

## ADVANCED OXIDATION PROCESSES – CURRENT STATUS AND PROSPECTS

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**Abstract.** The paper provides an overview of theoretical basis, efficiency, economics, laboratory and pilot plant testing, design and modelling of different advanced oxidation processes (combinations of ozone and hydrogen peroxide with UV radiation and catalysts).

**Key words:** water, wastewater, chemical oxidation, ozone, hydrogen peroxide, UV radiation, solid catalyst.

### INTRODUCTION

Hazardous organic wastes from industrial, military, and commercial operations represent one of the greatest challenges to environmental engineers. Advanced oxidation processes (AOPs) [1–4] are alternatives to the incineration of wastes, which has many disadvantages. Conventional incineration is commonly thought to be a feasible alternative to landfill, but as presently practised, incineration may bring about serious problems due to releasing toxic compounds such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) into the environment via the incinerator off-gas emissions and/or fly ash.

The AOPs have proceeded along one of the two routes:

- oxidation with  $O_2$  in temperature ranges intermediate between ambient conditions and those found in incinerators Wet Air Oxidation (WAO) processes in the region of 1–20 MPa and 200–300°C); and
- the use of high energy oxidants such as ozone and  $H_2O_2$  and/or photons that are able to generate highly reactive intermediates – 'OH radicals.

In 1987, Glaze et al. [1] defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. The hydroxyl radical ( $\cdot\text{OH}$ ) is a powerful, non-selective chemical oxidant (Table 1), which acts very rapidly with most organic compounds (Table 2). The reaction rate constants of molecular ozone with different organic compounds are also given in Table 2. These reaction rate constants vary in quite a wide range from 0.01 to  $10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. Depending upon the nature of the organic species, two types of initial attack are possible: the hydroxyl radical can abstract a hydrogen atom from water, as with alkanes or alcohols, or it can add itself to the contaminant, as in the case of olefins or aromatic compounds.

**Table 1.** Relative oxidation power of some oxidizing species [2, 3]

Oxidizing 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, $\text{TiO}_2^+$	2.35

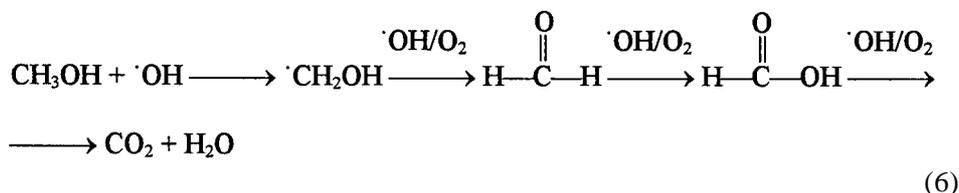
**Table 2.** Reaction rate constants ( $k$ ,  $\text{M}^{-1} \text{ s}^{-1}$ ) of ozone vs. hydroxyl radical [4]

Compound	$\text{O}_3$	$\cdot\text{OH}$
Chlorinated alkenes	$10^3$ – $10^4$	$10^9$ – $10^{11}$
Phenols	$10^3$	$10^9$ – $10^{10}$
N-containing organics	$10$ – $10^2$	$10^8$ – $10^{10}$
Aromatics	$1$ – $10^2$	$10^8$ – $10^{10}$
Ketones	1	$10^9$ – $10^{10}$
Alcohols	$10^{-2}$ –1	$10^8$ – $10^9$

A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation:



For example, reaction with methanol proceeds as follows:



The attack by the  $\cdot\text{OH}$  radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. The exact routes of these reactions are still not quite clear. For example, chlorinated organic compounds are oxidized first to intermediates, such as aldehydes and carboxylic acids, and finally to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and the chloride ion. Nitrogen in organic compounds is usually oxidized to nitrate or to free  $\text{N}_2$ , sulphur is oxidized to the sulphate. Cyanide is oxidized to cyanate, which is then further oxidized to  $\text{CO}_2$  and  $\text{NO}_3^-$  (or, perhaps,  $\text{N}_2$ ).

As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with  $\cdot\text{OH}$  radical. From Table 2 we can see that chlorinated alkenes are treated most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules (i.e., alkanes) react at a much slower rate and, therefore, are more difficult to oxidize. AOPs can often achieve oxidative destruction of compounds refractory to conventional ozonation or  $\text{H}_2\text{O}_2$  oxidation. AOPs are suited for destroying dissolved organic contaminants such as halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compounds (benzene, toluene, ethylbenzene, xylene – BTEX), pentachlorophenol (PCP), nitrophenols, detergents, pesticides, etc. AOPs can also be used to oxidize inorganic contaminants such as cyanide, sulphide, and nitrite.

In general, the AOPs when applied in a right place, give a good opportunity to reduce the contaminants' concentration from several hundreds ppm to less than 5 ppb. That is why they are called the *water treatment processes of the 21st century*.

Few AOPs have been examined in any detail under controlled experimental conditions, for many it is uncertain what the exact chemical mechanisms are, and few field tests have been carried out in such a manner that the entire process could be critically examined. Moreover, the practical applications of AOPs have been made largely by equipment manufacturers, who have not carried out systematic studies of AOPs with the view of understanding their advantages and disadvantages.

