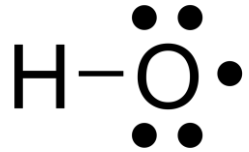
Advanced Oxidation Processes



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PASSION FOR CHEMISTRY

Definition

- Advanced oxidation processes (abbreviation: AOPs), in a broad sense, refers to a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals (·OH), Ozone or Hydrogen Peroxide/UV.
- If Oxidant generation is Electrochemical, the process is named EAOP.

.OH Radicals Are Very Strong Oxidizers

Oxidative species	Chemical formula	Oxidation potential (Volts)
Hydroxyl radical (1)	$OH^{\bullet}$	2.8
Ozone (1)	O_3	2.1
Peracetic acid (2)	CH_3CO_3H	1.8
Hydrogen peroxide (1)	H_2O_2	1.8
Hypochlorite ion (1)	OCl^-	1.7
Chlorine dioxide (1)	ClO_2	1.5
Hypochloric acid (3)	HOCl	1.5
Chlorine (3)	Cl_2	1.4
Oxygen (1)	O_2	1.2

[a] International Maritime Organization (2006).
[b] Madigan & Martinko, 2006.
[c] Wojtenko et al., 2002.

Typo: * Hypochlorous acid

Achievable Treatment Goals

- AOPs can reduce the concentration of contaminants from several-hundreds ppm to less than 5 ppb and therefore significantly bring COD and TOC down, which earned it the credit of "water treatment processes of the 21st century".
- AOP's breakdown organics into H2O and CO2 and sometimes other smaller molecules. The process is called mineralization.
- Some heavy metals can also be removed in the form of precipitated hydroxides $M(OH)_x$.

Specific Contaminants

- The AOP process is particularly useful for treating biologically toxic or non-biodegradable chemicals such as phenols, aromatics, pesticides, petroleum constituents, anti-biotics, various pharmaceuticals, EDC's PFAS, and volatile organic compounds in wastewater.
- TriChloroEthylene (TCE) and TetraChloroEthylene (PCE) are also destroyed by AOP.
- PFAS

Applications

- Oil and Gas Waste Water
- Tertiary Sewage Effluent Polishing
- Swimming Pools
- Pharmaceutical Waste Water
- Removal of Pesticides and Biocides
- Pulp and Paper Waste
- Hospital Waste Water
- Ground Water Remediation
- PFAS and PFOS

Conditions

- The reaction, using H_2O_2 for the formation of ·OH, is carried out in an acidic medium (2.5-4.5 pH) and a temperature between 10 °C - 50 °C, in a safe and efficient way, using optimized catalysts and hydrogen peroxide formulations.
- OH radicals are indiscrimate towards organics hence, it is useful to lower the TOC as much as possible before trying to remove the COD. For example, PureBlue Water use anion exchange to remove humics and fulvics from treated waste water BEFORE they try to remove POP's.
- Nitrates Absorb UV light and are converted to Nitrites

Ozone (O_3) + UV

- Ozone generation systems work by discharging a corona discharge into pure O2. Air used as feed needs to be concentrated as O2 otherwise toxic NOx are formed as a by-product.
- Ozone system suppliers:

  - https://www.prominent.co.uk/en/Products/Products/Disinfection-Systems-and-Oxidation-Systems/Ozone-Systems/pg-ozone-systems.html - Prominent
  - https://www.watertechnologies.com/products/disinfection-oxidation/ozonia-ozone-systems - Ozonia
  - https://www.denora.com/our-brands/Capital-Controls/Capital-Controls-Ozone-AOP.html DeNora

Hydrogen Peroxide (H_2O_2) + UV

- Hydrogen Peroxide can be dosed as a chemical or generated in-situ by electrolytic systems that convert demin Water + O2 into H2O2. Such an electrochemical AOP system has been tried and tested by https://www.hpnow.eu/ and shown to improve growth characteristics of plants in the agricultural industry.

Fenton’s Reagent

- A small concentration of ferrous ions catalyses the breakdown of H2O2 into Hydroxyl ions. This is classical chemistry.

- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} +$ **HO·** $+ OH^-$ (initiation of Fenton's reagent)
- $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$ (regeneration of Fe^{2+} catalyst)
- $H_2O_2 \rightarrow HO\cdot + HOO\cdot + H_2O$ (Self scavenging and decomposition of H_2O_2)

- The Fenton's reaction was first discovered by British chemical H.J.H. Fenton in the year 1894

TiO_2 Photocatalytic Oxidation

Photocatalytic oxidation with TiO_2:

$TiO_2 + UV \rightarrow e^- + h^+$ *(irradiation of the photocatalytic surface leads to an excited electron* (e^-) *and electron gap* (h^+)*)*

$Ti(IV) + H_2O \rightleftharpoons Ti(IV)\text{-}H_2O$ *(water adsorbs onto the catalyst surface)*

$Ti(IV)\text{-}H_2O + h^+ \rightleftharpoons Ti(IV)\text{-}\cdot OH + H^+$ *the highly reactive electron gap will react with water*

EAOP – Electrochemical AOP

- Boron Doped Diamond electrodes can generate Hydroxyl radicals at the anode that can oxidise recalcitrant organics
- Suppliers:
  - Clear Fox https://clearfox.com/clearfox-eo-diox/
  - Arvia https://arviatechnology.com/

Disadvantages

- Most prominently, the **cost** of AOPs is fairly high, since a continuous input of expensive chemical reagents is required to maintain the operation of most AOP systems. As a result of their very nature, AOPs require hydroxyl radicals and other reagents proportional to the quantity of contaminants to be removed.
- Some techniques require pre-treatment of wastewater to ensure reliable performance, which could be potentially costly and technically demanding. For instance, presence of bicarbonate ions (HCO_3^-) can appreciably reduce the concentration of ·OH due to scavenging processes that yield H_2O and a much less reactive species, $\cdot CO_3^-$. As a result, bicarbonate must be removed from the system or AOPs are compromised. Also TOC needs to be as low as possible to avoid the extra cost of removal of TOC.
- Note: Ozone can form Bromate which is toxic.

Materials/Piping

- Need SS piping. OH. Radicals will attach plastic piping.
- Need to use chemical resistant gaskets.

Suppliers/System Designers

- http://www.escouk.com/
- https://www.watertechnologies.com/products/disinfection-oxidation/aop-systems
- https://genesiswatertech.com/blog-post/how-gwt-aop-advanced-oxidation-systems-helped-companies-to-achieve-better-water-treatment-results/
- https://www.poolmagazine.com/features/products/aop-advanced-oxidation-process-what-it-is-how-it-works/
- https://pureblue.nl/en/
- https://www.lenntech.com/processes/pfas-removal-by-ozonation/advanced-oxidation.htm
- Trojan UV

Online Lectures

- https://www.youtube.com/watch?v=ni6NtEjrFLA
- https://www.youtube.com/watch?v=ZcuXU9dbnYc
- https://www.youtube.com/watch?v=uTLh0tdfiN4