The Power of Three

Combining UV & ozone for increased disinfection & oxidation efficacy

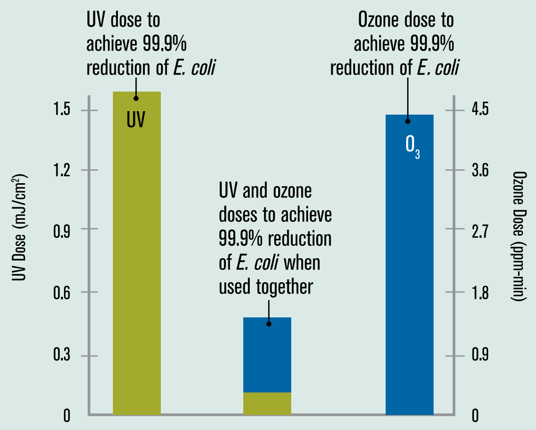
By Ray Denkewicz

Ultraviolet (UV) and ozone are clearly established as viable secondary disinfection methods to chlorine for combating recreational waterborne illnesses (RWIs). As recommended by the Centers for Disease Control and Prevention (CDC) in its recently issued Model Aquatic Health Code, UV and ozone help inactivate *Cryptosporidium*, the primary causal agent of RWIs.[1] Chlorine, unfortunately, is not effective against *Cryptosporidium*—it is not the end-all, be-all sanitizer, but neither is UV or ozone, which is why, when they are used as a complement to chlorine, greater microbial efficacy is achieved.

It is logical, then, to ask, "If UV and ozone are potent in their own rights, then might the combination of the two be even better?"

Microbial inactivation studies employing a combination of UV and ozone have been reported for decades in water treatment.[2,3,4,5,6] These studies have been made almost exclusively in non-swimming pool applications, so less notice may have been taken of them within the pool and spa industry. In these research investigations, which span multiple water treatment applications, researchers observed a synergistic effect when UV and ozone were used in combination for disinfection and oxidation purposes. That is to say, the observed results were greater than the expected contributions of their parts. The synergistic action, as observed by many investigators, has been attributed to the formation of hydroxyl radicals when UV light interacts with ozone.[7] The use of hydroxyl radicals in water treatment is commonly referred to in scientific literature as advanced oxidation.[8] The potent nature of hydroxyl radicals results in what is effectively a one-two-three punch when UV and ozone are used together.

Figure 1. Synergy of UV & Ozone Against *E. coli*[9]



Synergy of UV & Ozone

A landmark study published in 2006 by Magbanua, et al., clearly and systematically delineated the synergistic effect of a UV/ozone combination against *E. coli*.[9] At first, the researchers studied the efficacy of UV and ozone against *E. coli* in separate, independent tests. In doing so, the team was able to establish the requisite dosages of each disinfectant to affect a specific level of microbial reduction. In a second series of tests, the team utilized UV and ozone together to determine if the resulting microbial reduction was simply the sum of the contributions from each disinfectant.

The results were nothing short of astounding (see Figure 1). It was discovered that the individual UV and ozone doses required to destroy *E. coli* to the same extent (e.g., 99.9%) could be reduced by factors of 18 and four, respectively, when the two disinfectants were used together.

In essence, there was a synergistic effect on the microbial reduction of *E. coli* when UV and ozone were paired in a dual disinfection strategy.

According to Magbanua, et al., the synergy associated with UV/ozone water treatment is attributed to the presence of supplementary hydroxyl radicals. In pure water, ozone reacts with hydroxide ions to form hydroxyl ions via a complicated pathway. The combined use of UV and ozone promotes the formation of additional hydroxyl radicals by photolysis of ozone through a hydrogen peroxide pathway (see Figure 2).

