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ALTERNATIVE TO BROMINE IMPROVES COOLING WATER MICROBIAL CONTROL AND OVERALL TREATMENT

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ABSTRACT

Ammonia in the cooling loop poses an additional challenge for hypochlorite or oxidizing biocides in controlling the microbiological activity since chloramines are typically seen as less effective biocides as compared to free chlorine. Often, cooling tower biocidal treatment is accomplished with bromine based non-oxidizing biocides coupled with the occasional application of isothiazolin or gluteraldhyde. This paper demonstrated that Mixed Oxidant Solution (MOS), a biocide produced through the electrolysis of sodium chloride brines, is a highly effective biocide. Without overcoming ammonia, and in high pH environments, MOS was able to successfully control the microbial populations in the cooling tower waters of a major semiconductor facility in the US, where ammonia contaminated wastewater is used as part of the makeup water for cooling towers.

INTRODUCTION

Awareness of the broad issues surrounding the increasing scarcity of freshwater supplies, especially in the western and southwestern US, is driving many companies to find ways to increase the use lifetime of waters used in various industrial processes. This is especially true in the semiconductor manufacturing industry, where industry leaders are engaged in a number of programs aimed at minimizing freshwater consumption and increasing the amount of water reuse within manufacturing facilities. Internal reuse of process wastewaters for cooling systems is often an easy approach which can lead to the increased use of water in an industrial setting, however, proper treatment of these waters is required to ensure the reuse water does not interfere with cooling processes.

Oxidizing halogen biocides, typically aqueous chlorine or bromine, are often used as the primary biocide in cooling tower disinfection applications. Both aqueous chlorine and bromine are highly effective at inactivating bacteria responsible for forming biofilms, such as *Pseudomonas aeruginosa*, as well as bacteria responsible for causing human illness, such as *Legionella pneumophila*. Often, when the pH of the water in a cooling tower is greater than 8, bromine has traditionally considered to be the oxidizing biocide of choice. However, emerging experience indicates that Mixed Oxidant Solution (MOS), produced using on-site generation (OSG) systems (Figure 1), can be more effective than bromine as a disinfectant for cooling system waters.

Depending on the compositional makeup of the wastewater, internal wastewater reuse for cooling applications can present a number of treatment challenges to facility operators. One common wastewater stream repurposed for cooling applications in semiconductor manufacturing facilities are ammonia-laden wastewaters derived initially from ultrapure water (UPW) sources. UPW waters are beneficial for cooling system operations from the standpoint that they will not contribute calcium or magnesium hardness to the water within the cooling system, thereby helping to minimize the formation of scale within the cooling system. However, the presence of ammonia in the water can potentially interfere with oxidizing biocides which are typically part of the overall cooling water treatment regimen.

Aqueous chlorine reacts with ammonia to produce monochloramine (NH_2Cl), dichloramine ($NHCl_2$), trichloramine (NCl_3), and ultimately nitrogen gas through a series of chemical reactions. Cooling tower waters typically have a pH in the range of 8 – 9, and in this range, the predominant chlorine species is the hypochlorite ion (ClO^-) and the predominant ammonia species is the ammonium ion (NH_4^+). Reactions between these two components result in the production of various chloramine species:

$$ClO^- + NH_4^+ \leftrightarrow NH_2Cl + H_2O$$

$$ClO^- + NH_2Cl \leftrightarrow NHCl_2 + HO^-$$

$$ClO^- + NHCl_2 \leftrightarrow NCl_3 + HO^-$$

Similar reactions occur between aqueous bromine and ammonia, resulting in the production of bromamine species. Due to the complex chemistry and microbial inactivation efficacy of chloramine and bromamine produced *in situ* during cooling tower disinfection, the formation of these chemicals often presents a unique challenge to a cooling system operator.

Overall, use of ammonia-laden wastewaters as a source of cooling tower makeup water can provide a substantial benefit to the facility operator in terms of decreasing wastewater production as well as fresh water consumption, but also presents a substantial challenge in tailoring an appropriate biocidal treatment regimen. Biocidal treatment of these waters must account for the expected decreased biocidal treatment efficacy as well as to navigate the complex chemistries which occur in these treatment scenarios due to the presence of ammonia to both effectively removal microbial contaminants from the water and preserve worker and reputational safety.

