OZONE-BASED ADVANCED OXIDATION PROCESSES

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Summary

Advanced oxidation processes (AOPs) are defined as the oxidation processes which generate very powerful, non-selective hydroxyl radicals that are utilized in water treatment. AOPs are comparatively new and intensively developing technique. Ozone-based AOPs are the processes where ozonation is applied simultaneously with UV-radiation, hydrogen peroxide, activated carbon, catalysts, ultrasound that rely primarily on oxidation with hydroxyl radicals. Such approach aims to improve the efficacy of ozonation: to enhance the oxidation rate of contaminants (and consequently ascertain higher COD and BOD reduction); to lower the ozone consumption; to improve the biodegradability of the by-products, etc. AOPs have high potential to degrade organic water contaminants that are not attacked by chlorine and ozone. Ozone-based AOPs have developed from the laboratory to full-scale applications and are successfully used for both the wastewater and drinking water treatment. None of the individual AOPs is universally applicable or highly effective for every kind of the wastewater. They are not to be employed whenever cheaper technologies are effective. However, they are indispensable for special water treatment needs.

1. Introduction

1.1. Advanced Oxidation Processes (AOPs)

The concept of “advanced oxidation processes” was established by Glaze and co-workers in 1987. AOPs were defined as the oxidation processes, which generate hydroxyl radicals in sufficient quantity to affect water treatment. The hydroxyl radical ($^{\bullet}OH$) is a powerful, non-selective chemical oxidant that acts very rapidly with most organic compounds. A free radical is not an ionic species but is formed from an equal cleavage of a two-electron bond.

Many systems are qualified under this broad definition of AOP. Most of these systems use a combination of strong oxidants, e.g. O_3 and H_2O_2, catalysts, e.g. transition metal ions or photocatalyst, and irradiation, e.g. ultraviolet (UV), ultrasound (US), or electron beam. Table 1 lists typical AOP systems.

Non-photochemical	**Photochemical**
O_3 at elevated pH (> 8.5)	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/US	O_3/H_2O_2/UV
O_3/AC (activated carbon)	H_2O_2/Fe^{2+}/UV (photo-Fenton)
O_3/catalyst	UV/TiO_2
Fe^{2+}/H_2O_2 (Fenton system)	H_2O_2/TiO_2/UV
electro-Fenton	O_2/TiO_2/UV
pulsed plasma	UV/US
ultrasound (US)	vacuum UV
H_2O_2/US	
microwave	
wet air oxidation	
supercritical water oxidation	

Table 1. List of typical AOP systems

Thus, AOPs may be sorted into three main groups: photocatalysis and hydrogen peroxide photolysis, the Fenton reaction based processes, and ozonation processes, such as O_3 at elevated pH, O_3/UV, O_3/H_2O_2, O_3/catalyst (CAT); O_3/GAC. The key difference between the ozonation and AOP processes is that the ozone process relies mainly on the direct oxidation with aqueous ozone while AOPs rely primarily on oxidation with hydroxyl radicals.

As stated above the aim of AOPs is to produce the hydroxyl radical in aqueous medium. As it can be seen from the Table 2 the hydroxyl radical is able to oxidize a wide range of organic compounds significantly faster (with reaction rate constants usually in order of 10^8-10^{10} M^{-1} s^{-1}) than ozone.

Compound	**O_3**	**$^{\bullet}OH$**
Chlorinated Alkenes	10^3 to 10^4	10^9 to 10^{11}
Phenols	10 to 10^4	10^9 to 10^{10}
N-containing Organics	10^{-2} to 10^2	10^8 to 10^{10}
Aromatics	1 to 10^2	10^8 to 10^{10}

Ketones	1	10^9 to 10^{10}
Alcohols	10^{-2} to 1	10^8 to 10^9

Table 2. Reaction Rate Constants (k, M^{-1} s^{-1}) of Ozone vs. Hydroxyl Radical

Hydroxyl radicals are secondary oxidants that can be produced from decomposed ozone. They are stronger oxidizing agents than ozone itself, as a matter of fact, they are the most reactive oxidants used in water treatment having a standard reduction potential of 2.8 V (see Table 3). Only fluorine gas has a higher electronegative oxidation potential, but it is not used in water treatment. The hydroxyl radicals´ concentration is elevated by accelerating ozone decomposition rate. Once a free radical reaction is initiated a large number of subsequent reactions occur making the prediction of all oxidation products extremely complicated. The oxidation rate is strongly dependent on radical concentration, which is affected by pH, presence of ions, temperature, type of the contaminant, and presence of radical scavengers. Most of the $^{\bullet}OH$ are produced from ozone in chain reaction where OH^- (high pH) or HO_2^- (hydrogen peroxide) act as initiator.

Oxidation species	**Oxidation potential (*V*)**
Fluorine	3.06
Hypochlorous Acid	1.49
Chlorine	1.36
Hydrogen peroxide	1.78
Ozone	2.07
Perhydroxyl radical	1.70
Hydroxyl radical	**2.80**
Atomic oxygen	2.42

Table 3. Relative oxidation power of some oxidizing species

Hydroxyl radicals have low selectivity towards species present in water. The ozone decomposition can be inhibited with the species that terminate the radical chain by reacting with hydroxyl radical. The inhibitor is also called hydroxyl radical scavenger as its presence limits or inhibits the action of free radicals on the target compound. The classic hydroxyl radical scavenger tert-butyl alcohol is not usually present in natural water and wastewater. However, hydroxyl radicals are consumed by competitive reactions with the water matrix that includes carbonate, bicarbonate ions and other species. Carbonate acts as radical scavenger since $CO_3^{-\bullet}$ is much less reactive than $OH^{\bullet}$:

$$HCO_3^- + OH^{\bullet} \rightarrow CO_3^{-\bullet} + H_2O \qquad (1)$$

$$CO_3^{2-} + OH^{\bullet} \rightarrow CO_3^{-\bullet} + OH^- \qquad (2)$$

The presence of radical scavengers in water matrix is in many cases cutting down the total efficacy of AOPs

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Biographical Sketch

Marina Trapido, was born in Tallinn, Estonia in June 9, 1952. She graduated from the Tallinn University of Technology in 1976 as a chemical engineer. During the beginning of the scientific career her interests were focused on the environmental aspects of carcinogenic substances and she obtained the Ph.D. in 1986 from N.Petrov's Institute of Oncology in Leningrad (USSR). During the next two decades she served as senior research scientist at the Institute of Chemistry (Estonian Academy of Sciences). In September 2005 she was appointed as the associate professor at the Department of Chemical Engineering Tallinn University of Technology. The areas of her scientific activities include environmental chemistry and technology, ozonation and advanced oxidation technologies, environmental protection, environmental pollution and monitoring, and chemical carcinogens in the environment. She was rewarded with Estonian Science Award in 2001 and published more than 175 papers.