On the other hand, few AOPs have been operated for very long periods of time so that the reliability of equipment and accurate costs could be evaluated. Despite the limited understanding, the scale of pilot and process installations has begun to reach substantial proportions. One of the pioneers in the field of practical application of AOPs has been the company Solarchem Environmental

Systems, Canada (now Chemviron Carbon, USA). The reference list of this company consists of more than 50 full-scale installations of UV, UV/H<sub>2</sub>O<sub>2</sub>, or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> systems worldwide, treating a variety of contaminants in process wastewater, groundwater, and drinking water. Well water is currently being treated by the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (ozone/peroxide) AOP for trichloroethylene (TCE) and tetrachloroethylene (PCE) removal at a scale of 450 m<sup>3</sup>/h in Los Angeles. An O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system has been used for atrazine removal from the water of the River Seine in Paris at a scale of 5000 m<sup>3</sup>/h, etc. UV disinfection is found in drinking water treatment plants throughout Europe and USA. Many bacteria and viruses are inactivated and many organic compounds undergo photolysis in the presence of UV radiation.

Some of pilot plant or full-scale elaborations of AOPs are known already as registered trademarks such as ULTROX, RAYOX, WEDECO, UVOX, ECOCLEAR, and BioQuint.

At the same time the knowledge about the exact mechanisms of AOPs is still incomplete. AOPs are to be important tools for environmental technology and they must be placed on more sound scientific and engineering basis. The reaction mechanisms, comparative efficiency of different AOPs, and their mathematical modelling have been the key subjects of the joint research group of the Department of Chemical Engineering of Tallinn Technical University (TTU) and of the Institute of Chemistry at TTU since 1993.

## ADVANCED OXIDATION METHODS

Several methods are available for generating <sup>•</sup>OH radicals. These include both **non-photochemical** and **photochemical** methods:

- Ozonation at elevated pH (>8.5)
- Ozone + hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)
- Ozone + catalyst (O<sub>3</sub>/CAT)
- Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)
- O<sub>3</sub>/UV
- H<sub>2</sub>O<sub>2</sub>/UV
- O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV
- Photo-Fenton/Fenton-like systems
- Photocatalytic oxidation (UV/TiO<sub>2</sub>)

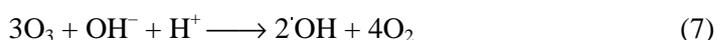
### Non-photochemical methods

There are four well-known methods for generating hydroxyl radicals without using light energy. Two of the methods involve the reaction of ozone while one uses Fe<sup>2+</sup> ions as the catalyst. These methods are ozonation at elevated values of pH (>8.5), combining ozone with hydrogen peroxide, ozone + catalyst, and the Fenton system.

### Ozonation at elevated pH

As the pH rises, the decomposition rate of ozone in water increases. For example, at pH 10, the half-life of ozone in water can be less than 1 min. Oxidation of organic species may occur due to a combination of reactions with molecular ozone and reactions with  $\cdot\text{OH}$  radicals.

The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical  $\text{O}_2^{\cdot-}$  and hydroperoxyl radical  $\text{HO}_2\cdot$ . By the reaction between ozone and the super-oxide anion radical the ozonide anion radical  $\text{O}_3^{\cdot-}$  is formed, which decomposes immediately giving  $\cdot\text{OH}$  radical. Summarizing, three ozone molecules produce two  $\cdot\text{OH}$  radicals [5]:

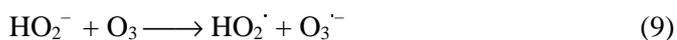


Bicarbonate and carbonate play an important role as scavengers of  $\cdot\text{OH}$  radicals in natural systems. The products of a reaction between  $\cdot\text{OH}$  radical and carbonate or bicarbonate ions are passive carbonate or bicarbonate radicals, which do not interact further with ozone or organic compounds. *tert*-Butyl alcohol also suppresses the chain reaction, if present.

The rate of the attack by  $\cdot\text{OH}$  radicals is typically  $10^6$  to  $10^9$  times faster than the corresponding reaction rate for molecular ozone. The major operating cost for the ozone oxidation process is the cost of electricity for ozone generation. The energy requirement for ozone synthesis using air as a feed gas ranges from 22 to 33 kWh/kg  $\text{O}_3$ , including air handling and ozone contacting with water [2]. The energy requirement for ozone production from pure oxygen is in the range from 12 to 18 kWh/kg  $\text{O}_3$ , to which the cost of oxygen should be added.

### Ozone + hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ) – (peroxone)

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of  $\cdot\text{OH}$  radicals [5]:



The reaction continues along the indirect pathway described above and  $\cdot\text{OH}$  radicals are produced [6]. The combination of different reaction steps shows that two ozone molecules produce two  $\cdot\text{OH}$  radicals:



Paillard et al. [7] studied the elimination of atrazine in filtered Seine River water. Results showed better degradation of the pesticide in water treated with ozone–hydrogen peroxide combination as compared to ozone alone. The optimum  $\text{H}_2\text{O}_2/\text{O}_3$  mass ratio was from 0.35 to 0.45. The performance of the process depends on the ozone dose, contact time, and alkalinity of water. Duguet et al. [8], when treating Lake Cholet water, established the importance of  $\text{H}_2\text{O}_2$  introduction point: the best performance was achieved when  $\text{H}_2\text{O}_2$  was added

after the oxidation of highly reactive substances with ozone alone. The implementation of a radical system makes oxidation of refractory molecules possible: it allows getting full advantage of selective molecular ozone reactions before converting the process to non-selective free radical attack.

Hydrogen peroxide is a relatively inexpensive, readily available chemical oxidant. It is produced by electrolysis of ammonium bisulphate or by oxidation of alkyl hydroanthraquinones. The electrolytic process consumes approximately 7.7 kWh per 1 kg of H<sub>2</sub>O<sub>2</sub> produced [2].

### **Ozone + catalyst (O<sub>3</sub>/CAT)**

Another opportunity to accelerate ozonation reactions is to use heterogeneous or homogeneous catalysts. Several metal oxides and metal ions (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-Me, MnO<sub>2</sub>, Ru/CeO<sub>2</sub>, TiO<sub>2</sub>-Me, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, etc.) have been studied and sometimes a significant acceleration in the decomposition of the target compound has been achieved, although the reaction mechanism in most cases remained unclear.

