Advanced Oxidation Process Basics and Emerging Applications in Water Treatment

James P. Malley, Jr.

Professor of Civil/Environmental Engineering, Environmental Research Group,
University of New Hampshire, Room 344 Gregg Hall, 35 Colovos Road, Durham, NH 03824

ABSTRACT

UV/H2O2 and Ozone/H2O2 (Peroxone) are the most promising AOP technologies for water reuse and drinking water treatment applications. Recent growth in UV/H2O2 applications including facilities at PWN in The Netherlands; Aurora, CO USA and Brisbane, Australia shows it to be a very good technology for reuse or difficult to treat source waters. Improvements in bromate control and the continued recognition of the multiple benefits that ozone can provide in drinking water treatment suggests a renewed interest in Peroxone for drinking water applications solely aimed at taste and odor control and partial disinfection credit. It remains a myth and a misconception that the benefits of UV/H2O2 can be gained from minor modifications and simply adding H2O2 to existing UV disinfection systems. Design, operation and costs of UV/H2O2 are entirely different than those of UV disinfection systems. Each technology, UV/H2O2, UV disinfection, ozone and Peroxone, has its application and its niche. AOP processes remain costly in terms of total life cycle costs relative to conventional treatment alternatives and research efforts need to continue into making these processes more kinetically favorable more energy efficient and more optimized in terms of residual H2O2 control.

BACKGROUND

Advanced oxidation processes can be thought of as a subset of free radical chemistry and some of the reactions (e.g., Fenton's) have been known and used since the 1890's. In the environmental field applications first emerged in industrial wastewater treatment in the 1950's for the oxidation of phenolic compounds and other recalcitrant complex organics. Applications in hazardous waste remediation emerged in the 1980's and grew somewhat over the next 25 years with particular emphasis on groundwater remediation in the 1990's. More recently, there has been interest around the world for using AOPs to treat difficult source waters or waters in reuse applications. This recent interest has focused on applications of UV and hydrogen peroxide due in part to the widespread interest in UV disinfection applications, the many attractive features of UV-peroxide that will be discussed as well as and aggressive information and marketing campaign by manufacturer's of UV-peroxide systems.

The pros of AOPs include:

- Very rapid processes requiring relatively little time and small footprints to treat large water flowrates

- Potential for complete detoxification of a wide range of emerging organic pollutants and pathogens (disinfection) through complete oxidation often called mineralization in the hazardous waste treatment field for example:
  TCE + AOPs ‡ CO2 + H2O + Cl-

- AOP Treatment processes do not generate solid residuals (such as spent carbon adsorbents or biological sludge)

- The relatively non-selective oxidative nature of AOPs makes them an attractive tool for simultaneously addressing multiple treatment objectives such as control of tastes and odors, disinfection, oxidation of emerging organic compounds (e.g., EDC's PhAC's and other contaminants found on the UCMR (CCL2) list.

The cons of AOPs include:

- Limited track record in water reuse and drinking water applications.

- Very significant capital and O&M costs (particularly power). Not the same as UV disinfection, a much different application in terms of costs.

- Radical chemical reactions can be difficult to predict due to site specific water quality conditions that can result in free radical initiators or scavengers.

- There can be site specific questions about chemical by-products and biologically stable water after the AOP process (increased formation of AOCs, BDOC)

- Removal of hydrogen peroxide residuals after the AOPs needs to be addressed in the integrated design of the treatment facilities.

CHEMISTRY AND KINETICS

AOPs involve the generation of chemical radicals which are very strong oxidizing agents. Of these hydroxyl radicals (•OH) are the best known and most commonly studied. The processes are termed "Advanced" because the chemical reactions are highly accelerated oxidation reactions compared to typical environmental transformations that occur in the environment. The •OH radicals react with many reduced compounds to initiate a series of oxidative degradation reactions.

AOPs are chemical processes and performance in water treatment is a function of hydraulics and kinetics •OH radicals react with organic compounds by several mechanisms (e.g., methanol oxidation chemistry) including hydrogen abstraction from aliphatic compounds:

•OH + CH3OH ◊ •CH2OH + H2O

and the addition to unsaturated compounds

•OH + CH2=CH2 ◊ •CH2CH2OH

These steps are followed by reaction with oxygen initiating a series of degradation reactions. The general sequence of reactions is that pollutants react to form aldehydes which are further oxidized to carboxylic acids which are ultimately converted to carbonates.