Aqueous ozone absorbs UV radiation at wavelengths of 200 to 310 nm, and, in turn, decomposes to form hydrogen peroxide. Hydrogen peroxide then further reacts with UV to produce hydroxyl radicals. The reaction pathway in Figure 2 also suggests that hydrogen peroxide, when added to a UV system, would provide a similar benefit in the production of hydroxyl radicals. For this reason, hydrogen peroxide/UV systems and hydrogen peroxide/ozone/UV systems are in use for many water treatment applications where oxidation is a primary objective.[10]

Figure 2. Formation of Hydroxyl Radicals in UV/Ozone Applications

$$O_3 + H_2O \xleftrightarrow{UV} H_2O_2 + O_2$$

$$H_2O_2 \xleftrightarrow{UV} 2\ HO^{\bullet}$$

Table 1. Relative Oxidizing Power of Select Oxidants[10]

Oxidant	Relative Oxidizing Power (mV)
Hydroxyl radical	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Hypochlorous acid	1.10
Chlorine	1.0

Hydroxyl radicals are extremely fast-reacting, potent, non-selective chemical species.[10] In fact, their oxidation power is recognized as being far more potent than chlorine gas, hypochlorous acid or ozone (see Table 1). Furthermore, the reactivity of hydroxyl radicals has long been recognized as extremely fast—in some instances as much as 1 million times faster-acting than ozone for bond breaking via chemical oxidation.[11] For these reasons, the inactivation rate of waterborne pathogens is much greater due to the additional oxidizing power provided by the supplementary hydroxyl radicals.

The Trio of UV, Ozone & Hydroxyl Radicals

Scientific literature is replete with studies on the use of UV and ozone together for water treatment. This dual

Table 2. Research Findings on Use of UV/Ozone in Various Applications

Investigation/Application	Research Findings	Reference
Disinfection of *E. coli*	Synergistic disinfection performance against *E. coli* using UV/ozone combination	9
Oxidation of disinfection byproducts	Total trihalomethanes (TTHMs) and total organic halides reduced by 90% and 98%, respectively, using UV/ozone combination	12
Oxidation of organic carbon and disinfection byproducts	Total organic carbon reduced by 50% over ozone or UV alone; TTHMs and haloacetic acids (HAAs) reduced by 80% and 70%, respectively	13
Drinking water treatment	Overall, the combination of ozone and UV treatment led to improved water quality with regard to disinfection, oxidation of micropollutants (atrazine, MTBE, 17-a-ethinylestradiol, etc.) and minimization of bromates.	2
Disinfection of poultry feedwater	Fifty-fold improvement in disinfection against *E. coli*	14
Treatment of surface water	Complete removal of methylisoborneol and geosmin and 40% reduction in bromates with UV/ozone	15
Removal of disinfection byproducts	Increased reaction rate for the destruction of HAAs	16

Figure 3. Synergy of UV & Ozone Against Adenovirus & *Naegleria fowleri*[17]

Note that the UV and ozone doses were unchanged when the two disinfectants were used together. The results achieved are far greater than the sum of the individual contributions.

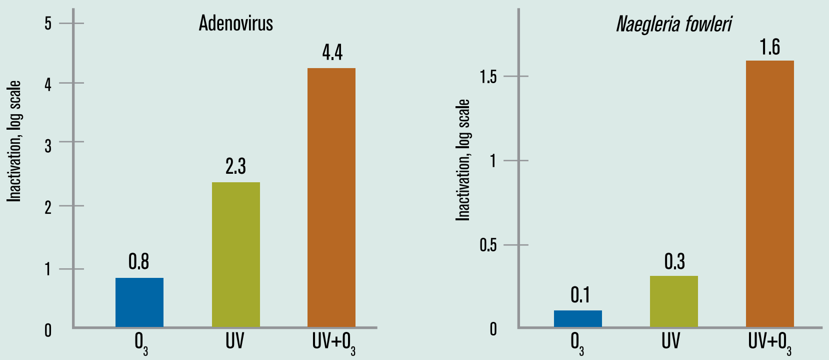


Figure 4. Chlorine & Chloramine Reduction With UV/Ozone

Note that the chlorine demand was lowered by about 53%, and combined chlorine by 54%, when UV and ozone were employed with chlorine on a 28,000-gal outdoor, in-ground pool.