Cortes et al. [9] studied advanced oxidation of chlorobenzenes in wastewater as well as in model solutions using iron and manganese ions as heterogeneous catalysts. They concluded that the reduction of total organic carbon (TOC) and chemical oxygen demand (COD) from wastewater was more efficient with the ozone/catalyst system than oxidation with ozone at high pH values. The O<sub>3</sub>/Mn(II) and O<sub>3</sub>/Fe(II) systems were more effective in the removal of organochloride compounds than the O<sub>3</sub>/Fe(III) and O<sub>3</sub>/high pH systems.

The study of Karpel Vel Leitner et al. [10] concerned the catalytic ozonation of one model compound – succinic acid, which is barely oxidized by ozone alone. Ru/CeO<sub>2</sub> was used as a catalyst. Legube et al. [11] studied the catalytic ozonation process using Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> in its anatase form, and clay as the support for metal catalysts. Salicylic acid was chosen as a model compound. In contrast to unassisted ozonation, TOC measurements showed complete removal of organics in catalytic ozonation.

Paillard et al. [12] compared the efficiency of catalytic ozonation O<sub>3</sub>/TiO<sub>2</sub> with plain ozonation and a combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. Oxalic acid was chosen as a model compound. As a result the O<sub>3</sub>/TiO<sub>2</sub> system was preferable in terms of process efficiency in TOC reduction.

Ozone-Granulated Activated Carbon systems (O<sub>3</sub>/GAC) make a special case of catalytic ozonation. Quite well-known is the combined system O<sub>3</sub>/GAC for biorefractory compounds (for example, pesticides) destruction where the GAC's bed life is prolonged due to the ozonated water [13]. Using the GAC as a catalyst for free radicals formation in ozonated water is much less studied and some results are quite contradictory.

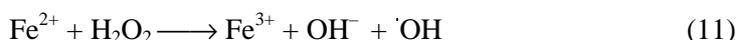
Kaptijn [14] elaborated the *Ecoclear* process – oxidation of biorefractory organics in the ozonation column filled with the GAC bed by the radicals such as O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, and O<sub>3</sub><sup>-</sup> (not by ·OH radicals!) formed on the surface of GAC. This

process has been in commercial operation since 1992 at an ozone consumption of 1.7 kg ozone per 1 kg COD removed.

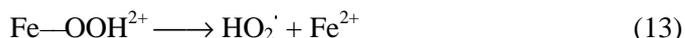
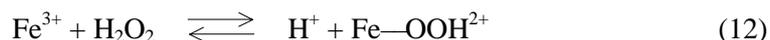
In their recent publication [15] Jans & Hoigne declare that a few milligrams of activated carbon or carbon black per litre in ozone-containing water initiate a radical-type chain reaction that then proceeds in the aqueous phase and forms 'OH radicals.

### **Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)**

The Fenton process was reported by Fenton [16] already over a hundred years ago for maleic acid oxidation:



The rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe(II) oxidizes to Fe(III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. Hydrogen peroxide decomposes catalytically by Fe(III) and generates again hydroxyl radicals according to the reactions:



etc.

For this reason, it is believed that most waste destruction catalyzed by Fenton's reagent is simply a Fe(III)–H<sub>2</sub>O<sub>2</sub> system catalyzed destruction process, and Fenton's reagent with an excess of hydrogen peroxide is essentially a Fe(III)–H<sub>2</sub>O<sub>2</sub> process (known as a Fenton-like reagent). Thus, the ferrous ion in Fenton's reagent can be replaced with the ferric ion [5].

Iron salts act as a catalyst for hydrogen peroxide decomposition, further reactions (13, 14) regenerate iron(II). It has been demonstrated that Fenton's reagent is able to destroy different phenols, nitrobenzene, and herbicides in water media as well as to reduce COD in municipal wastewater [17–20].

The usefulness of the Fe(II)/H<sub>2</sub>O<sub>2</sub> system as a potential oxidant for soil contaminants has also been investigated. It has been shown that PCP and trifluralin are extensively degraded while hexadecane and dieldrin are partially transformed in a soil suspension at acidic pH [21].

The use of Fe(II)/H<sub>2</sub>O<sub>2</sub> as an oxidant for wastewater treatment is attractive due to the facts that: (1) iron is a highly abundant and non-toxic element, and (2) hydrogen peroxide is easy to handle and environmentally benign.

Thus, the Fenton process is very effective for 'OH radicals generation; however, it involves consumption of one molecule of Fe<sup>2+</sup> for each 'OH radical produced, demanding a high concentration of Fe(II).

## Photochemical methods

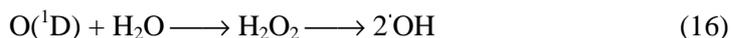
Conventional ozone or hydrogen peroxide oxidation of organic compounds does not completely oxidize organics to CO<sub>2</sub> and H<sub>2</sub>O in many cases [2]. In some reactions, the intermediate oxidation products remaining in the solution may be as toxic as or even more toxic than the initial compound. Completion of oxidation reactions, as well as oxidative destruction of compounds immune to unassisted ozone or H<sub>2</sub>O<sub>2</sub> oxidation, can be achieved by supplementing the reaction with UV radiation.

UV lamps must have a maximum radiation output at 254 nm for an efficient ozone photolysis. Many organic contaminants absorb UV energy in the range of 200–300 nm and decompose due to direct photolysis or become excited and more reactive with chemical oxidants. However, commercially available high-power UV lamps have an energy efficiency of only 15%. Solarchem Environmental Systems (Ontario, Canada) [5] has improved this efficiency to over 30%, with a substantial output below 240 nm, where many pollutants absorb UV directly. One 30 kW Solarchem lamp can replace 200 to 500 low-pressure lamps, resulting in systems that require much less maintenance and space.

