



Hydroxyl Radical Based Advanced Oxidation Process

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DESCRIPTION

The Advanced Oxidation Process (AOP) was first proposed in the 1980 for the treatment of drinking water and has subsequently been extensively studied for the treatment of different types of wastewater. During AOP wastewater treatment, hydroxyl radicals ($\text{OH}\cdot$) or sulphates ($\text{SO}_4^{\cdot-}$) are generated in sufficient quantities to remove refractory organic matter, traceable organic contaminants, or other contaminants, or certain inorganic contamination to increase the biodegradability of wastewater during pre-treatment prior to treat upon a biological treatment. In general, the effectiveness of treatment depends strongly on type of AOP selected, the physical and chemical properties of the target pollutants, and the operating conditions. It should be noted that other mechanisms, other than oxidation based on hydroxyl radicals or sulphates, may interfere in AOP treatment and contribute to the reduction of target pollutants. In particular, recent advances in AOP treatment of landfill leachate, as well as enhanced oxidation of wastewater organic matter (EfOM) in Biologically Treated Secondary Wastewater (BTSE) for water reuse.

Ozone-based PDO

Ozone (O_3) is a strong oxidant with an oxidation potential of 2.07 V relative to SCE. However, the direct oxidation of O_3 is a selective reaction, with a typical reaction rate constant of $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, where O_3 reacts preferentially with other compounds. Under certain conditions, $\text{OH}\cdot$ is generated from O_3 to initiate indiscriminate oxidation (indirect mechanism). Various detailed mechanisms have been proposed to explain the complication of $\text{OH}\cdot$. In the presence of other oxidizing or irradiating agents, the $\text{OH}\cdot$ yield can be significantly improved. For example, in the so-called perozone ($\text{O}_3/\text{H}_2\text{O}_2$) system, O_3 decomposition and $\text{OH}\cdot$ production are enhanced by the hydroperoxide (HO_2) generated from the decomposition of H_2O_2 . In O_3 /ultraviolet (UV) irradiation, H_2O_2 is produced as an additional oxidant mainly by O_3 photolysis. Accordingly, $\text{OH}\cdot$ can be generated, at minimum, by three pathways: Ozonation; $\text{O}_3/\text{H}_2\text{O}_2$; and The photolysis of H_2O_2 .

UV-based AOP

The hydroxyl radicals can be initiated by photons in the presence of a catalyst or oxidant. The most common catalyst is titanium dioxide (TiO_2), and RO-type semiconductor. The excited TiO_2 particles generate positive holes in the valence band ($h\nu^{+vb}$) with oxidizing capacitance and negative electrons on the conduction band (e^{-cb}) with reduced capacitance, as follows:

With the reactions of OH , H_2O and $\text{O}_2\cdot$ on the surface of TiO_2 , these holes and electrons can form additional hydroxyl radicals. In the presence of oxidizing agents such as H_2O_2 or O_3 , additional $\text{OH}\cdot$ can be generated by UV irradiation. For example, one molecule of H_2O_2 is cleaved by UV irradiation to produce two $\text{OH}\cdot$. Furthermore, at wavelengths below 242 nm, $\text{OH}\cdot$ can also be produced by photolysis of H_2O .

Among these metals that are able to activate H_2O_2 and produce hydroxyl radicals in water, iron is the most frequently used metal in Fenton process; H_2O_2 reacts with Fe^{2+} to generate strong reactive species. The reactive species produced are traditionally recognized as hydroxyl radicals, though other substances such as ferryl ions are proposed. The classical Fenton radical mechanisms primarily involve the following reactions:

$\text{OH}\cdot$ is generated through electron transfer. However, the $\text{OH}\cdot$ generated can be recovered with Fenton's reagents. Therefore, the optimal molar ratio of ferric ion to hydrogen peroxide must be determined experimentally to minimize unwanted garbage recovery. Although this indicates that the generated Fe^{3+} can be reduced to Fe^{2+} , iron cannot be a catalyst in the Fenton system because the rate constant in is the order of magnitude lower in the equation. Therefore, Fe^{3+} forms iron slurry under typical wastewater and water treatment conditions. Waste sludge must be treated separately, increasing treatment complexity and operating costs of the generation of hydroxyl radicals during the Fenton reaction and it is the most effective in acidic pH condition. As a result, the application of Fenton reaction for wastewater treatment is restricted in practice. Based on the classical Fenton treatment scheme, three modified Fenton

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processes are proposed, including the Fenton-like system, photo-Fenton system, and electro-Fenton system.

In the Fenton-like reaction, Fe^{2+} is replaced by ferric ion (Fe^{3+}) namely the series of reactions in the Fenton system are initiated from the Fenton-like system, rather than the traditional Fenton treatment. In the photo-Fenton reaction, UV irradiation is

applied with the traditional Fenton system with a major purpose of enhancing the UV induced reduction of dissolved Fe^{3+} to Fe^{2+} . In the electro-Fenton reaction, either or both of the Fenton reagents may be generated through electrochemical methods.