Mixed Oxidant Solution (MOS) has been previously shown to be a highly effective biocidal treatment for cooling towers, even under the typically high pH environment often found in cooling waters. MOS has demonstrated enhanced microbial inactivation efficacy over bromine under these treatment conditions, as well as effectively treat challenging waters such as those where high levels of ammonia are present. MOS is a chlorine-based oxidant solution produced through the electrolysis of sodium chloride brines through two, distinct, electrochemical mechanisms. At the anode, chloride ions are oxidized to produce chlorine, which eventually results in the production of sodium hypochlorite with and overall chemical transformation of:

$$NaCl + H_2O \rightarrow NaOCl + H_2$$

Simultaneously, oxygen can be reduced at the cathode to produce hydrogen peroxide according to the electrochemical transformation of:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

Combined, the hypochlorite and hydrogen peroxide result in a highly potent biocide with superior microbial inactivation efficacy as compared to standard hypochlorite.[1]

In this paper, data from a field installation conducted at a site where ammonia containing wastewater is used as part of the make-up water for a large cooling tower system is also presented. Here, historic treatment outcome data from a bromine-based biocide treatment regimen is compared with results where MOS produced from an OSG system is used to displace the bromine and other biocidal agents. Results here will show that MOS, even when applied at a substantially lower effective dosage, was able to effectively control the microbial population in these waters.

OSG SYSTEM INSTALLATION AND COMPARATIVE STUDY DESIGN

Working with the facility operator, an OSG system capable of producing MOS was installed at the cooling tower site in early 2014. Validation of the efficacy of MOS for the treatment of this water was accomplished by conducting an extensive study of the outcomes of the biocidal treatment during the initial weeks of the use of the OSG system at this site. This study was conducted from January to July of 2014, with the first 11 weeks of the study using the previously existing biocidal treatment regimen and the following 18 weeks utilizing only MOS as the biocide. During this time, water quality parameters (including pH, conductivity, alkalinity, corrosion, ammonia concentration, and chlorine residuals), microbial populations, and overall chemical consumption were monitored. This data then enabled an accurate comparison of MOS with the previously utilized bromine-based biocide treatment regimen in terms of both ability to control microbial populations as well as in regards to the relative operational expenses.

BIOCIDE TREATMENT PROGRAMS

Prior to the installation of the MOS OSG system at the location, the microbial treatment of the cooling water focused on the use of a 4:1 chlorine/bromine oxidizing biocide, which was provided as a concentrate to the facility and slug fed into the water twice per day with a goal of having an Oxidation Reduction Potential (ORP) of ~400 mV in the cooling water. In addition to oxidizing biocide, isothiazolin, gluteraldehyde, and an algaecide were periodically slug fed into the water as needed. Biocidal treatment using MOS was accomplished by a continuous feed operation where MOS was fed into the cooling water to maintain a target maximum ORP of 275 mV in the water. No other biocides were used once the use of MOS as the oxidizing biocide was initiated. Corrosion inhibition and anti-scalant treatment chemicals and their dosage amounts were unchanged as a result of the transition to the use of MOS as the biocide.

TREATMENT COMPARISON

During this study, a number of water quality parameters, as well as the relative amount of oxidizing biocide present in the water, were observed to change as a result of the transition from a chlorine/bromine biocide to MOS (Table 1). Core water properties such as pH (Figure 2) and conductivity (Figure 3) were both observed to decrease once the use of MOS was initiated. During this study period, the average pH of the water before and after the use of MOS was found to be 8.63 and 8.57, respectively, while the average conductivity of water before and after the transition to MOS was found to be 993 mS and 667 mS, respectively, and was likely due to the decreased oxidant dosage added to the water. Other water quality parameters, such as alkalinity and hardness, were found to be essentially unchanged during the study period.

Residual biocide concentrations were also seen to decrease after the transition to the use of MOS (Figure 4). Residual biocides were measured both as the Free Chlorine residual and Total Chlorine residual. Here, the Chlorine residuals measured the presence of both chlorine and bromine during the chlorine/bromine phase of treatment since the measurement test used does not discriminate between the two chemicals. Free Chlorine refers to either bromine or chlorine that has not reacted with ammonia to make chloramine or bromamine, while the total chlorine measurement is both the free chlorine or bromine as well as the chloramine and bromamine. As can be seen, the free chlorine residual decreased from an average of 0.27 mg/L to an average of 0.09 mg/L and the total chlorine residual decreased from an average 0.38 mg/L to an average of 0.16 mg/L after the transition to MOS. Effectively, once the MOS was used as the biocide, the water was being treated with 60% less biocide as compared to the chlorine/bromine treatment regimen. Moreover, this data also demonstrates that, under both biocidal regimens, the oxidizing biocide is mostly in the form of chloramine or bromamine.