In recent years, new, excimer lamps with emission wavelengths at 172 and 222 nm have been developed for direct photolysis of water, producing  $\cdot\text{OH}$  and  $\text{H}^{\cdot}$  radicals, which are very effective in UV-oxidation processes [22].

### Ozone–UV radiation (O<sub>3</sub>/UV)

Ozone readily absorbs UV radiation at 254 nm wavelength (the extinction coefficient  $\epsilon_{254\text{ nm}} = 3300\text{ M}^{-1}\text{ cm}^{-1}$ ) producing H<sub>2</sub>O<sub>2</sub> as an intermediate, which then decomposes to  $\cdot\text{OH}$  [5]:



Common low pressure mercury lamps generate over 80% of their UV energy at this wavelength. Photolysis of ozone therefore appears only to be an expensive way to make hydrogen peroxide that is subsequently photolyzed to  $\cdot\text{OH}$  radicals. Although photochemical cleavage of H<sub>2</sub>O<sub>2</sub> is conceptionally the simplest method for the production of hydroxyl radicals, the exceptionally low molecular absorptivity of H<sub>2</sub>O<sub>2</sub> at 254 nm ( $\epsilon_{254\text{ nm}} = 18.6\text{ M}^{-1}\text{ cm}^{-1}$ ) limits the  $\cdot\text{OH}$  yield in the solution. Table 3 shows that photolysis of ozone yields more radicals than the UV/H<sub>2</sub>O<sub>2</sub> process.

The absorptivity of H<sub>2</sub>O<sub>2</sub> can be increased by using UV lamps with output at lower wavelengths. In practice, the power requirement for UV lamps in the process of ozone photolysis is in *watts* range versus *kilowatts* for hydrogen peroxide photolysis.

**Table 3.** Formation of  $\cdot\text{OH}$  from photolysis of ozone and  $\text{H}_2\text{O}_2$  [2]

Oxidant	$\epsilon_{254\text{ nm}}$ , $\text{M}^{-1}\text{ cm}^{-1}$	Stoichiometry	$\cdot\text{OH}$ formed per incident photon
$\text{H}_2\text{O}_2$	20	$\text{H}_2\text{O}_2 \longrightarrow 2\cdot\text{OH}$	0.09
$\text{O}_3$	3300	$3\text{O}_3 \longrightarrow 2\cdot\text{OH}$	2.00

If water solutions contain organic compounds strongly absorbing UV light, then UV radiation usually does not give any additional effect to ozone because of the screening of ozone from the UV by optically active compounds such as phenol, 5-methylresorcinol, xylenols, etc. [23, 24]. Although phenolic compounds (phenol, *p*-cresol, 2,3-xylenol, 3,4-xylenol) are easily oxidizable by ozone, complete mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is uncommon. Using the  $\text{O}_3/\text{UV}$  system complete mineralization of organic compounds with a short molecular chain (glyoxal, glyoxylic acid, oxalic acid, formic acid) can be achieved according to Gurol & Vatistas [25] and Takahashi [26].

Peyton et al. [27] demonstrated the efficiency of  $\text{O}_3/\text{UV}$  system for  $\text{C}_2\text{Cl}_4$  elimination from water compared to ozonation and photolysis only.

#### Hydrogen peroxide–UV radiation ( $\text{H}_2\text{O}_2/\text{UV}$ )

The direct photolysis of hydrogen peroxide leads to the formation of  $\cdot\text{OH}$  radicals [5]:



Also  $\text{HO}_2^-$ , which is in an acid–base equilibrium with  $\text{H}_2\text{O}_2$ , absorbs the UV radiation of the wavelength 254 nm:



$\text{H}_2\text{O}_2/\text{UV}$  process has been successfully used for the destruction of chlorophenols [28] and other chlorinated compounds [29, 30]. Bischof et al. [31] showed that molecules of atrazine, desethylatrazine, and simazine can be mineralized finally to carbon dioxide within reasonable irradiation times in the presence of hydrogen peroxide. Sundström et al. [32] investigated the  $\text{H}_2\text{O}_2/\text{UV}$  process in detail for water disinfection purposes.

#### Ozone–hydrogen peroxide–UV radiation ( $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ )

The addition of  $\text{H}_2\text{O}_2$  to the  $\text{O}_3/\text{UV}$  process accelerates the decomposition of ozone, which results in an increased rate of  $\cdot\text{OH}$  generation [2]. In processes involving pollutants that are weak absorbers of UV radiation, it is more cost effective to add hydrogen peroxide externally at a reduced UV flux. If direct

photolysis of pollutants is not a major factor, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> should be considered as an alternative to photooxidation processes.

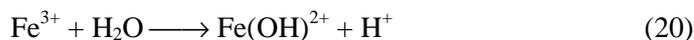
The capital and operating costs for the UV/O<sub>3</sub> and/or H<sub>2</sub>O<sub>2</sub> systems vary widely depending on the wastewater flow rate, types and concentrations of contaminants present, and the degree of removal required. Table 4 presents a comparison of the operating costs of various AOPs.