Chrorine Reduction

28,000-gal in-ground pool with OPR-controlled salt chlorination system

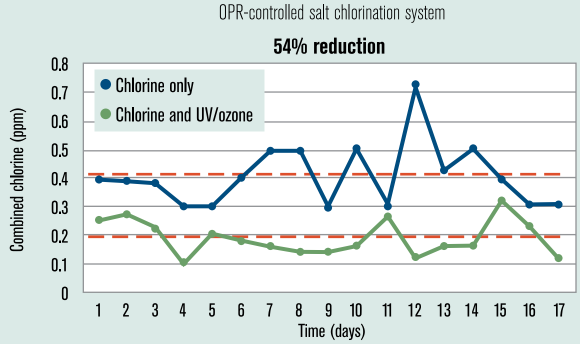
Test #1	Chlorine only	0.62 lb/day of chlorine (-1.5 months)
Test #2	Chlorine and UV/ozone	0.29 lb/day of chlorine (-1 month)

% Chlorine Reduction

$$\frac{(0.62 - 0.29)}{0.62} \times 100\% = 53\%$$

Combined Chlorine Reduction

28,000-gal in-ground pool with OPR-controlled salt chlorination system



technology approach, commonly referred to as advanced oxidation, has the capability of achieving oxidation and disinfection. Table 2 provides a list of just some of the reported research on advanced oxidation in water treatment and the applications in which it has been employed. It is clear that the breadth of the applications for the trio of UV, ozone and hydroxyl radicals within water treatment is vast, owing to the potency of the combination for disinfection and oxidation.

The Trio as Disinfectants

In addition to the research by Magbanua, et al., the combined effects of UV, ozone and hydroxyl radicals as disinfectants were demonstrated in work performed at the University of Arizona's Water Quality Center under a grant sponsored by the U.S. Department of Homeland Security.[17] In that research, the disinfection performance of UV and ozone against adenovirus and *Naegleria fowleri* was shown to be remarkably improved when paired together (see Figure 3). Importantly, this study established the synergistic effect of UV and ozone against viruses and amoebas, augmenting prior results against bacteria and parasites. Taken together, the potency of a UV/ozone combination as a disinfection approach seems unparalleled.

The Trio as Oxidizers

The benefits of pairing UV with ozone do not stop with disinfection performance. While UV has virtually no oxidizing ability, the resulting hydroxyl radicals created from UV and ozone are tremendous oxidizers. As is the case with disinfection, the literature is replete with studies that reflect the superior oxidation performance of hydroxyl radicals formed from UV and ozone.[2,12,13,15,16]

In Hayward Industries' laboratories, it has been established that hydroxyl radicals are highly effective at reducing chlorine and combined chlorine (i.e., chloramines) by 50% or more in swimming pools, as well as oxidizing urea, a major component of sweat and urine (see Figure 4). These findings were expected, owing to the potency of hydroxyl radicals. The implications of these findings are significant for swimming pool and spa applications, because urea and chloramines limit chlorine's effectiveness and affect bather comfort. Furthermore, chloramines can volatilize, creating an unpleasant "fishy" or "chlorine" odor, and wreak havoc on indoor materials due to their corrosive nature.

The Trio as a Water Treatment Strategy

It should come as no surprise that a pairing of UV and ozone is gaining attention as a strategy for a variety of water treatment applications, although as recently as 1999, the U.S. Environmental Protection Agency had not discussed the UV/ozone combination in its comprehensive Alternative Disinfectants and Oxidants Guidance Manual.[6,18,19]

If UV and ozone are potent in their own rights, then might the combination of the two be even better?

The synergy that is provided with respect to both oxidation and disinfection is invaluable in most instances. Unfortunately, neither UV nor ozone, nor the resulting hydroxyl radicals, provide a lasting disinfection residual. Therefore, in some applications, such as pools and spas, chlorine is still a necessary part of the overall treatment strategy.

As discussed in my article, "UV & Ozone for Secondary Disinfection" in the May 2015 issue of WQP, the manner in which chlorine is complemented by UV and ozone makes their use together a logical and prudent water treatment approach for the highest level of water sanitization. To this end, CDC's recommendation to use either UV or ozone as a secondary disinfectant to chlorine for swimming pools and spas is a wise approach; however, utilizing both UV and ozone provides an even more robust treatment regimen, not only for pools and spas but for many water treatment applications.

This article is the second in a three-part series on secondary disinfection in recreational water applications. The final installment will appear in the July 2015 issue of WQP. **WQP**

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