

UV DISINFECTION AND ADVANCED OXIDATION

A NEW WAY OF TACKLING OLD PROBLEMS

Written by: Jon McClean, VP of Research, Design & Engineering and Patrick Bollman, P.E., UV Product Specialist

Introduction

Modern wastewater and drinking water facilities face an array of complex and sometimes contradictory problems. On one hand, they need to treat microorganisms that are becoming increasingly chlorine tolerant while driving down the disinfection byproducts caused by high doses of chlorine. While on the other, treat the new contaminants that are emerging, such as pesticides caused by intensive land use, pharmaceutical products consumed in increasing quantities by an aging population, or synthetic organics washing into the aquifer. These emerging contaminants are referred to as Compounds of Emerging Concern (CEC).

Water scarcity will lead to relying more on the reuse of water and has accelerated the urgency to develop and add process barriers to remove these contaminants from the water supply without exacerbating this issue. Few conventional drinking water treatment processes can address these emerging issues and almost no conventional municipal wastewater processes are capable of targeting these problematic compounds.

Metabolized and un-metabolized Pharmaceutical and Personal Care Products (PPCPs) are not new, however their potential to cause effects on living tissue is now subject to scrutiny. A study by the U.S. Geological Survey published in 2002 brought attention to PPCPs in water (USGS, 2002). Following sampling of 139 susceptible streams in 30 states, detectable quantities of PPCPs were found in 80 percent of the streams.

PPCPs Include:

- Sun-screen products
- Prescription, over-the counter, and veterinary drugs
- Diagnostic agents

- Fragrances and cosmetics
- Nutraceuticals (e.g., vitamins)

Sources of PPCPs:

- Agribusiness
- Residues from hospitals and pharmaceutical manufacturing
- Human activity
- Illicit drugs
- Veterinary drug use, especially antibiotics and steroids

The USEPA maintains an active program called the Contaminant Candidate List (CCL) to identify contaminants in public drinking water that warrant detailed study and may require regulation under the Safe Drinking Water Act (SDWA). The most recent Contaminant Candidate List, CCL4 was finalized on November 17, 2016, and contained 97 chemicals or chemical groups, 12 microbiological contaminants, and 10 pharmaceutical compounds.

The list includes antibiotic pharmaceuticals such as erythromycin, and nine hormones: 17 alpha-estradiol, 17 beta-estradiol, equilenin, equilin, estriol, estrone, ethinyl estradiol, mestranol, and norethindrone.

Ultraviolet (UV) alone or in combination with selected chemical oxidants has the ability to produce large amounts of the hydroxyl radical ($\cdot\text{OH}$) or chlorine ($\text{Cl}\cdot$) radical from hypochlorite ($\text{ClO}\cdot$). These species aggressively attack organic compounds, either by the abstraction of hydrogen atoms from water, (alkanes and alcohols), or it can add itself to the compound (olefins and aromatic compounds).

RELATIVE OXIDATION POWER OF PRINCIPAL OXIDIZING SPECIES

Species	Relative Oxidation Power
Chlorine	1.00
Hypochlorous Acid	1.10
Permanganate	1.24
Hydrogen Peroxide	1.31
Ozone	1.52
Atomic Oxygen	1.78
Hydroxyl Radical	2.05
Positively charged hole on Titanium Dioxide, TiO ₂ ⁺	2.35

Table 1. Illustrates how powerful the hydroxyl radical is. It is non-selective and initiates a complex cascade of oxidation reactions leading to mineralization of the organic compound.

History

Advanced Oxidation Processes (AOP) can be usefully defined as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantities to effect water purification” (Glaze et al, 1987).

The earliest evidence of this phenomenon was recorded by Bach (1889), who observed the photolysis of carbonic acid. The decomposition of H₂O₂ by UV was later observed by Thiele (1907). Kornfeld (1922) developed the reaction products from the photolysis of H₂O₂. Therefore, the basic concepts of the modern AOP technologies are over 100 years old.

Today these processes are an essential tool in the removal of a number of microconstituent compounds such as N-nitrosodimethylamine (NDMA). NDMA is a known carcinogen and is effectively removed using only UV light. UV light at or close to 228 nm is used to photolyze this compound – effectively breaking the bonds within the molecule. In the United States, California has established a notification level of 10-ng/L for NDMA, which will likely serve as a future regulation in the state.

In the north of Holland, the PWN Water Supply Company successfully replaced breakpoint chlorination at their Andijk drinking water treatment plant by using the UV/H₂O₂ process. The plant wanted to provide control against emerging organisms that are

chlorine tolerant while reducing by-product formation and controlling organic contaminants. The effect of UV and H₂O₂ on 12 pesticides was studied. For an electric energy of 1 kWh/m³ degradation varied from 18% for trichloroacetic acid to 70% for atrazine. For a combination of ≤1 kWh/m³ and ≤15 g/m³ H₂O₂ all pesticides could be degraded by more than 80% (Kruithof et al., 2005).