Reaction rate determinations for AOPs are an important kinetic step in evaluation and design. AOP chemical kinetics are usually modeled as zero or first order depending upon the specific environmental applications. For most water applications the AOP kinetics are approximated as first order so if we define performance as percent removal then:

% Removal = [(Co – Ce)/Co] x 100% = [1 – Ce/Co] X 100%

(Co and Ce are initial and final pollutant concentrations)

For first order kinetics with ideal hydraulics:

$$r_c = dC/dt = kC \text{ and } t = V/Q$$

$$Ce/Co = \exp[-k(V/Q)]$$

So ideally for a given flow (Q) and a given percent removal needed, the larger the rate constant (k) the smaller the overall contact time and/or reactor volume (V) needed, hence the lower cost.
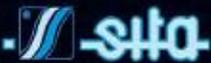
DETERMINATION OF EEO

In almost all cases, AOPs are driven by electrical energy so AOP performance can be compared based on power use. A useful term is Electrical Energy Dose (EED) which can be calculated for a given process as:

EED (kWh/m³) = (P T) / 60 V

where:

     P   = Power (kW)
     T   = Irradiation time (min)
     60 = min/hour
     V   = total system volume (m³)

In most applications in water treatment, the pollutant is normally in relatively low concentrations (< 100 mg/L) so it is useful to calculate the Electrical Energy Used per Order of Magnitude Reduction (EEO) which can be calculated from EED for a given process as:

EEO (kWh/m³) = EED / (log C_o/C_e)

It is useful to linearize this equation to determine EEO for a given set of data:

log C_e = log C_o + (– 1/EEO)(EED)

Experimental data can then be plotted as C_e vs. EED and the resulting slope will be equivalent to -1/EEO which allows computation of the EEO for a given system. EEO data derived experimentally is a function of scale and in most cases full scale EEO derived data will be lower than bench or pilot scale EEO derived data. Research by Bolton and Stefan (*Res. Chem. Intermediates*, 28:857, 2003) clearly demonstrated that the EEO for a given pollutant drops off dramatically as the test reactor radius goes from 2.5 cm to 10 cm and this effect is most pronounced at larger values of UVT.

Since AOP reactions follow first order kinetics, AOP reactor hydraulics should be designed to approach plug flow conditions. Optimum AOP reactor designs are determined through modeling efforts (CFD for ozone reactors, fluence models and particle track analysis for UV reactors etc.) and from empirical pilot data.

TYPES OF AOPS

AOPs can be divided into two general categories, the homogeneous AOPs and the heterogeneous AOPS. Although the heterogeneous AOP that uses UV irradiation and a TiO2 catalyst has received extensive study by numerous researchers, the process has not gained widespread acceptance or use in the environmental engineering field. Therefore, this paper will focus on the homogeneous AOPs.

For many of the homogeneous AOPs there is a photolytic component to the reaction. Photolysis requires that the Molar Absorption (_) and Quantum Yield (_) must both be favorable. Quantum yield can be defined simplistically as _ ~ [1/(number of photon hits needed to break a bond)]. Therefore, _ = 1 is optimum; _ = 0.5 implies 2 hits needed to break a bond and an _ = 0.01 implies 100 hits are needed to break a bond (an unfavorable yield).

Direct photolysis occurs when photons emitted by a lamp source are directly adsorbed by the target chemical substrate resulting in excitation and chemical reactions leading to bond breakage and rearrangement. Kinetics are generally modeled as first order. Direct photolysis can be advantageous in many water applications if kinetics are favorable since it does not require additional chemicals. It is important to match lamp output spectra with target compound absorption spectra (Figure 1). The first law of photochemistry basically states that photochemical reactions cannot occur unless photons of the emitted UV light are adsorbed by the target compound   Typical examples where direct photolysis is an important mechanism in environmental engineering applications for water treatment includes UV disinfection through thymine dimerization reactions; direct UV photolysis of NDMA; and the often unwanted effect of UV reduction of nitrate to nitrite by polychromatic medium pressure UV lamps.

Direct vacuum UV (< 190nm) photolysis of water has been applied in the ultrapure water field often to remove low levels of TOC since it requires no additional chemicals; there is rapid molar adsorption of the UV by water within microns and there is a reasonable quantum yield (_ = 0.33) for the process.

FENTON'S PROCESSES

Ferric complexes can absorb in the near UV and up to about 500 nm visible range. These reactions generate ferrous iron Fe(II) and in the presence of hydrogen peroxide and optimum pH of 3 to 4 the reactions generate hydroxyl radicals. Fenton's reactions also occur without photochemical initiation in some reduced organic matrices. Typical reactions are:

Fe^{3+} + h_ ◊ Fe^{2+}

Fe^{2+} + H_2O_2 ◊ Fe^{3+} + OH^- + •OH

R-H + •OH ◊ •R + H_2O

•R + Fe^{3+} ◊ R(oxidized) + Fe^{2+}
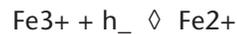
The process has been used effectively when pollutant concentrations are high, or the UVT of the water is low and/or when natural iron levels are high. Good success has been reported for insitu groundwater remediation at sites where there are high concentrations of iron in the soils or groundwater.