Microbial populations within the water were found to be typically 1,000 CFU/mL both before and after the transition to the use of MOS (Figure 5). Importantly, this data validates that MOS is a highly effective biocide for the challenging water in this tower. Even under the high pH environment and in the presence of ammonia, MOS was shown to be as effective as the prior chlorine/bromine-based biocide regimen even though no additional biocides were used and the MOS was used as an effective dose rate about 60% smaller than the chlorine/bromine biocide.

Other treatment benefits were also realized as a result of the decreased biocide dose used in this tower. Corrosion analysis found that there was reduced corrosion after the transition to MOS occurred (Figure 6). Average corrosion rates for mild steel decreased from 0.5 mpy to 0.1 mpy after the transition while the average corrosion rates for copper were observed to decrease from 0.02 mpy to 0.015 mpy after the transition to MOS.

COST COMPARISON

During the study timeframe, close monitoring of the chemical consumption both before and after the transition to MOS occurred allowed the site operator to assess the impact of using OSG equipment to provide the biocide component of the cooling water treatment program. With an estimated operational expense of less than $1,000 per year, including the cost of both salt and electricity required to produce the full amount of biocide needed at this tower, the tower operator was able to realize a cost savings of $240,000-$280,000 per year. This cost savings translates into a highly attractive Return on Investment of less than one year for the OSG system installed at this location. Given the reduced corrosion rates observed, it is likely that the consumption of corrosion prevention chemicals could also be decreased, thus allowing for additional cost savings.

CONCLUSIONS

Results from this study clearly demonstrated that MOS is a highly effective biocide for cooling tower disinfection, even in high pH environments and in the presence of ammonia in the water. Here, it was found that an effective MOS dose that was 60% less than the chlorine/bromine disinfectant used before the implementation of MOS was able to maintain a similar control over the microbial population in the cooling tower water. Using less biocide had the added benefit of a significant reduction in the observed corrosion rates, potentially allowing for a reduction in the use of corrosion prevention chemicals. Financially, this site is expected to achieve a cost savings of at least $240,000-$280,000 per year as a result of replacing the chlorine/bromine biocide with MOS, resulting in a highly attractive Return on Investment for the OSG system in place.

ACKNOWLEDGEMENTS

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APPENDIX: LABORATORY COMPARISON OF MOS AND BROMINE

Laboratory testing was conducted to further differentiate the microbial inactivation efficacy of MOS and bromine. Studies utilized simulated cooling tower waters spiked with *P. aeruginosa* and *L. pneumophila*. Test waters were prepared to have an alkalinity of 200 mg/L as sodium bicarbonate, hardness of 400 mg/L as calcium carbonate, and pH adjusted to 8.5. After sterilization, these waters were inoculated with *P. aeruginosa* and *L. pneumophila* to at least 10,000 cfu/mL. MOS or bromine was then dosed into the waters to a Free Available Chlorine concentration (as measured using standard DPD methodology) of 0.25 to 0.5 mg/L, and the oxidant dosed samples allowed to sit at room temperature for 5 or 10 minutes. After the desired exposure time had elapsed, a portion of the sample was filtered through a sterile membrane filter to capture the bacteria cells, with the filter then washed with sterile phosphate buffer to remove remaining biocide. Filter membranes were then transferred to a petri dish containing solidified, sterile media using sterile forceps. After incubation at 35-37^{o}C for 48 hours, the active bacteria were quantitated in cfu/mL, and these results used to calculate the log reduction compared to control samples.