In the UK, operators at the Mid Southern Water drinking water plant at Boxall’s Lane used UV light to effectively remove a wide variety of pesticide species from well water being abstracted from chalk aquifers (McClean, 2000). Atrazine, simazine and diuron in concentrations 0.1 to 0.5 µg/L were successfully removed using UV light alone and a higher removal rate was achieved when UV was combined with H₂O₂.

A 12-month study undertaken at Greater Cincinnati Water Works examined the ability of a low pressure and medium pressure UV system to reduce 7 contaminants of interest (Atrazine, Metolachlor, MTBE, MIB, Ibuprofen, Gemfibrozil and 17-α-ethynylestradiol), some of which have been found in the Ohio River (Metz, 2011).



Figure 1. ETS-UV™ systems used as part of an AOP pilot study at the Greater Cincinnati Public Water Works

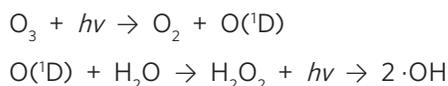
The study examined the addition of up to 10 mg/L of H₂O₂ in conjunction with the UV systems, and recorded encouraging degradations under different process conditions (Meyer, 2009). This facility also compared UV-mediated AOP using chlorine (Cl₂) rather than the conventional H₂O₂. The improvement in performance and probable cost savings they measured were striking at this facility.

Studies carried out by Watts and Linden (2007) and Watts et al. (2012) have shown that UV/Cl₂ AOP is significantly more cost effective than UV/H₂O₂ as an AOP (Watts et al., 2012). Additional studies undertaken by Rosenfeldt et al. (2013) at Greater Cincinnati Water Works, using the ETS-UV™ system, showed that UV/Cl₂ AOP is capable of reducing MIB by up to 90%, and that this combination outperforms UV/H₂O₂ at low oxidant concentrations with significantly lower costs by avoiding the need for quenching agents. Interestingly, the study showed no evidence of disinfection by-products formation; this is likely due to the highly reactive nature of the oxidizing species within the AOP environment.

The Science of Photolysis

Conventional ozonation or H₂O₂ oxidation of organic compounds does not completely oxidize many species to CO₂ and H₂O. In a number of reactions, the intermediate oxidation products can be more toxic than the initial compound. Completion of the oxidation reactions is regularly achieved using UV light.

Ozone readily absorbs UV light to form ·OH from a H₂O₂ intermediate, as shown below:



The molar absorption coefficient of H₂O₂ for UV light at 254 nm (the wavelength produced by low pressure) is very low. The H₂O₂ absorbance increased when polychromatic lamps (medium pressure lamps with broader spectral output) are used and further increased when high quality synthetic quartz is selected with enhanced UV transmittance below 240 nm. The process is however still inefficient due to the low absorbance of UV above 220 nm.

The direct photolysis of hydrogen peroxide leads to the formation of hydroxyl radicals.



The ·OH radicals are unselective and so react quickly. At H₂O₂ concentrations over 100 mg/L, the species are scavenged by H₂O₂.

These reaction mechanisms are complex and varied. The illustration below highlights some of the potential breakdown pathways.

OXIDATION OF ORGANIC CONTAMINANTS PHOTO-OXIDATION REACTIONS

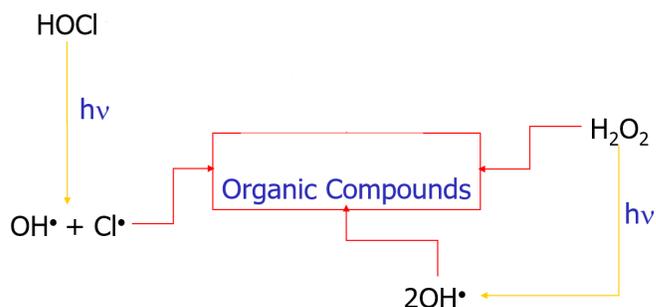
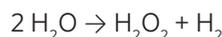


Figure 2. Potential reaction pathways

The active chlorine species, and indeed chlorine mediated AOP processes are gaining traction. Operating cost, ease of chemical handling, and safety are essential considerations. The conventional practice of dosing H₂O₂, to then need to quench it with expensive chemicals looks to be obsolete.

A Better Way

The Evoqua approach to UV-mediated AOP is to combine an advanced electrode arrangement upstream of the UV lamps into the AOP system. The electrode consists of anode and cathode plates that are highly efficient in converting TDS and other mineral salts found in most ground or surface water into the active chlorine species and cleaving the water into ·OH, via the formation of H₂O₂.



The anode and cathode work together to produce trace amounts of ·OH and ClO⁻/HOCl (the ratio depends on the pH of the water), which are formed in situ immediately upstream of the UV lamps. The electrodes use a switching power supply to remove any hard water deposits off them. This has the obvious benefit of not requiring the bulk storage of H₂O₂ on site nor does it require the addition of quenching agents due to the inherent inefficiency of the conventional H₂O₂ AOP.