OZONE/PEROXIDE (PEROXONE)

AwwaRF and MWDSC studied this process they named Peroxone extensively in the 1990's for Taste and Odor Control. Hydrogen peroxide initiates a base catalyzed cyclic decomposition of ozone yielding intermediate radical oxidant species and hydroxyl radicals.

H_2O_2 ⇓◊ H^+ + HO_2^-

HO_2^- + O_3 ◊ HO_2 + O_3^- ◊ O_2^- ◊ •OH

Interest in Peroxone has diminished somewhat in drinking water applications in part due to costs, operational
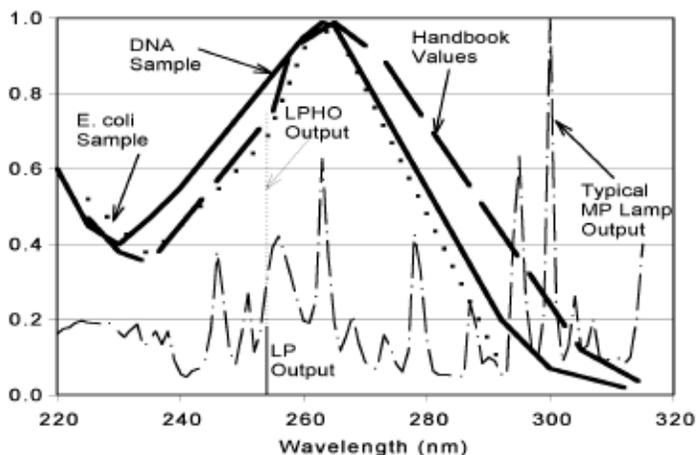
Figure 1: D*NA Absorbance Spectra Versus Commercial UV Lamp Outputs.*

complexities and issues related to bromate formation during the 1990's. However, in recent years, significant improvements in ozone generation efficiency and process control as well as research developments in the control of bromate formation suggests that Peroxone may be a cost effective solution in applications where bromate levels are not a concern.
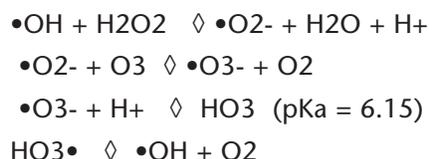
UV/OZONE

Ozone (O_3) absorbs UV in the 200-300 nm range resulting in singlet oxygen generation that leads to hydroxyl radical formation and formation of hydrogen peroxide as shown below:

$$O_3 + h\_ \lozenge O_2 + \bullet O \qquad \_ = 1.0 \text{ (good)}$$

$$\bullet O + H_2O \ \lozenge \ 2\,[\bullet OH] \lozenge H_2O_2$$
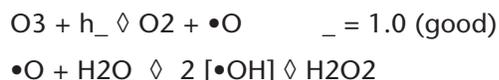
This process is rarely used as it is not cost competitive with Peroxide-Ozone (Peroxone) or UV-Hydrogen Peroxide processes. Its early promise was diminished with further understanding of AOP chemistry and mechanisms showing that it is basically an inefficient way of making hydrogen peroxide. Literature search shows that the treatment of munitions wastes with UV/Ozone remains in use for some locations.

UV/PEROXIDE/OZONE

As previously mentioned, the UV photolysis of ozone leads to generation of H_2O_2. If additional H_2O_2 is also added to the solution, it can act as an enhancer of radical generation and overall oxidation rate from a series of radical oxidation reactions:

$$\bullet OH + H_2O_2 \ \ \lozenge \bullet O_2\text{-} + H_2O + H+$$

$$\bullet O_2\text{-} + O_3 \ \lozenge \bullet O_3\text{-} + O_2$$

$$\bullet O_3\text{-} + H+ \ \ \lozenge \ HO_3 \ (pKa = 6.15)$$

$$HO_3\bullet \ \ \lozenge \ \bullet OH + O_2$$

This approach has been used in some hazardous waste applications for organics removals, in particular polyaromatic hydrocarbons (PAHs), but is generally not necessary nor cost competitive with the other AOP options used in typical water treatment.

