

APPLICATION OF ADVANCED OXIDATION PROCESSES (AOP) IN WATER TREATMENT



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ABSTRACT

Conventional oxidation processes are used in water treatment to disinfect water, to reduce toxins, odour and colour or to reduce manganese and iron levels in potable water. These processes may not destroy all toxins and have the potential to create dangerous disinfection by-products (DBPs). Advanced oxidation process (AOP) utilises the strong oxidising power of hydroxyl radicals that can reduce organic compounds to harmless end products such as carbon dioxide and water. For many water treatment plants this level of treatment is currently not deemed to be necessary to meet statutory requirements. However, this situation may change driven primarily by concerns over water quality arising from the retention and accumulation of recalcitrant organic compounds in water systems.

KEYWORDS

Advanced oxidation processes AOP, Water treatment, Wastewater treatment

1.0 INTRODUCTION

The topic of advanced oxidation has over the past 40 years, been subject of a large research output Comminellis (2008), counted 4500 Journal articles published between 2005 to 2007 alone. AOPs have been used extensively in industry such as textile dying for many decades and reliable equipment exists. In what might be one of the largest such schemes, the water factory WF21 in Orange County Cal injects treated wastewater (currently 378500m³/d) after MF-RO-AOP, into a major water supply aquifer.

Processes such as gravity settling, filtration, air stripping, or adsorption to activated carbon are separation processes that leave a waste stream to be treated and disposed. AOPs can be similar to denitrification (which produces nitrogen N₂ gas from nitrate), since AOPs offer the possibility of complete destruction – mineralization - to CO₂, H₂O and salts, or at least reduction/change in molecular structure such that toxicity is removed. The fragmented molecule or compound may then become biodegradable and biological treatment to CO₂ and biomass, can dispose of the rest.

Industries or locations using AOPs for the removal or reduction of degradation resistant (recalcitrant/refractory) compounds include places where petroleum products were stored or produced, textile dying, pulp and paper, explosives production and use, landfill leachate, slaughterhouse waste, hospital waste (e.g. destruction of prions), removal of pathogens and persistent endocrine disrupting chemicals, metal plating wastes, pesticides, heavy metals such as chromium, and arsenic. This large and growing range of mostly organic compounds includes those that start off with very small concentrations in water bodies but, because they are not broken down by conventional treatment plant and natural processes, persist in the environment and are recycled within the water cycle or accumulate within organisms becoming more concentrated and toxic as they move up the food chain.

The list includes compounds that must not enter a wastewater treatment plant i.e. toxic or inhibitory to bacteria, or that pass through the plant unchanged accumulating in the environment. Similarly there are compounds and organisms that must not leave a potable water treatment plant including algal toxins, disinfection resistant pathogens, toxic organics from the various raw water sources including from aquifers near current/former industrial sites and metal, odour and colour contaminants.

AOP is also of interest in general COD and sludge reduction. An MBR plant where some of the sludge is pumped through an AOP may reduce sludge treatment and handling costs significantly.

2.0 DISCUSSION

Chemists distinguish between conventional oxidation e.g., with chlorine, oxygen, ozone, or potassium permanganate and Advanced Oxidation Processes (AOPs) where for example; combinations of ozone (O₃), UV, and hydrogen peroxide (H₂O₂) are used.

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant) which has a higher affinity for electrons. These electron transfers result in the chemical transformation of both the oxidant and the reductant. Typically chemical species are produced that have lost their colour or odour forming capacity, or it is causing dissolved metals to form particles that can be filtered out. This chemically disruptive process will also destroy a range of pathogenic microorganisms.

In advanced oxidation processes AOPs the hydroxide radical $\bullet\text{OH}$ not the OH^- hydroxyl ion as in bases (the radical is also indicated OH^\bullet or OH' in the literature), is produced in a first step. This molecule has a very strong oxidizing and disrupting ability that may, depending on conditions, turn a complex (recalcitrant or refractory), organic molecule into CO₂ and H₂O i.e. lead to the mineralization or complete disappearance of the molecule.

The first reaction of $\bullet\text{OH}$ with many volatile organic compounds (VOCs) is the removal of a hydrogen atom, forming water and an alkyl radical ($\bullet\text{R}$). $\bullet\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \bullet\text{R}$
Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants, (both organic and inorganic), until stable oxidation products are formed.

Summarizing at this point; AOPs are reactions where first, hydroxyl radicals are produced, secondly, these radicals react with and destroy degradable organic and inorganic compounds. Typically methods such as UV, ozone O₃, Hydrogen peroxide H₂O₂, Fenton's and titanium dioxide TiO₂ are combined (synergistic effect) to increase $\bullet\text{OH}$ formation. Combining methods increases reaction rates 100 – 1000 times compared to using either ozone, H₂O₂ or UV alone. The ability of an oxidant to initiate chemical reactions is measured in terms of its oxidation potential, that is, its ability to disrupt, break up and so destroy molecules, as listed in Table 1.