**Table 4.** Comparative operating costs of some AOPs [2]

Process	Cost of oxidant	Cost of UV
O <sub>3</sub> /UV	High	Medium
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	High	0
H <sub>2</sub> O <sub>2</sub> /UV	Medium	High
Photocatalytic oxidation	Very low	Medium to high

#### Photo-Fenton and Fenton-like systems

When Fe<sup>3+</sup> ions are added to the H<sub>2</sub>O<sub>2</sub>/UV process, the process is commonly called photo-Fenton-type oxidation. At pH 3, the Fe(OH)<sup>2+</sup> complex is formed because of the acidic environment:



When exposed to UV irradiation, the complex is further subjected to decomposition and will produce ·OH and Fe<sup>2+</sup> ions:



It is apparent that the photo-Fenton-type reaction relies heavily on the UV irradiation to initiate the generation of ·OH. If desired, organic pollutants can be mineralized completely with UV/visible irradiation. For example, Sun & Pignatello [33] showed that a number of herbicides and pesticides can be totally mineralized by the hv–Fe(III)/H<sub>2</sub>O<sub>2</sub> process, and the mineralization of chloro-phenol by the photo-Fenton process was demonstrated by Ruppert et al. [34].

The increased efficiency of Fenton/Fenton-like reagents with UV/visible irradiation is attributed to:

– *Photo-reduction of ferric ion*: irradiation of ferric ion (and/or ferric hydroxide) produces ferrous ion according to reaction 22. The ferrous ion produced reacts with hydrogen peroxide generating a second hydroxyl radical and ferric ion, and the cycle continues;

– *Efficient use of light quanta*: the absorption spectrum of hydrogen peroxide does not extend beyond 300 nm and has a low extinction coefficient beyond 250 nm. On the other hand, the absorption spectrum of ferric ion (and/or hydroxy ferric ions) extends to the near-UV/visible region and has a relatively large

extinction coefficient, thus enabling photo-oxidation and mineralization even by visible light.

As a photo-active catalyst ferrioxalate can be used [5]. Its photoreactivity was first discovered in 1833 and it was later suggested as a chemical actinometer for light intensity measurements. Irradiation of ferrioxalate in an acidic solution generates Fe(II) and carbon dioxide:



The quantum yield of Fe(II) formation is about 1.0–1.2, independent of irradiation wavelength in the range of 250–450 nm (UV/visible) and decreases with further increase in the irradiation wavelength. The photolysis of ferrioxalate produces ferrous (free or complexed with oxalate) ion, which in combination with hydrogen peroxide provides a continuous source of Fenton's reagent and hydroxyl radicals. The formation of hydroxyl radicals in the photolysis of ferrioxalate/H<sub>2</sub>O<sub>2</sub> mixtures was demonstrated by Zepp et al. [35] and Safarzadeh-Amiri et al. [36].

#### Photocatalytic oxidation (UV/TiO<sub>2</sub>)

The basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, often, but not exclusively, in the near UV spectrum. Under near UV irradiation a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation respectively. At the surface of the TiO<sub>2</sub> particle these may react with absorbed species [37]:



Holes possess an extremely positive oxidation potential and should thus be able to oxidize almost all chemicals. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible:



Numerous observations can indeed be explained by the intermediacy of OH<sup>•</sup>. However, due to the short life-time and high reactivity of this radical no experimental evidence for the formation of hydroxyl radicals has been given so far.

Authors of [38–40] found that there is no need to bubble the air through the reaction mixture as the performance does not depend on aeration. The absorption of oxygen by the surface of solution is sufficient for photocatalytic oxidation (PCO). This means that the absorption of oxygen by the liquid phase is not the stage limiting the process rate.

Titanium dioxide, both in the forms of anatase and rutile, is one of the most widely used metal oxides in industry. Its high refractive index in the visible range permits preparation of thin films, and thus its use as a pigment material. On the other hand, its use as a catalyst support or as a catalyst and photocatalyst itself is well known. Titanium dioxide acts not only as a catalyst support, but also interacts with the supported phase as a promoter [41]. Titanium dioxide (anatase) has an energy bandgap of 3.2 eV and can be activated by UV illumination with a wavelength up to 387.5 nm. At the ground level, solar irradiation starts at a wavelength of about 300 nm. Therefore only 4–5% of the solar energy reaching the surface of the earth could in principle be utilized as direct and diffused components when TiO<sub>2</sub> is used as a photocatalyst [42, 43].

Practically all kinds of toxic chemicals are degradable by PCO. Halogenated hydrocarbons are readily mineralized. Aromatic molecules are also quantitatively oxidized. Chlorinated phenols, biphenols, and even dioxins are also completely oxidized yielding CO<sub>2</sub> and HCl as final products. A proof that pertinent toxic by-products are not formed even in trace amounts is still not available in the literature. The mineralization of dyes, phthalates, DDT, and surfactants has been achieved.

The research activity over the world is mostly devoted to the PCO of wastewaters containing refractory and toxic organics. However, PCO and other AOPs may play an important role in dealing with today's challenging demand for new drinking water treatment technologies.

The pH value has a dominant effect on the photocatalytic reaction because many properties, such as the semiconductor's surface state, the flat-band potential, the dissociation of organic contaminant, are all strongly pH dependent. The solution matrix can influence the photocatalytic reaction rate of a particular compound in several ways [44]. Indeed, Weichgrebe [45] indicated that PCO is the best in terms of the process rate under the conditions of pH 3.0 (pH 3.0, 5.0, 7.0, and 11.0 were tested) when landfill leachate is treated by either H<sub>2</sub>O<sub>2</sub>/UV or TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV.

However, Way & Wan [46] found that acidic conditions with pH value less than 2 do not favour the PCO of phenol. The phenol degradation rate increases with increasing pH and has its maximum at pH ~6.5. As the pH value increases further, the removal percentage diminishes rapidly. However, when the pH value is above 11, the phenol oxidation rate will increase again.

Similar dependence of phenolics decomposition on the pH, although with some differences, was observed by Preis et al. [47]. In general, the optimum pH for the most effective PCO depends strongly on the character of the compound to be oxidized. Thus, aromatic amino compounds behave differently than phenolics [48].