Results from laboratory studies clearly show that MOS is the superior biocide as compared to bromine for the inactivation of *P. aeruginosa* (Figure 7) and *L. pneumophila* (Figure 8). Tests conducted with *P. aeruginosa* used an oxidant dose of 0.25 mg/L. At a contact time of 5 minutes, MOS achieved a 3.3 log inactivation, which was comparable to the 3 log inactivation achieved by bromine. After a 10 minute contact time, however, MOS achieved a log inactivation of 5.7 which the bromine sample showed a log inactivation of only 3.1. MOS was found to be similarly more effective than bromine for *L. pneumophila* inactivation as well, achieving a 5.8 with a 5 minute contact time while bromine was able to produce a log inactivation of only 2.9. As before, increased exposure time did not result in an increased inactivation for the bromine sample, and no effect was seen for MOS in this case since the maximum detection limit for this test was a log inactivation of ~5.7-5.8.

Laboratory data further validates earlier observations that MOS is a highly effective biocide when applied in a high pH environments simulating typical cooling tower waters. Further, this data also provides the first side-by-side comparison of MOS with aqueous bromine, which is often thought to be the best biocidal choice for high pH disinfection. It is very likely that the combined impact of hypochlorite and hydrogen peroxide thought to be present in MOS results in the observed superior disinfection seen in these tests.

REFERENCES

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Figure 1- Photograph showing an example of an OSG system.

Parameter	Pre-MOS Disinfection	MOS Disinfection
Free Chlorine Residual (mg/L)	0.27	0.09
Total Chlorine Residual (mg/L)	0.38	0.16
Ammonia (mg/L)	Not Measured	0.84
pH	8.63	8.57
Conductivity (mS)	993	667
Total Hardness (mg/L)	70	73
Alkalinity (mg/L)	149	153
ORP Set Point (mV)	400	275
Average Mild Steel Corrosion Rate (mpy)	0.5	0.1
Average Copper Corrosion Rate (mpy)	0.02	0.015
Typical Microbial Load (CFU/mL)	1,000	1,000

Table 1- General water quality parameters measured during the comparison period.

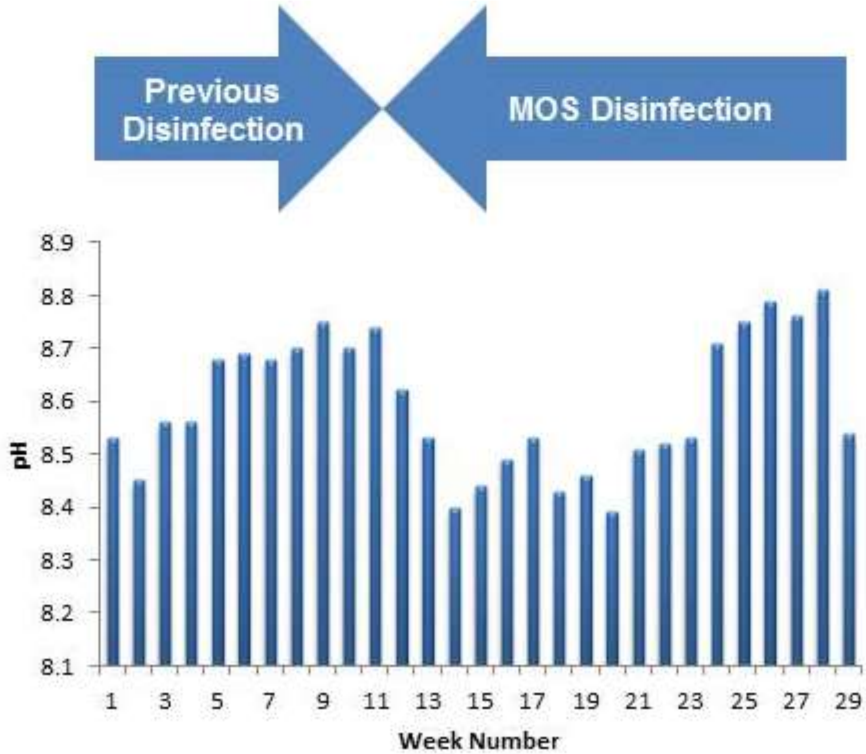

Figure 2- Graph showing the pH of the cooling water both before and after the transition to the use of MOS.