Taking the simple compound methanol as an example, the equations Figure 1 below show how the molecule CH₃OH is broken up by $\bullet\text{OH}$ via intermediates to produce CO₂ gas and water H₂O. The process with other larger or more complex molecules is similar but not always completely understood to date.

Organic compound \longrightarrow Intermediates in this example:
 Aldehydes e.g. formaldehyde \longrightarrow CO_2 and H_2O
 Carboxylic acids e.g. formic acid

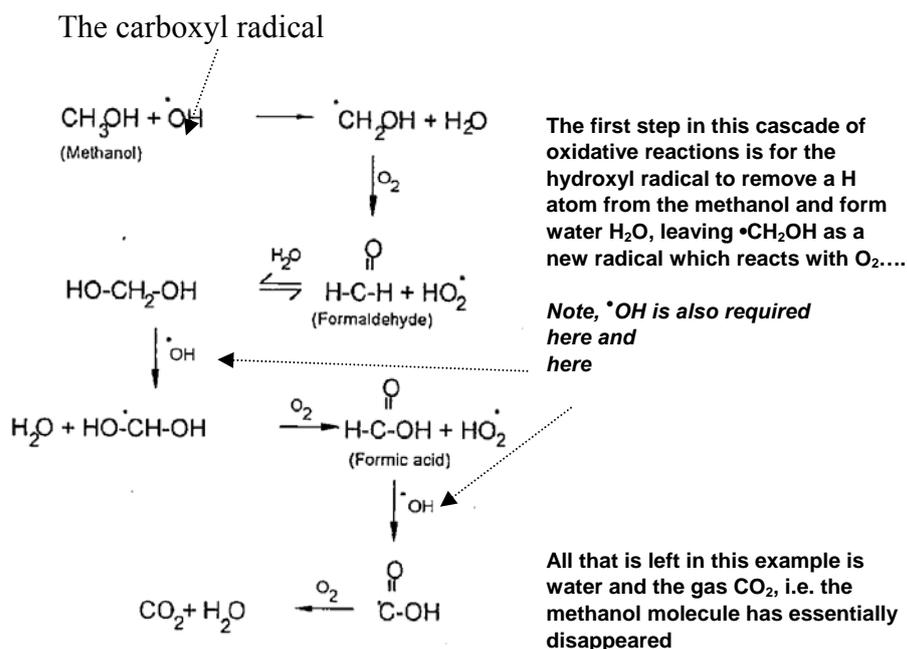


Figure 1: Using methanol as example for mineralization by AOP

Attack of the hydroxide radical on methanol in the presence of O_2 initiates a complex cascade of chemical reactions that requires a supply of $\bullet\text{OH}$ radicals and leads as in this example, to the disappearance of the contaminant. The issue of the possible production of intermediates in oxidation and AOP which may be more toxic than the original compound, if left un-oxidised, must always be considered. The production of intermediates may be indicated by a colour change or a change in pH. In theory all organic compounds can be mineralised completely by some method or other but, costs might be prohibitive.

AOPs effectiveness and efficiency depends greatly on the composition of the raw water or wastewater, the treatment combination chosen and careful fine-tuning. For example, the system works very successfully when a contaminant such as atrazine, 1-4 dioxane or NDMA, is removed from bore water, as happens in California (at different locations) where few alternative raw water sources exist.

Advantages of AOPs include removal of toxic/bio-degradation resistant molecules, reduced - or no waste, possibility of complete disinfection (sterilisation), no DBPs and very fast reaction rates. Lastly, the process can be batch or continuous and is amenable to automation.

Disadvantages of AOPs include costs for chemicals, plant and power, reduced efficiency if $\bullet\text{OH}$ sequestering molecules such as carbonate and bicarbonate are present - may need to control alkalinity, reduced efficiency from turbidity or UV absorbing compounds such as iron Fe or nitrate when UV is used, problems if toxic intermediate compounds are left over, and costs if excess O_3 or H_2O_2 have to be removed from the treated water.

Tables 1 and 2 below list AOP oxidation agents in the left hand column. In Table 1 they are arranged from weakest to strongest oxidising agent in the second and third columns.