Experiments with *tert*-butanol, added as an  $\cdot\text{OH}$  radical scavenger to the solutions of phenolic and aromatic amino compounds photocatalytically oxidized under different pH, showed that the radical oxidation mechanism prevails under alkaline medium conditions. Under acidic medium conditions,  $\cdot\text{OH}$  radicals seem not to play a significant role in PCO [49, 50].

### AOPs COMPARISON AND MODELLING

One thing is probably quite clear from the overview presented above – the most difficult problem in the practical application of AOPs is the choice or design of the most efficient oxidation system for the given pollutant(s). However, some considerations and suggestions are presented in the literature. Glaze et al. [51] conducted a bench scale study of the oxidation of concentrated nitrobenzene solutions using different AOPs: ozone at elevated pH,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2/\text{UV}$ , and  $\text{O}_3/\text{UV}$ . Advantages and disadvantages of each process were ascertained. This study showed the existence of severe limitations of the application of typical AOPs for the treatment of concentrated wastewaters. In contrast to the oxidation of some micro-pollutants in fairly pure water (groundwater, process water of semiconductors, etc.), the treatment of organic compounds in water at relatively high concentrations (>50 ppm) in complex matrices is energy and oxidant consuming. The most interesting result was that the oxidation rate of nitrobenzene by unassisted ozonation is almost the same as that achieved with  $\text{O}_3/\text{H}_2\text{O}_2$  or  $\text{O}_3/\text{UV}$  combination.

The UV and  $\text{UV}/\text{H}_2\text{O}_2$  systems were studied in detail by Tuhkanen [52]. Photolytic oxidation of naphthalene and PCP by the combined UV radiation and hydrogen peroxide treatment led to higher oxidation rates and shorter half lives of organic substances than mere photolysis. The  $\text{UV}/\text{H}_2\text{O}_2$  oxidation process seemed to involve the action of different radical species including not only hydroxyl radical but possibly also carbonate ion radicals. A kinetic model, where direct photolysis and both hydroxyl and carbonate ion radical reactions were considered, was used to simulate the effects of different parameters on the decomposition of the model organic compound, naphthalene.

Hirvonen et al. [30] studied the feasibility of  $\text{O}_3/\text{H}_2\text{O}_2$  and  $\text{UV}/\text{H}_2\text{O}_2$  treatments for the purification of groundwater contaminated with TCE and PCE (TeCE). Both methods showed rapid and extensive removal of the chlorinated ethylenes. Chloride ion measurements and by-product studies indicated a high level of mineralization. Owing to the partial stripping of TCE and PCE during ozonation treatment, the  $\text{UV}/\text{H}_2\text{O}_2$  system was selected for further studies.

Ruppert et al. [53] compared the photochemical mineralization of 4-chlorophenol with four different UV-assisted advanced oxidation methods. Under illumination with a 150 W high pressure mercury lamp, the TOC degradation efficiency for 4-chlorophenol had the following order: UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> > UV/O<sub>3</sub> > UV/H<sub>2</sub>O<sub>2</sub> = UV/TiO<sub>2</sub>. The combinations UV/TiO<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> were found to be less efficient for bleaching and degradation of the dye waste.

Advanced oxidation of polyaromatic hydrocarbons (PAHs) and its mathematical modelling was studied by Trapido et al. [54]. It was concluded that the order of the efficiency of AOPs for anthracene oxidation is the following: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> = O<sub>3</sub> > O<sub>3</sub>/UV > O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV > UV. Similar results were obtained for other PAHs [55], indicating that the 'OH radicals obviously play a minor role in anthracene destruction.

Oxidation of nitrophenols with ozone and ozone combined with hydrogen peroxide and/or UV radiation was also studied by Trapido et al. [56]. All these processes enabled to degrade nitrophenols. The combinations of ozone with UV or H<sub>2</sub>O<sub>2</sub> accelerated the degradation of nitrophenols and decreased the ozone specific consumption mainly at low pH values. The combination of ozone with UV radiation and hydrogen peroxide was found to be the most effective system for the degradation of nitrophenols: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV > O<sub>3</sub>(pH 9.5) > O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> > O<sub>3</sub>/UV > O<sub>3</sub> (pH 2.5). To achieve an increase in the reaction rate and a reduction of ozone consumption, the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV combination has to be used definitely at low pH values.

From the above given data it is quite clear that the efficiency of AOPs is strongly compound specific. Glaze et al. [1] tried to generalize the experience of different researchers giving the theoretical quantities of oxidants required to obtain a certain quantity of 'OH radicals (Table 5).

**Table 5.** Theoretical amount of oxidants and UV required for the formation of 'OH radicals in O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV systems [1]

System	Moles of O <sub>3</sub> /mole 'OH	Moles of UV photons, einsteins/mole 'OH	Moles of H <sub>2</sub> O <sub>2</sub> /mole 'OH
O <sub>3</sub> /OH <sup>-</sup>	1.5	0	0
O <sub>3</sub> /UV	1.5	0.5	0.5 (H <sub>2</sub> O <sub>2</sub> <i>in situ</i> )
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	1.0	0	0.5
H <sub>2</sub> O <sub>2</sub> /UV	0	0.5	0.5

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> combination gives a good yield of 'OH radicals, it is easy to adapt to existing ozonation facilities and should have the lowest relative process cost based on 'OH oxidation. Ozonation at elevated pH values is of limited use. Although the O<sub>3</sub>/UV combination seems difficult to implement on a large scale, it can be successfully used for lower flow rates etc.

