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Chemical and Biological Approach using Mixed Oxidants for the Disinfection of Drinking Water Supplies

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Abstract

The use of mixed oxidants for disinfection as a public health measure reduces the spread of countless diseases and is the future of public safety. Mixed oxidant solutions, which have typically formed electrochemically through the electrolysis of brine, have emerged as an effective and potentially significant method of disinfection of drinking water supplies. Many solutions have been tested and documented regarding inactivation rates relating to mixed oxidant solutions, including chlorine, ozone, hypochlorite, and several others. Advanced technologies are interesting, however many are still in the research state, while conventional technologies are the most used and far along. However, although some of the conventional technologies are not fully verified, a vast majority of them are very significant and vital methods when it comes to disinfection. Some of the many benefits of mixed oxidant solutions include a decreased generation of potentially harmful disinfection byproducts (DBPs), inhibition of biofilm formation within distribution systems, improved residual power, safer operating environments, and lower operating costs. Disinfection byproducts (DBPs) are chemical, organic, and/or inorganic substances that are commonly found in drinking water supplies and can form during chemical reactions of a disinfectant and drinking water. The use of mixed oxidant solutions in public safety provides a safer working environment and a safer supply of drinking water, while also providing a cheaper and more effective solution to promote public health and safety.

Keywords:disinfection, drinking water treatment, DBP

1. Introduction

Mixed oxidant solutions, typically formed electrochemically through the electrolysis of brine, have emerged as an effective, and a potentially significant method of the disinfection of drinking water supplies. Numerous studies have documented the efficacy of mixed oxidant solutions in the disinfection of microorganisms including Coliphage MS2, *Escherichia coli, Bacillus subtilis, Cryptosporidium parvum* oocysts, and *Clostridium perfringens* spores (Son *et al.*, 2003; Venczel *et al.*, 1997; Casteel *et al.*, 2000); however, the active disinfectant species present in mixed oxidant solutions have not been fully verified, necessitating the need for continued research in this realm. Species suspected in mixed oxidant solutions generated through the electrolysis of brine include, but may not be limited to, ozone, chlorine dioxide, hypochlorite, hypochlorous acid, chlorine, hydrogen peroxide, and OH- radicals. It has been suggested that chlorine is the effective component of electrochemically mixed

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oxidant solutions responsible for disinfection (Clevenger *et al.*, 2007). However, studies documenting increased inactivation rates observed with mixed oxidant disinfection compared to disinfection with hypochlorite alone, as well as the ability of mixed oxidant solutions to inactivate chlorine-resistant organisms like *C. parvum*, indicate that chlorine species are not the only mixed oxidant constituents in effect (Hamm 2002; Son *et al.*, 2003; Venczel *et al.*, 1997; Casteel *et al.*, 2000). Based on reviewed literature, the inactivation rate, as well as the extent of the increase in disinfection efficacy by electrochemically and mechanically generated mixed oxidants compared to that of chlorine- based disinfectants, it is highly dependent on the type of microorganism used in the study. Accordingly, the assessment of the major oxidant species at work is also influenced by the biological indicator used. Lastly, the literature reviewed demonstrated that synergistic effects due to pH, temperature, and the combination of different oxidant types also play an important role in the disinfection efficacy of mixed oxidant solutions (Son *et al.*, 2003).

2. pH and Temperature Effects on Mixed Oxidant Disinfection

In the first half of the study presented by (Son *et al.,* 2003), *E. coli* and *B. subtilis* were used to investigate the disinfection efficacy of an electrochemically generated mixed oxidant solution compared to that of free available chlorine (FAC). The study also evaluated the effects of pH and temperature on inactivation rates of both microorganisms. Son *et al.* found that at a pH of 8.2, electrochemically generated mixed oxidant solutions were between 20 and 50 percent more efficient in inactivating *E. coli* and *B. subtilis* spores in comparison with disinfection with free available chlorine (FAC). The synergistic effect observed with the electrochemically mixed oxidants at a pH of 8.2 was not observed for *E. coli* or *B. subtilis* spores at lower pH levels of 5.7 or 7.1. As a point of clarification, the inactivation rates of *E. coli* and *B. subtilis* spores were the highest for both electrochemically mixed oxidants and FAC at lower pH levels; it was only at pH of 8.2 that a significant difference was recorded between the inactivation rate observed using electrochemically mixed oxidants versus the inactivation rate observed using FAC as the form of disinfection.