Table 1: Common chemical/physical AOP technologies

Oxidising Agent From Weak  to  Strong	Relative Oxidising Potential (relative to Chlorine Cl₂ which is set to 1)	Oxidising Potential (EOP) V	AOP Methods/ technologies	Comments Advanced oxidation processes are those producing high levels of hydroxyl radicals. Usually a combination of two or more processes. React by removing H or adding OH to molecule.
UV <200nm UV at 254nm with O ₃ to form •OH			O ₃ +UV H ₂ O ₂ +UV H ₂ O ₂ +O ₃ +UV	Major drawback - require low turbidity and low concentration of UV absorbing chemicals. Usually UV not used alone in AOPs.
Oxygen O ₂	0.90	1.23		
Chlorine dioxide ClO ₂	0.93	1.27		
Chlorine Cl ₂	1.00	1.36		Oxidation of organic matter leads to disinfection by-product formation.
Hypochlorous acid HOCl	1.10	1.49		
Potassium Permanganate KMn ₄	1.24	1.67		Relatively expensive, used for iron Fe and manganese Mn oxidation.
Hydrogen Peroxide H ₂ O ₂	1.30	1.78	O ₃ +H ₂ O ₂ UV + H ₂ O ₂	Commonly used with UV and/or O ₃ , relatively safe and simple to use.
Ozone O ₃ Must be produced on site, with electrical discharge or with UV light	1.52	2.08	O ₃ /GAC O ₃ +Cat O ₃ +H ₂ O ₂ (less affected by water quality) or UV +O ₃ (greater yield of •OH)	Oxidises organic compounds selectively and partly. Used for disinfection, toxin, taste, odour, Fe/Mn removal. May generate •OH at elevated pH >8.5 but, for AOP usually used in combination with other agents such as UV/H ₂ O ₂ , get faster more complete oxidation.
Oxygen radical ½O ₂ or atomic oxygen O	1.78	2.42		Often a short life by-product in oxidation reactions.
Hydroxide Radical •OH	2.05	2.80		Aim of AOP is to produce high levels of available hydroxide radicals •OH, the reactions are not selective i.e. react rapidly with almost any compound and may lead to complete removal as CO ₂ , H ₂ O and salt – no waste or sludge to dispose, but such complete mineralisation may be too expensive.
Fluoride F ₂	2.25	3.06		Strongest oxidant but industrial use not possible.

Table 2: *AOP technologies (not all processes are listed here)*

AOP methods continued	Comments
Fenton's reagent (ferrous sulphate) +UV or +H ₂ O ₂	System generates hydroxyl radicals - used in trade waste and wastewater treatment. For example $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$
Cavitation by Ultrasound (Sonochemical oxidation)	Can be generated by ultra sound and occurs when liquid is subject to rapid changes of pressure. It is based on the formation and immediate implosion of liquid free zones - bubbles or cavities. Forces are sufficiently strong to cause wear on concrete or metal surfaces, e.g. pump impellers. Cavitation is normally avoided by appropriate design, but will produce $\bullet OH$ and other radicals which will cause oxidation reactions. Will generate temperatures of 2000-5000 ⁰ C and pressures > 500 atm. Not affected by turbidity, requires no chemicals.
Cavitation by Hydrodynamics	If water flows around objects under pressure and at high speed i.e. is forced through a nozzle - venturi or orifice plate, it creates areas of low pressure. This causes a bubble of vapour to erupt and grow explosively into vapour cavities, these tiny bubbles implode with forces large enough to split water molecules H ₂ O to produce $\bullet OH$ as noted above, which will attack and break apart organic and inorganic molecules. Systems have been combined for example; hydrodynamic with ultrasound (acoustic) cavitation or with other AOPs e.g. with UV.
Anodic oxidation or Electrochemical mineralisation (EM)	For example using boron doped diamond electrodes, high voltages generated produce $\bullet OH$ at the surface of the anode in water.
TiO ₂ + UV Relative oxidation power 2.35	Photocatalytic oxidation with titanium dioxide TiO ₂ , generates hydroxyl and other radicals, a very strong oxidant, used in wastewater treatment.
Other contaminant removal methods Wet air oxidation WAO Air stripping Resin sorption GAC adsorption Incineration of GAC Thermal catalytic oxidation of gas	WAO is used for high strength waste/COD reduction (soluble or suspended) at very high temperature and pressure (150-320 ⁰ C pres. 10-220bar) in systems such as the Zimpro process. Air stripping, resin sorption and GAC adsorption produce a phase change for the contaminant (s) that is, contaminants are not destroyed but taken out and moved to another carrier such as air or the GAC and the disposal problem remains. Incineration may generate toxic gases.

The table above provides a description of cavitation (see ABC Catalyst program Thu. 29 March 2012, on the destructive forces cavitation can generate), cavitation has the potential for reduction of COD and removal of persistent organics in trade waste, wastewater plant influent and sludge without use of chemicals and with 'relatively' simple equipment.

3.0 CONCLUSION

AOPs are used only in some locations in Australian municipal WTPs, part of the reason is that dam, river and bore waters are generally free of excessive levels of organic contaminants. Compared to North America and Europe there is little indirect recycling of treated wastewater. The situation will be reversed if another drought requires recycling of treated wastewater or if regulations are introduced that mandate greater reduction of chemical compounds including DBPs, in drinking water and in water discharged into sensitive environments. However, AOPs including cavitation may be of interest to wastewater treatment plant operators because costs for sludge treatment and deposition increase constantly and developments here hold the potential for possible cost reductions and process simplification.

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