In the last ten years several models of AOPs giving a better idea of the process mechanism have been presented. Glaze & Kang [57] described a kinetic

model of the  $O_3/H_2O_2$  process based on experiments with PCE as a model compound. The model takes into account the doses of ozone and hydrogen peroxide, mass transfer of ozone, and reactions of radical scavenging. Peyton et al. [27] presented a kinetic model of the  $O_3/UV$  process. The model takes into consideration the radiation flux, ozone concentration in the liquid phase, and the ozonation reaction rate constant.

A quite remarkable contribution to the modelling of different AOPs was made by Beltran et al. [58–63]. They presented interesting mathematical models of ozonation and advanced oxidation of PAHs [58–61], nitroaromatic compounds [62, 63], etc. in water and water solutions.

Mathematical models of advanced oxidation of PAHs and chlorophenols were also composed by Kallas et al. [64] and Hautaniemi et al. [65, 66]. In [64] mathematical models of the advanced oxidation of three PAHs (anthracene, phenanthrene, and pyrene) using  $O_3/H_2O_2$ ,  $O_3/UV$ ,  $O_3/H_2O_2/UV$ , and  $O_3$  (pH 9.5) are presented. The model of chemical reactions takes into consideration 31 possible reaction routes. Quantum yield as well as molecular ozone and hydroxyl radical reaction rate constants for PAHs were evaluated from experimental data. It was established that for the treatment of PAHs the role of AOPs is modest as the radical reaction rate constants have relatively low values, between  $10^6$  and  $10^8 M^{-1} s^{-1}$ .

In [65, 66] the mathematical models of advanced oxidation of three chlorophenols (2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol) in basic and acidic conditions were developed. Under the basic conditions (pH 9.5) even unassisted ozonation of chlorophenols proceeds so rapidly that no ozone can be detected in the liquid bulk, and in modelling it became necessary to account for the reactions in the liquid film. Hydroxyl radical reactions did not make any contribution to the oxidation rate of chlorophenols under basic conditions. In an acidic medium the oxidation mechanism is quite different. A model was developed to simulate the treatment of chlorophenols by  $O_3$  and  $O_3/UV$ . The degradation rate of chlorophenols was not enhanced by the addition of UV radiation compared to ozonation alone, i.e. oxidation at low pH values in both processes proceeds mainly through reactions with molecular ozone.

### **SOME EXAMPLES OF PRACTICAL APPLICATION OF AOPs**

Ozonation and its combinations with hydrogen peroxide and/or UV radiation are excellent treatment methods for different hazardous wastes. Full-scale ozone/UV systems were installed at Tinker Air Force Base (Oklahoma, USA) to treat metal complexed cyanides and refractory organics. In 1978 ozone treatment was installed at the Cadillac Motor Car Division of General Motors Corporation in Detroit, Michigan (USA). Since then the total cyanide levels in the effluent below 1 mg/L and greater than 99% ozone utilization in gas have been achieved consistently [1].

In the manufacture and processing of integrated circuits, water of very high purity is a necessity. Zmolek [67] described a water treatment system developed and installed at Bell Telephone Laboratories in 1973, which incorporates the use of ozone for the control of bacteria, which can easily plug the 0.2 micron filters and thus cause serious failure of circuit elements. Similar problems of killing bacteria are encountered in the pulp and paper industry. Korhonen & Tuhkanen [68] proved the advantages of ozone and ozone/hydrogen peroxide treatment for the control of microbiological growth in the white water system of the paper machine.

Ozone is also applied in full scale for the decoloration of textile industry wastewaters in several countries [69]. Before the plants are designed, a laboratory evaluation of the capability of ozone to decolorize the specific dyestuffs is needed.

Ozone together with GAC is a good choice for the solution of environmental problems in the petroleum industry as well. ARCO Products Company has been treating ca 1 million gallons of oily wastewater annually at its Richmond, CA (USA), petroleum product storage and transportation facility since 1991 [70]. This facility was so successful that the company had installed four additional ozone/GAC facilities by 1993.

Ozone, ozone/UV, and ozone/H<sub>2</sub>O<sub>2</sub> are able to reduce the acute toxicity of the effluents from the pulp and paper industry [71]. And what is the most important – ozone is effective at destructive oxidation of dibenzo-*p*-dioxin and dibenzofuran, which are precursors to their polychlorinated compounds. Ozonation of pulp prior chlorine bleaching reduces the formation of these toxic compounds significantly.

Wable et al. [72] described studies of ozone and ozone/H<sub>2</sub>O<sub>2</sub> for treating landfill leachates in France. In order to comply with new French regulations, landfill leachates must be treated before being discarded to the environment. Leitzke [73] discussed the application of chemical oxidation in combination with ozone and UV light to German landfill leachates pretreated biologically. Chemical oxidation is used to reduce the levels of volatile pollutants such as hydrocarbons, chlorinated hydrocarbons, sulphur compounds, etc. at 15–20 local treatment plants in Germany and Austria.

The UV/oxidation technology (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV system) has been applied successfully for the removal of volatile organic contaminants (VOC) (benzene, acetone, dichloroethane, tetrachloroethane, etc.) from groundwater in San Jose, CA (USA) [74]. Greater than 90% removal efficiencies were achieved for most VOC. During 1994, a UV/oxidation system was installed at the Milan Army Ammunition Plant (Milan, TN, USA) to treat holding ponds contaminated with explosive compounds (2,4,6-trinitrotoluene, 2,4- and 2,6-dinitrotoluenes, nitrobenzene, etc.) [75]. GAC filtration follows the UV/ozone oxidation step. In 1994, UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment was installed at the Bofors Nobel Superfund Site, located near Muskegon, MI (USA), for the decomposition of hazardous wastewaters containing benzene, toluene, chlorobenzene, tetrachloroethane, benzidine, etc. [76].