The effects of pH on the inactivation efficacy of different disinfectants including free chlorine, ozone and chlorine dioxide are demonstrated in the single step application experiments run in a sequential disinfection study using *B. subtilis* spores. Results of the study showed that free chlorine was most efficient at lower pH levels (5.6 versus 8.2), whereas faster inactivation rates were observed at higher pH levels in single step treatment with ozone (Cho *et al.*'s 2006). The inactivation of *B. subtilis* spores by chlorine dioxide was not affected by a change in pH. These findings, specifically that of a single step application of ozone resulted in increased inactivation rates at a pH of 8.2, are consistent with the greater synergistic effect observed in the inactivation of *E. coli* and *B. subtilis* by mixed oxidants at a pH of 8.2 (Son *et al.*, 2003). They also suggest that mixed oxidant solutions, composed of several oxidant types, have the ability to be effective at varying pH levels.

Table 1. Summary of the CT values (mg/L x min) for the 2-log inactivation of *E. coli* and *B. subtilis* observed by Son *et al.* (2003).

		Electrochemically mixed oxidants	**FAC**	**Electrochemically mixed oxidants**	**FAC**
Micro organism	pH	20° C	20° C	4° C	4° C
E. coli	5.7	$3.5x10^{-2}$	$3.2x10^{-2}$	-	-
	7.1	$7.1x10^{-2}$	$7.6x10^{-2}$	-	-
	8.2	0.13	0.18	0.24	0.36
B. subtilis	5.7	46	50	204	221
	7.1	97	94	-	-
	8.2	240	280	670	800

In examining the effects of temperature (20°C vs. 4°C) at pH 8.2, Son *et al.* (2003) found that both *E. coli* and *B. subtilis* spores exhibited increased inactivation rates at the higher temperature of 20°C with both methods of disinfection; however, the percent effectiveness of inactivation by mixed oxidants versus FAC was greater for both organisms at 4°C versus 20°C. Specifically, at 4°C, the electrochemically mixed oxidants were approximately 50% and 19% more effective than FAC in inactivation of the 2-log inactivation of *E. coli* and *B. subtilis*, respectively; whereas at 20°C, the electrochemically mixed oxidants were approximately 35% and 17% more effective than FAC in inactivation of the-2 log of *E. coli* and *B. subtilis*. These results suggest that at pH 8.2, the inactivation rates of *E. coli* and *B. subtilis* may be less affected by a drop in temperature when treated with mixed oxidants versus FAC alone. In other words, mixed oxidant solutions may be a more effective disinfectant than FAC alone across a larger spectrum of temperatures.

3. Disinfection using Electrolytically Generated Mixed Oxidants

Son *et al.*'s (2003; 2005)) findings are somewhat in contrast to the study conducted by Clevenger *et al.*, in which three strains of *B. subtilis* and the bacteriophage MS2 were used to compare the disinfection potency of three electrolytic generation systems of mixed oxidants as well as hypochlorite (at pH 7, 22° C). While all three mixed oxidant generating systems were slightly more effective than hypochlorite in the inactivation of the macrophage, all three systems were similarly effective as hypochlorite in the inactivation of the three strains of *B. subtilis* spores. MS2, which was inactivated much more rapidly and effectively by all four methods of disinfection than the *B. subtilis* spores, displayed no apparent change in chlorine residual for the four disinfectants (since MS2 phages are very sensitive to free chlorine, very little chlorine was required for their inactivation). A more pronounced, but uniform, decrease in chlorine concentrations occurred in the inactivation of *B. subtilis* spores for all four disinfectants, leading Clevenger *et al.* to conclude that the effective disinfection component in the three mixed oxidant generating systems was chlorine alone. (Clevenger *et al.*, 2007)