UV/PEROXIDE

This process is receiving most of the interest in drinking water treatment and reuse applications at present. This interest is due in part to the growing interest in UV disinfection as a barrier for Giardia and Cryptosporidium and the ability of UV-hydrogen peroxide to remove organic micropollutants either by direct photolysis or by hydroxyl radical formation or through both mechanisms. Since hydrogen peroxide absorbs UV in 200-300 nm range the quantum yield is optimum:

$$H_2O_2 + h\_ \ \lozenge \ 2\,[\bullet OH] \qquad \_ = 1.0$$
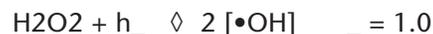
However, the molar absorption coefficients for H_2O_2 in the range of typical UV lamp output wavelengths are small, so significant concentrations (>5 ppm) of H_2O_2 are required to produce the desired radical formation from UV energy. It is important to have a UV lamp with strong output in the 200-300 nm region (MP and LPHO Lamps are both being used in current applications).

The UV/H_2O_2 process has been shown to be highly effective for disinfection of *Giardia, Cryptosporidium* and virus. The issue of adenovirus requiring higher UV doses (186 mJ/cm2 for 4-log inactivation) than typically used in disinfection is not an issue with UV/H_2O_2 since the typical UV doses applied in a UV/H_2O_2 AOP system are above 300 mJ/cm2. UV/H_2O_2 has also been shown to effectively remove many organic contaminants including NDMA, atrazine, 1,4 dioxane, and numerous EDC's and PhAC's. UV/H_2O_2 is also highly effective for taste and odor control through oxidation of compounds such as MIB and geosmin.

However, radical chemistry reactions can be extremely complicated and difficult to predict. It is clear that the UV dose and the H_2O_2 dose are important for this process. In addition, other key water quality parameters that affect UV/H_2O_2 in drinking water are in order:

• UV Transmittance (UVT) – affected by TOC
• pH
• Temperature
• Inorganics – particularly carbonate alkalinity

The effects of iron and manganese on UV/H_2O_2 processes have been examined in many studies but the results have been inconclusive. Perhaps the most significant effect reported has been the iron fouling of the UV system by the presence of iron thus reducing process efficiency.

COSTS OF AOPS

Cost effectiveness of using AOPs is very much a balancing act between multiple treatment objectives versus competing technologies. Costs are very site specific and are most influenced by UV Transmittance, design flows; duration of required treatment; specific pollutants and

needed percent removals; UV dose, and or ozone demand and decay kinetics and or H2O2 dose. The practicality of using ozone related AOPs, in particular Peroxone, is also a function of the bromate levels produced and/or the prevailing bromate standard. For applications where compliance with the USEPA bromate standard of 10 _g/L is adequate, use of Peroxone with practical bromate control strategies remains viable. If the water quality objective is to ensure bromate levels remain below 5 _g/L or even below 1 _g/L then the use of Peroxone is unlikely to be viable.

Therefore, the best that can be done in terms of describing the costs of AOPs is to provide "ball park" estimates based upon different scenarios. For applications in water reuse or in the treatment of highly impacted source waters where AOPs are being used to achieve removals of organic pollutants and disinfection in a 24 hour/day-7 day/week-365 day/year mode it is likely that UV-peroxide will be the technology of choice and the total life cycle costs will range between $1.00 - $5.00/1,000 gallons treated. For more tapered applications where seasonal taste and odor control and full time disinfection of bacteria, virus, *Giardia* and *Cryptosporidium* is the goal, the total life cycle costs range from $0.30 - $2.50/1,000 gallons treated if UV/H2O2 is chosen. However, depending upon the concerns over bromate and the existing plant conditions, it is often more cost effective to use ozone for taste and odor control as well as virus disinfection and partial disinfection credit for *Giardia* and *Cryptosporidium* followed by UV disinfection at doses (e.g., 25 to 40 mJ/cm^2) that provide a final *Giardia* and *Cryptosporidium* barrier; than it is to design, build and operate a UV/H2O2 system.

AOP RESEARCH NEEDS

The total life cycle cost for AOPs remains high due to capital costs for equipment and the power costs. Research is ongoing and needs to continue to find ways to more cost effectively produce hydroxyl radicals and improve oxidation kinetics. All AOP processes produce residual H2O2 levels that can be problematic to or increase the costs of downstream treatment processes. Therefore, improved process control strategies to minimize H2O2 levels need to be developed. The complexities of AOP chemistry and growing concerns with unregulated organic chemicals and DBPs (in particular N-DBPs) suggests that the byproducts of incomplete oxidation produced from AOPs must continue to be studied in terms of potential toxicity and in terms of the biostability (AOC, BDOC) of the water after treatment.

ACKNOWLEDGEMENTS