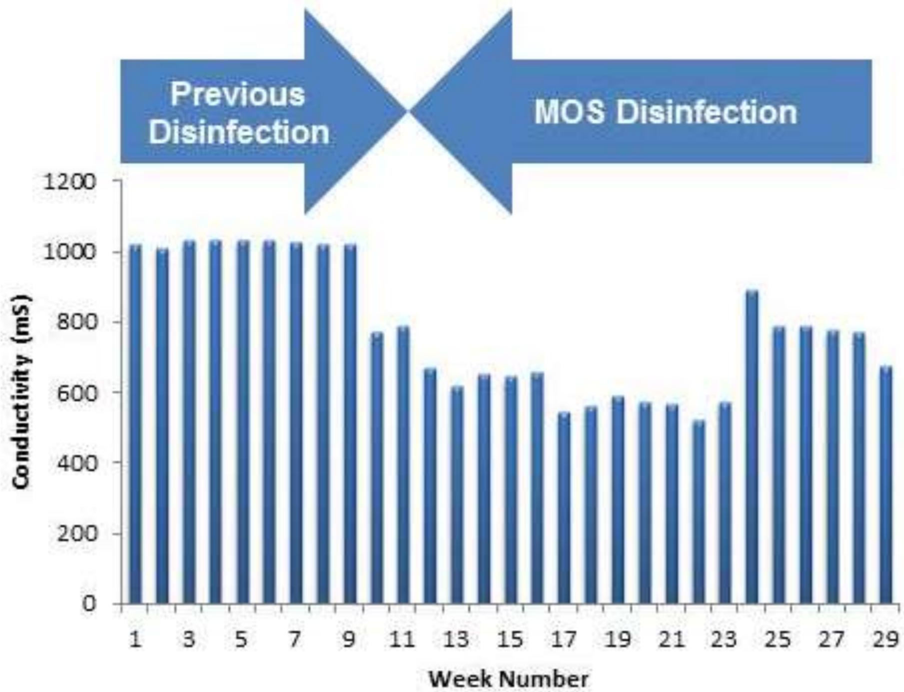

Figure 3- Graph showing the conductivity of the cooling water both before and after the transition to the use of MOS.

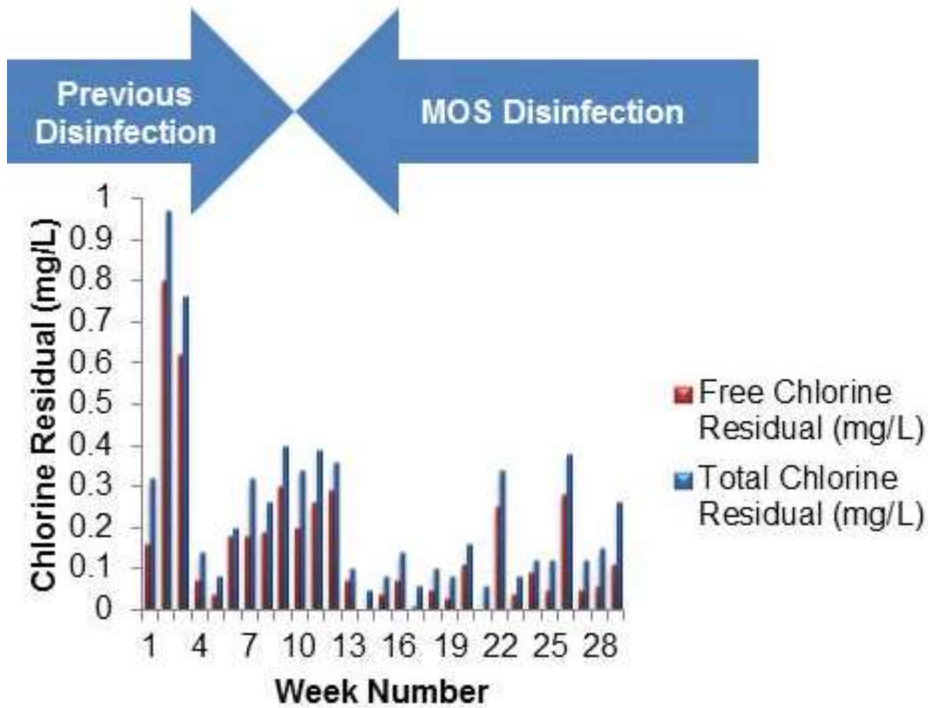

Figure 4- Graphs showing the Free Available Chlorine and Total Chlorine residuals present in the cooling water measured both before and after the transition to the use of MOS.