The rapid inactivation of bacteriophage MS2 by an electrochemically generated mixed oxidant solution was also reported in Casteel *et al.* (2000), in which a 2 log reduction of the macrophage occurred in 30 seconds. The study also reported a relatively high percentage of the initial dose (2.4 mg/L) of mixed oxidant solution remained throughout the experiment, with 1.6 mg/L mixed oxidant remaining after one hour contact time. This is generally consistent with the lack of a decrease in chlorine residual observed for MS2 after 30 minutes in Clevenger *et al.* (2007). Casteel *et al.* observed similar inactivation characteristics for *E. coli* treated with electrochemically mixed oxidants (2 log reduction within 30 seconds with a 2.4 mg/L dose of mixed oxidant solution, with 1.6 mg/L mixed oxidant remaining after one hour contact time). In contrast, chlorine-resistant *C. parvum* oocysts and *C. perfringens* spores exhibited much slower inactivation rates at higher doses of mixed oxidants. As indentified in the table below, *C. parvum* oocysts treated with 2 mg/L of electrochemically mixed oxidants experienced a 0.7 log reduction with 30 minutes contact time and a 1 log reduction after 240 minutes; *C. parvum* oocysts treated with 4 mg/L experienced a 2.1 log reduction at 30 minutes and a 2.9 log reduction after 240 minutes. The inactivation rate of *C. perfringens* was similar to that of *C. parvum* when treated with the same two doses of electrochemically mixed oxidants.

Table 2. Inactivation of *C. parvum* and *C. perfringens* by electrochemically mixed oxidants in oxygen demand-free water at pH 8 and at 25° C (Casteel *et al.*, 2000)

Micro organism	Dose of Mixed Oxidants	Contact Time	Log(10) inactivation
C. parvum	2 mg/L	30 min	0.7
		240 min	1
C. parvum	4 mg/L	30 min	2.1
		240 min	2.9
C. perfringens	2 mg/L	30 min	0.7
		240 min	1
C. perfringens	4 mg/L	30 min	1
		240 min	1.5

Both *C. parvum* and *C. perfringens* exhibited declining rate inactivation kinetics by mixed oxidants. This study demonstrates that the rate and extent of inactivation by mixed oxidants is dependent on the type of microorganism, the initial does of mixed oxidants, the contact time, and in the case of *C. parvum* and *C. perfringens*, the mixed oxidant residual (or oxidant demand) (Casteel *et al.*, 2000).

4. Mixed Oxidants vs. Free Chlorine Disinfection

Prior to Casteel *et al.*'s study, Venczel *et al.* (1997) demonstrated the inactivation of *C. parvum* oocysts and *C. perfringens* spores by electrochemically mixed oxidants, in contrast to disinfection by free chlorine alone. The declining rate inactivation, or "retardant die-off," kinetics also observed by Casteel *et al.*, were also observed by Venczel *et al.* with disinfection of *C. parvum* and *C. perfringens* with electrochemically mixed oxidants. As identified in Table 3, 5 mg/L of electrochemically generated mixed oxidants inactivated both *C. parvum* oocysts and *C. perfringens* spores in water at pH 7 and at 25° C, with greater than 2.3 log (>99.5%) inactivation in four hours. With an equivalent dose of free chlorine and four hour contact time period, there was essentially no inactivation of *C. parvum* and reduced inactivation of *C. perfringens* spores (1.5 log inactivation, or 97%). No inactivation of *C. parvum* spores treated with free chlorine was recorded after 24 hours of contact time, and only a 0.2 log increase in inactivation was recorded for *C. perfringens* beyond four hours contact time.

Table 3. Inactivation of *C. parvum* and *C. perfringens* by electrochemically mixed oxidants and FAC in oxygen demand-free water at pH 7 and at 25° C (Venczel *et al.* 1997). The inactivation rates in the table are the averages of four replicate experiments.

