cu(I) by the reaction with PMS (reaction 1).

$$HSO_5^- + Cu(II) \rightarrow Cu(I) + SO_5^{\bullet-} + H^+ \quad (1)$$

Then, Cu(I) can reductively decompose PMS to generate reactive oxidants. The decomposition of PMS by one-electron reduction yields either $SO_4^{\bullet-}$ or $^{\bullet}OH$ (reactions 2 and 3). However, the two-electron reduction of PMS yields Cu(III) (reaction 4).

$$HSO_5^- + Cu(I) \rightarrow Cu(II) + SO_4^{\bullet-} + OH^- \quad (2)$$

$$HSO_5^- + Cu(I) \rightarrow Cu(II) + SO_4^{2-} + {}^{\bullet}OH \quad (3)$$

$$HSO_5^- + Cu(I) \rightarrow Cu(III) + SO_4^{2-} + OH^- \quad (4)$$

Meanwhile, Cu(I) (generated by reaction 1) is known as a strong biocide, and mainly responsible for antimicrobial actions of copper compounds (Park *et al*. 2012, Smith and Reed 1992).

4.2 Effects of biocides generated by the Cu(II)/PMS system on microbial inactivation

As described in the previous section, all the biocides in the Cu(II)/PMS system (i.e., $SO_4^{\bullet-}$, $^{\bullet}OH$, and Cu(III), and Cu(I)) are generated through the catalytic cycle of Cu(II)/Cu(I). This explanation is consistent with the observation that the copper-chelating agents (EDTA and DMP) almost completely suppressed the microbial inactivation (Fig. 3).

We observed contradictory findings for the effects of reactive oxidants on microbial inactivation by Cu(II)/PMS. Oxidant scavengers (MeOH and *t*-BuOH) failed to inhibit the *E. coli* inactivation by Cu(II)/PMS (Fig. 3), whereas the level of intracellular oxidants greatly increased for the *E. coli* cells treated by Cu(II)/PMS (Fig. 5). A possible explanation for these observations is that the intracellular reactive oxidants mainly responsible for the *E. coli* inactivation are not effectively scavenged by externally supplied oxidant scavengers. The higher oxidant level in the intracellular region than in the extracellular region in Cu(II)/PMS (Fig. 5) indicates that the generation of reactive oxidants is accelerated inside the cells, which may result from the enhanced reduction of Cu(II) into Cu(I) by cellular components (Park *et al*. 2012). We believe that the added reagents (Cu(II) and PMS) bound onto or penetrated the cell membranes and generated reactive oxidants at accelerated reaction rates, exerting fatal oxidative damage on the cells. The higher inactivation rates of *E. coli* by sequentially adding the reagents (Fig. 4) can be explained by the improved penetration of the reagent: The reagent added first had sufficient contact time to penetrate the cells before the reaction with the second reagent.

In addition to the damage from reactive oxidants, the direct biocidal actions of Cu(I) could also contribute to the microbial inactivation; Cu(I) is known to denature cellular proteins by interacting with thiol functional groups (Park *et al*. 2012, Smith and Reed 1992). The decreased inactivation rate of *E. coli* and MS2 at high concentrations of PMS (Fig. 2b and Fig. 6b) can be associated with the role of Cu(I). Increasing the input concentration of PMS will enhance the generation of reactive oxidants (which explains the increase in inactivation rate at lower PMS concentrations), but it will decrease the steady-state concentration of Cu(I) (responsible for the decrease at higher PMS concentration). However, it is also possible that the excess PMS scavenges the reactive oxidants, decreasing the intracellular oxidants.

From the observations in this study, it is unclear which oxidant among $SO_4^{\bullet-}$, $^{\bullet}OH$, and Cu(III) is mainly responsible for the microbial inactivation. The contributions of reactive oxidants may be different depending on the target microbial species (*E. coli* and MS2). However, it appears that Cu(III) does not play a key role in the microbial inactivation by Cu(II)/PMS; MS2 is known to be much more susceptible to the oxidative stress by Cu(III) than *E. coli* (Nguyen *et al*. 2013), but the Cu(II)/PMS system inactivated *E. coli* more rapidly than it did MS2 (compare the values of Fig. 2b and Fig. 6b).

5. Conclusions

Major conclusions and potential implications from this study are summarized as follows. The disinfection system using Cu(II) in combination with PMS (i.e., the Cu(II)/PMS system) effectively inactivated both *E. coli* and MS2 coliphage in natural water. The system exhibited synergistically enhanced microbicidal activity compared with using either Cu(II) or PMS alone. We believe that multiple biocidal effects result in the microbial inactivation by Cu(II)/PMS. Reactive oxidants generated by the reaction of Cu(II) with PMS can exert oxidative damage on cells and viral particles. In addition, the toxicity of Cu(I) (reduced by PMS or cellular components) could also be responsible for the microbial inactivation. We propose a Cu(II)/PMS system as a potential alternative technology for water disinfection with low concentration of Cu(II); we used 10 μM Cu(II) in this study. This concentration is as low as the drinking water quality standards for copper, which are 1 mg/L (= 15.7 μM) and 1.3 mg/L (= 20.5 μM) in Korea and the United States, respectively.

Acknowledgements

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through GAIA

Project (RE201805163) and Industrial Facilities & Infrastructure Research Program (88107), funded by Korea Ministry of Environment.

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