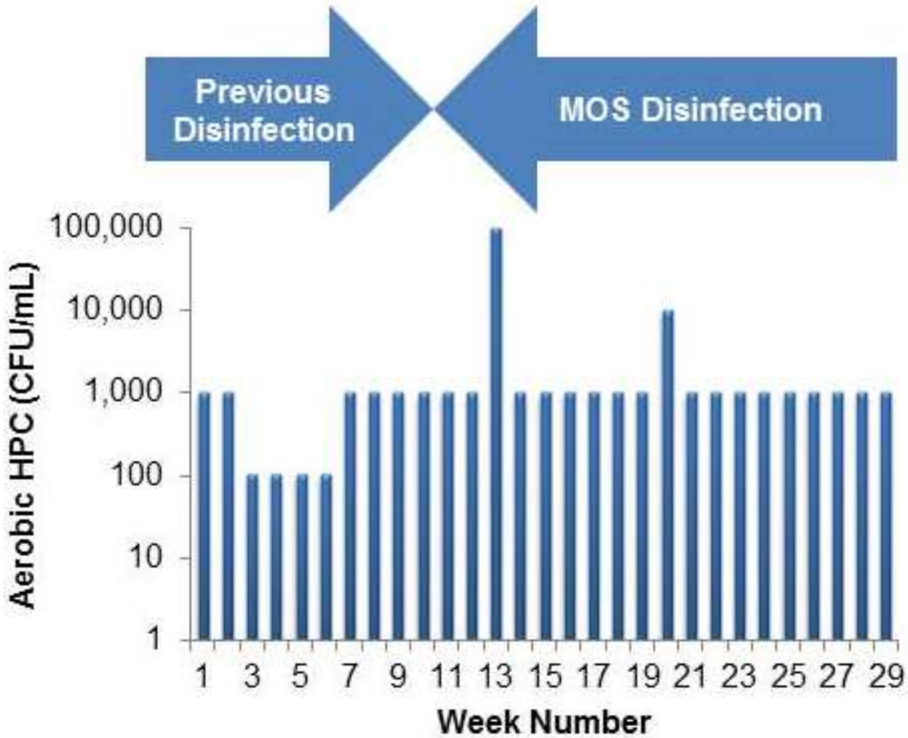

Figure 5- Graph showing the weekly enumeration of the microbial population in the cooling tower water both before and after the transition to the use of MOS.

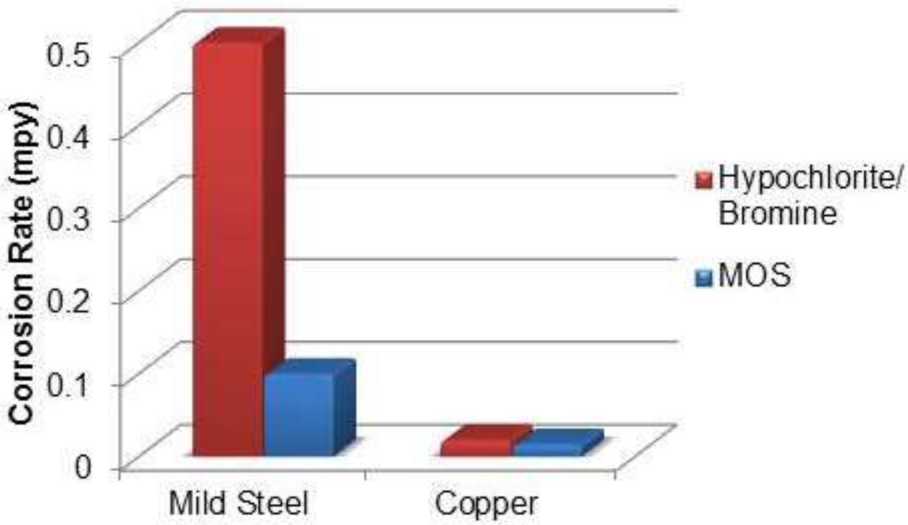

Figure 6- Graph showing cooling mild steel and copper corrosion rates using hypochlorite/bromide and MOS disinfection chemistries.