Micro organism	Disinfectant	Contact Time	Log(10) inactivation
C. parvum	electro-chemically mixed oxidants	1 h	1.3
		4 h	>3.5
		8 h	>4.3
		12 h	>4.6
		24 h	>3.8
C. parvum	FAC	1 h	no inactivation
		4 h	
		8 h	
		12 h	
		24 h	
C. perfringens	electro-chemically mixed oxidants	1 h	2.2
		3 h	2.6
		4 h	2.7
		8 h	3.3
		12 h	3.6
		24 h	3.7
C. perfringens	FAC	1 h	1
		3 h	1.3
		4 h	1.5
		8 h	1.6
		12 h	1.7
		24 h	1.7

Based on the results observed by Venczel *et al.* (1997) and Casteel *et al.* (2000), electrochemically mixed oxidants were effective in inactivating chlorine-resistant microorganisms such as *C. parvum* and *C. perfringens* (*C. parvum* being more resistant to chlorine than *C. perfringens* (Venczel *et al.*, 1997)). As cited in Venczel *et al.* (1997), Korich *et al.* (1990) reported that when exposed to a free chlorine dose of 80 mg/L, a 1 log inactivation of *C. parvum* oocysts was observed after 90 minutes; however, such a high dose of chlorine would never be used in the disinfection of drinking water. Thus, for microorganisms such as *C. parvum* and *C. perfringens*, an alternative to disinfection by chlorine alone is needed, and mixed oxidant solutions appear to be a viable approach.

5. Synergistic Effects of Mixed Oxidants on Disinfection

In addition to the optimal pH and temperature conditions, another factor influencing the increased disinfection efficacy by mixed oxidant solutions may be synergism of certain oxidant species. Synergistic effects of oxidant species can be investigated through sequential disinfection experiments. In Liyanage *et al.* (1997), the enhanced inactivation of *C. parvum* oocysts was attributed to synergistic effects of combining ozone and chlorine dioxide in sequential disinfection. The study reported that the expected inactivation by single oxidants was 0.8 log units for ozone and 1.4 log units for chlorine dioxide, for a total of 2.2 log inactivation; whereas, 3.4 log inactivation was documented when *C. parvum* oocysts were exposed to 0.8 mg/L of ozone for 4.4 minutes followed by a 2.0 mg/L chlorine dioxide treatment for 60 minutes. Thus, the sequential treatment of *C. parvum* oocysts with ozone and chlorine dioxide resulted in an additional 1.2 log units of inactivation due to synergism of the two disinfectants (Liyanage *et al.*, 1997). It is quite possible that a similar synergistic effect between ozone and chlorine dioxide occurs in electrochemically mixed oxidant solutions, helping make mixed oxidant solutions effective disinfectants in the inactivation of *C. parvum* oocysts and *C. perfringens* spores. Applying the results of other sequential disinfection studies, synergism of oxidant species may also be an important factor in the increased disinfection efficacy of mixed oxidants in the inactivation of other microorganisms, including *B. subtilis* (Cho *et al.*, 2006) and *E. coli* (Yang *et al.*, 2012; Beber de Souza and Daniel, 2011). Synergism observed in subsequent disinfection studies has been attributed to the activity of the disinfection species reacting with specific chemical groups of the bacterial cell wall (H. Son *et al.*, 2005).

In Son *et al.* (2003; 2005), synergism of oxidant species appeared to be a contributing factor to the enhanced inactivation of *B. subtilis* spores by mechanically mixed oxidants versus disinfection by FAC alone. Four mechanically mixed oxidant solutions were prepared by adding small amounts of ozone (1 mg/L), chlorine dioxide (1.8 mg/L and 18 mg/L), hydrogen peroxide (9.2 mg/L) and chlorite (40 mg/L) into 200 mg/L FAC stock solution at pH 2.5. The chlorite/FAC solution was prepared to take into account expected chlorite production from the reaction between FAC and ozone. The pH and concentrations of each oxidant were chosen to replicate the reported concentrations of the oxidants produced (FAC), and claimed to be produced (ozone, chlorine dioxide, hydrogen peroxide and chlorite), by the MIOX electrolytic generation system. Son *et al.* (2003; 2005) explained that the concentration of chlorite used in the study (40 mg/L) was much greater than that reported in MIOX literature so that the product of FAC and chlorite, chlorine dioxide, could be detected by UV absorbance.