Figure 3. Electrode assembly being inserted into an ETS-UV™ AOP system, directly upstream of the UV lamps

Initial testing of the electrode/UV technology has shown great success. The first study occurred at a drinking water facility in New York to show the effectiveness of MIB destruction. The results showed a greater than 75% reduction (testing analysis only showed <9.8 ng/L in the effluent concentration, so reduction could have been much higher). The second study was performed at a direct potable reuse demonstration facility in California targeting 1,4-dioxane. Once again, the technology showed to be effective providing a >0.5-log reduction which is industry standard for 1,4-dioxane. Results of pilot are shown below. Additional pilot/testing is scheduled to begin by the end of 2017 with additional data expected in 2018.

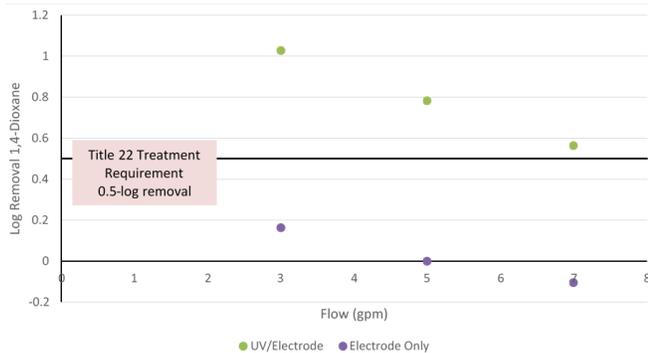


Figure 4. Electrode based AOP removal of 1, 4 dioxane

UV will continue to play an active role as a disinfection barrier against the chlorine tolerant organisms. As the available water supply dwindles, and we are forced to use and eventually reuse water, so the removal of micro-contaminants, CECs and PPCPs will become more pressing. Conventional wastewater plants were not built as a barrier to these nuisance compounds so cannot be expected to effectively remove them. Oxidation using UV light and a number of oxidants would seem to be a logical next step.

Hydrogen Peroxide alone probably isn't the answer to AOP process, and UV mediated AOP using chlorine and the active chlorine species offers significant operational and safety benefits (Rosenfeldt et al., 2013).

References

- Bach, A 1899. On the relation between the reduction by nascent hydrogen, the electrolysis, and the photolysis of carbonic acid. *J. Phys. Chem.* 3(3): 181.
- Glaze, W H; Kang, J W; Chapin, D H. 1987. The chemistry of water treatment processes involving ozone hydrogen peroxide and ultraviolet radiation, *Ozone: Sci. Eng.*, 9: 335-352.
- Gmelin.1994, Handbook of inorganic and organometallic chemistry, Parthé, E; Gelato, L; Chabot, B; Penzo, M; Cenzual, K; Gladyshevskii, R, Eds. ISBN 3-540-93684-X, 3: 331-348.
- Kornfeld. 1922 cited in Oppenlander T. 2003, Photochemical Purification of Water and Air, Wiley, New York.
- Kruithof, J; Kamp, P; Martin, B; Belosevic, M; Williams, G. 2005 UV/H2O2 treatment for primary disinfection and organic contaminant control at PWN's water treatment plant Andijk, Proc. Third International Congress on Ultraviolet Technologies, Whistler, BC, Canada International Ultraviolet Association, Ayr, ON, Canada.
- Meyer, M. 2009, Greater Cincinnati Water WQTC.
- McClellan J. 2000, IUVA News, 2(5): 4.
- Metz, D H; Meyer, M; Dotson, A; Beerendonk, E; Dionysiou, D D. 2011, The effect of UV/H2O2 treatment on by-product formation potential under simulated distribution system conditions, *Water Res.* 45(13): 3969-3680.
- Rosenfeldt, E; Boal, A K; Springer, J; Stanfod, B; Rivera, S; Kashinkunti, R D; Metz, D H. 2013, Comparison of UV-mediated Advanced Oxidation, 105(7): 29-33.
- Thiele, V H. 1907, Einige Reaktionen im ultravioletten lichte, *Zeit. Angew. Chim.*, 51: 2472-2484.
- Watts, M J; Linden, K G. 2007, Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. *Water Res.* 41(13): 2871-2878.
- Watts, M J; Hofmann, R; Rosenfeldt, E J. 2012, Low pressure UV/Cl2 for advanced oxidation of taste and odor, *J. Amer. Water Works Assoc.*, 104(1): E58-E65.
- USGS. 2002, Water-quality data for pharmaceuticals, hormones and other organic wastewater contaminants in U.S. Streams, 1999-2000 USGS Open File report 02-94.

Contact Us

ets-uv@evoqua.com
Jon McClellan - VP of Research, Development & Engineering
 jon.mcclellan@evoqua.com
 +1 (513) 652-2465
Patrick Bollman - UV Product Specialist
 patrick.bollman@evoqua.com
 +1 (859) 760-7365



238 Commercial Drive, PO Box 392, Beaver Dam, WI 53916

+1 (877) 885-4628 (toll-free)

+1 (920) 885-4628 (toll)

www.evoqua.com

ETS-UV is a trademark of Evoqua Water Technologies LLC, its subsidiaries or affiliates in some countries.

All information presented herein is believed reliable and in accordance with accepted engineering practices. Evoqua makes no warranties as to the completeness of this information. Users are responsible for evaluating individual product suitability for specific applications. Evoqua assumes no liability whatsoever for any special, indirect or consequential damages arising from the sale, resale or misuse of its products.