## CONCLUSIONS

If properly used, AOPs generally result in higher oxidation rates than ozone alone. However, they need to be evaluated for effectiveness, costs, and possible side effects. It should be noticed that AOPs need not be very effective for treating highly concentrated effluents with the concentrations of organics several hundreds up to 1000 mg C/L. From the chemical point of view, the effect of O<sub>3</sub>/UV is comparable to the system O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> if direct photolysis is negligible. When comparing the O<sub>3</sub>/UV and H<sub>2</sub>O<sub>2</sub>/UV systems, the stoichiometric yield of <sup>•</sup>OH is the greatest from the photolysis of H<sub>2</sub>O<sub>2</sub>, but the photolysis of ozone actually yields more <sup>•</sup>OH than that from H<sub>2</sub>O<sub>2</sub> because of the higher molar extinction coefficient of ozone compared to H<sub>2</sub>O<sub>2</sub>.

It is important to notice that this comparison is only theoretical. In reality, a high production of <sup>•</sup>OH can even lead to a lower reaction rate because the radicals recombine and are not useful for the oxidation process. Therefore, taking into consideration that the efficiency of AOPs is compound specific, the final choice of the AOP system can be made only after preliminary laboratory tests. In the general comparison the effects of different inorganic/organic compounds in the water were not considered.

For removing taste and odour and for the disinfection of drinking water, ozone alone is sufficient without any doubt. In the case of some micro-pollutants in water (pesticides, chlorinated organics, etc.) the combination O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, followed by an O<sub>3</sub>/UV system, is the most efficient and inexpensive technology for drinking water treatment plants. An advantage of the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process is that it does not require maintenance such as cleaning and replacement of the UV lamps, and the power requirements are usually lower. Treatment plants that already use ozone as a treatment step can easily add H<sub>2</sub>O<sub>2</sub> to increase the reaction rate.

Photocatalytic oxidation in water treatment has proved its efficiency at many pilot-scale applications. However, wide marketing of commercially available solar detoxification systems is obstructed by the general market situation: a new water treatment procedure has an opportunity to be implemented only when its cost is at least two-fold lower than the cost of a procedure currently in use.

There are still many research needs in the field of AOPs for water, wastewater, and polluted air treatment, including further R & D to provide:

- a better understanding of the mechanisms of candidate AOPs;
- measurements of the efficiency of candidate processes under controlled experimental conditions;
- realistic evaluations of the relative costs of candidate processes for selected treatment objectives versus other treatment processes such as WAO, SCWO (Supercritical Wet Air Oxidation), GAC adsorption, etc.;
- evaluation of by-products and their toxicity of candidate AOPs;
- reliability factors for candidate processes.

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## TÄIUSTATUD OKSÜDATSIOONIPROTSESSID – PRAEGUNE SEIS JA PERSPEKTIIVID

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Täiustatud oksüdatsiooniprotsessid (TOP) näiteks osooni, vesinikperoksiidi ja UV-kiirguse kombinatsioonide abil on tänapäeval arvestatav alternatiiv ohtlike jäätmete põletamisele, mille käigus emiteeritakse heitgaaside ja lendtuhaga kantserogeenseid dibensodioksiine ja/või dibensofuraane. TOP põhinevad osoonist 1,4 korda aktiivsemate hüdroksüülradikaalide ( $\text{OH}$ ) sihipärasel tootmisel töödeldavas keskkonnas. Õiges kohas ja õigesti rakendatuna tagavad TOP osoonimisest suurema keemilise oksüdatsiooni kiiruse, võimaldades saasteaineid mineraliseerida ning viia nende jääkkontsentratsiooni vees või heitvees 100–200 kuni 0,005 mg/l. Tuntumad TOP, mis on jõudnud ka praktikasse, põhinevad  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$  ja  $\text{H}_2\text{O}_2/\text{UV}$  kasutamisel. Esimesed kaks on oma efektiivsuselt täiesti võrreldavad juhul, kui otsese fotolüüsi tähtsus on tühine. Kui võrrelda esimest ja kolmandat, siis on vesinikperoksiidi madala ekstinktsioonikoeffitsiendi tõttu hüdroksüülradikaalide saagis palju suurem just osooni fotolüüsil. Tegelikuses aga ei tähenda suur radikaalide saagis alati protsessi efektiivsust, sest tihti toimub aktiivsete radikaalide rekombineerumine passiivsete osakeste tekkega. Seetõttu on väga oluline töödeldava vee ioonmaatriks. Viimase mõju selgitamine TOP efektiivsusele on ka üks selle valdkonna olulisemaid uurimisobjekte praegusajal.

TOP on selektiivsed, nende toime oleneb lähteaine keemilistest omadustest. TOP edukaks rakendamiseks vee, heitvee, saastatud pinnase ja heitgaaside töötlemisse on vaja kõigepealt tunduvalt laiendada vastavaid alusuuringuid, et võimalikult täpselt välja selgitada nende protsesside kulgemise reaktsioonimehhanisme, seejärel on vaja katsetada laboratoorsel ja pilootseadmel mitmeid TOP nn. kandidaatprotsesse. Kõigil uuritud juhtudel on vaja teha majanduslik analüüs ning võrrelda tulemusi alternatiivsete lahendustega (superkriitiline märgoksüdatsioon, adsorptsioon aktiivsoel jt.). Väga oluline on ka määrata kõigi katsetatud TOP puhul oksüdatsiooni vahe- ja lõppproduktide toksilisus. Alles pärast seda saab teha lõpliku otsuse ühe või teise TOP kasuks. Ei ole kahtlust selles, et keskkonnanõuete karmistumisega kogu maailmas kasvab nende protsesside osatähtsus lähiajal märgatavalt.