The inactivation experiments using the four mechanically mixed oxidant solutions were carried out at pH 8.2 at 20°C. The mechanically mixed oxidant solutions of FAC and ozone (0.01 mg/L), and FAC and chlorine dioxide (0.018 mg/L and 0.18 mg/L) were 21%, 26% and 45% more effective, respectively, than FAC alone in achieving 2 log removal of *B. subtilis* spores. No notable difference in inactivation rate was observed between the mechanically mixed oxidant solution of FAC and hydrogen peroxide (9.2 mg/L). The mechanically mixed oxidant solution of FAC and chlorite (40 mg/L) increased the inactivation rate by 52% compared to disinfection with FAC alone, but as previously mentioned, the amount of chlorite in the prepared solution was much higher than expected for chlorite generated from an electrochemical cell. Son *et al.* (2005) explained the enhanced disinfection efficacy of mechanically mixed oxidants containing ozone, chlorine dioxide and chlorite by the synergistic effects of the mixed oxidants, as well as by intermediates generated through the reaction of ozone, chlorine dioxide and chlorite with FAC. Throughout the measurement of UV absorbance at wavelengths specific to ozone, chlorine dioxide and chlorite, Son *et al.* (2003; 2005) were able to show that chlorite was produced as an intermediate from the reaction of FAC and ozone, and chlorine dioxide was generated from the reaction of FAC and chlorite.

6. Conclusion

The efficacy rate of mixed oxidant solutions compared to conventional chlorine disinfection is greatly affected by the type of microorganism used in the experiment, or found in the drinking water supply. While the bacteriophage MS2 and *E. coli* are inactivated rapidly by mixed oxidant solutions (Clevenger *et al.* 2007; Son *et al.* 2003; Casteel *et al.* 2000), *B. subtilis* spores, *C. perfringens* spores and *C parvum* oocysts are increasingly more resistant (Son *et al.* 2003; Casteel *et al.* 2000; Venczel *et al.* 1997); however, at higher doses and/or with greater contact times, mixed oxidant solutions have been found to be effective in inactivating these more resistant microorganisms (Son *et al.* 2003; Casteel *et al.* 2000; Venczel *et al.* 1997). This is especially significant for chlorine-resistant microorganisms like *C. parvum*, for which no inactivation was observed with treatment with free chlorine alone after 24 hours of contact time (Venczel *et al.* 1997).

Comparison of the inactivation rates of different microorganisms using the same method and dose of disinfection emphasizes the importance of selecting appropriate biological indicators. For instance, while

C. perfringens spores have shown to be reliable indicators for *C. parvum* oocyst inactivation by mixed oxidants in water, the bacteriophage MS2 and *E. coli* would be inappropriate as indicators for *C. parvum* oocyst inactivation (Casteel *et al.* 2000).

As observed by Son *et al.* (2003), the species in electrochemically generated mixed oxidant solutions likely play a larger role, or have a greater capacity for disinfection, at slightly basic conditions. Mixed oxidant solutions appear to be the most effective at temperatures between 20-25° C; however, mixed oxidant solutions may be able to better maintain their disinfection potency at lower temperatures (4° C) compared to FAC alone. Synergistic effects observed in sequential disinfection experiments from the reaction of disinfectant species (Liyanage *et al.*, 1997; Cho *et al.*, 2006; Yang *et al.*, 2012; Beber de Souza & Daniel, 2011) may also occur between the oxidant species in mixed oxidant solutions, contributing to the disinfection efficacy of electrochemically mixed oxidant solutions. Synergism of mechanically mixed oxidants, as well as the disinfection abilities of intermediates formed by the reaction of oxidant species, was observed in the enhanced inactivation of *B. subtilis* spores by mechanically mixed oxidants in concentrations believed to be similar to those generated by the electrolysis of brine (Son *et al.* 2003; 2005).

In addition to increased disinfection potency, noteworthy benefits of mixed oxidant solutions include, but are not limited to, decreased generation of potentially harmful disinfection byproducts (DBPs), inhibition of biofilm formation within distribution systems, improved residual power, safer operating environments, and lower operating costs (Venczel *et al.* 1997; Hamm 2002).

Based on the study, the use of mixed oxidants appears to be a viable approach in the disinfection of drinking water, and may prove to be very valuable with more research that investigates and confirms the constituents and mechanisms responsible for the enhanced inactivation of a number of microorganisms.

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