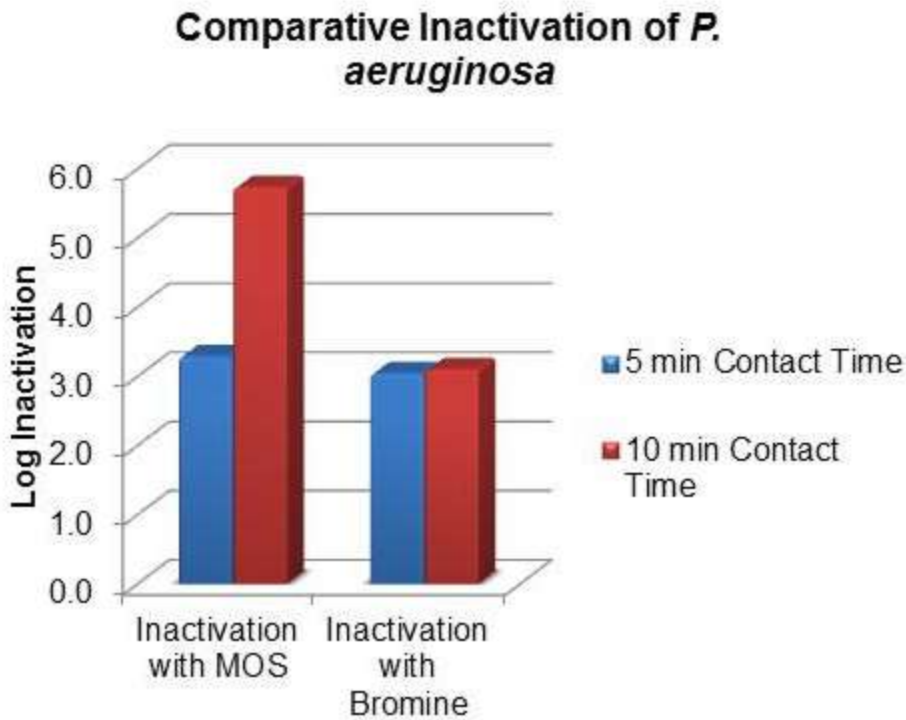

Figure 7- Graph showing the comparative inactivation of P. aeruginosa *by both MOS and bromine with a 0.25 mg/L dose for both 5 and 10 minute contact times.*

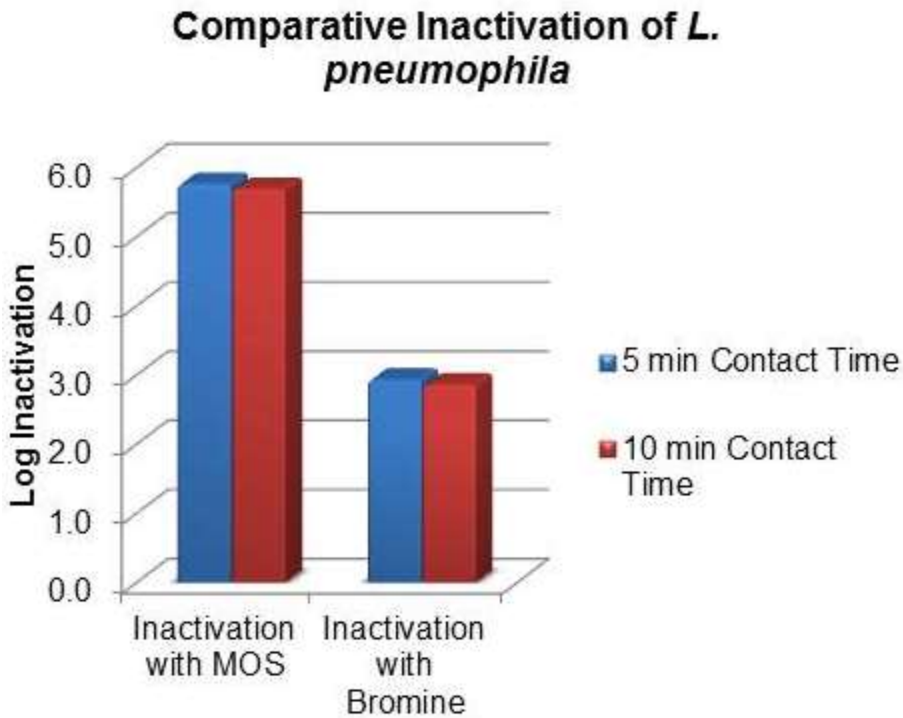

Figure 8- Graph showing the comparative inactivation of L. pneumophila *by both MOS and bromine with a 0.5 mg/L dose for both 5 and 10 minute contact times.*