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Advanced Oxidation Processes for Water Treatment

The contamination of fresh water supplies and growing demands for clean drinking water pose a serious threat to mankind and the planet Earth. Currently, more than one billion people do not have access to clean water, and within the next 10–15 years, two-thirds of the global population will face severe water shortages. The presence of pathogens and toxins in water causes more than two million deaths annually, mostly children under the age of 5.^{1,2} Traditional methods employing chlorination and ozone have been effectively employed for disinfection in municipal water treatment, but there are increasing concerns over the formation of hazardous by-products. Chlorination can lead to the formation of a variety of carcinogenic disinfection byproducts (DBPs), while ozone can be expensive and lead to the formation of highly toxic bromate.^{3,4} Disinfection is generally not effective for treatment of the variety of industrial pollutants and naturally occurring toxins often present in today's freshwater supplies. Growth in the global population, the diminishing supply of clean water, heightened environmental concerns, and the strong link between water quality and human health require the identification and employment of effective sustainable water treatments to meet the urgent global need for clean water.⁵

Advanced oxidation processes (AOPs) have shown tremendous promise in water purification and treatment, including for the destruction of naturally occurring toxins, contaminants of emerging concern, pesticides, and other deleterious contaminants. One of the first references to AOPs was by Glaze in 1987 as processes that “involve the generation of hydroxyl radicals in sufficient quantity to affect water purification”.⁶ The definition and development of AOPs have evolved since the 1990s and include a variety of methods for generating hydroxyl radical and other reactive oxygen species including superoxide anion radical, hydrogen peroxide, and singlet oxygen. However, hydroxyl radical is still the species most commonly tied to the effectiveness of AOPs. Most organic compounds react with hydroxyl radical by addition or hydrogen abstraction pathways to form a carbon-centered radical. The resulting carbon-centered radical reacts with molecular oxygen to form a peroxy radical that undergoes subsequent reactions, ultimately producing a host of oxidation products, that is, ketones, aldehydes, and alcohols.⁷ Hydroxyl radical can also abstract an electron from electron-rich substrates to form a radical cation, which in aqueous media is readily hydrolyzed, ultimately leading to an oxidized product. The oxidation products are often less toxic and more susceptible to bioremediation.

AOPs include UV/O₃, UV/H₂O₂, Fenton, photo-Fenton, nonthermal plasmas, sonolysis, photocatalysis, radiolysis, and supercritical water oxidation processes. Many AOPs are initiated by radiolysis, sonolysis, or photolysis. Radiolysis and sonolysis of aqueous media can generate hydroxyl radicals in the absence of chemical oxidants, whereas photochemical methods such as photo-Fenton type processes⁸ typically require the presence of a precursor or catalyst to produce hydroxyl radical. Sonolysis involves production and localization of hydroxyl radical at or near a gas–liquid interface,⁹ while

radiolysis of aqueous media results in the generation of hydroxyl radical, which is considered homogeneous for the time scales involved in water treatment.¹⁰ Operating costs are one of the primary challenges for the large-scale water treatment using sonolysis, while the cost of building large-scale electron beams is often a limiting economic factor for radiolytic treatments.

Fenton and photo-Fenton type processes have also received significant attention for water treatment applications.^{8,11} The consumption of Fe(II) and the need for disposing of the generated iron sludge during Fenton type advanced oxidation processes have limited its application for water treatment. These limitations can be overcome by photo-Fenton processes that effectively employ solar irradiation to regenerate the Fe(II) species, leading to hydroxyl radical production. The Perspective contributed by Wang, Chen, Ma, and Zhao in this issue of *The Journal of Physical Chemistry Letters* unravels important fundamental aspects of the redox cycling of ferrioxalate complexes and the effects of dissolved organic matter (DOM) under solar irradiation.⁸ The study is especially relevant to iron-mediated advanced oxidation processes, the environmental cycling of Fe(II)/Fe(III), and the fate of organic pollutants. The results presented in the Perspective establish the primary photochemical steps and the sensitivity of the subsequent redox processes to the nature of the ligand complexing iron. Dicarboxylic acids, oxalate and malonate, form strong complexes with Fe(III) and have strong light absorbances but interestingly exhibit vastly different photochemically initiated redox processes. Photolysis of the oxalate complexes generates a reductive CO₂^{•-} species, which can reduce another Fe(III), enhancing the regeneration of the Fe(II) critical to Fenton processes. The unique photochemistry of the malonate complex leads to the formation of two radical species, •CH₂CO₂H formed during photolysis via decarboxylation of the malonate and hydroxyl radical produced by photodissociation of Fe(III)(OH)²⁺ species. Other mono- and dicarboxylate ligands compete for hydroxyl radicals, thus inhibiting oxidation of Fe(II). DOM typically possesses polycarboxylate functionalities, which can form iron complexes that are susceptible to direct photolysis and can initiate photosensitized reactions. The paper demonstrates that the redox cycling of Fe(II)/Fe(III) and the photochemical processes associated with DOM can generate reactive radical species attractive for environmental remediation.

UV TiO₂ photocatalysis, a heterogeneous type AOP, has been extensively studied for solar energy conversion and purification of water and air. (See Table 1 for recent articles from *J. Phys. Chem. Lett.*) The generation of hydroxyl radicals by UV TiO₂ photocatalysis for water treatment occurs at the liquid–solid interface, and the subsequent hydroxyl radical reactions are subject to heterogeneous reaction dynamics. The primary drawbacks of TiO₂ photocatalysis have been the

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Table 1. Recent *J. Phys. Chem. Lett.* Articles on Photocatalysis

	reference	DOI
1	Rajeshwar, K. Solar Energy Conversion and Environmental Remediation Using Inorganic Semiconductor–Liquid Interfaces: The Road Traveled and Way Forward. <i>J. Phys. Chem. Lett.</i> 2011 , 2, 1301–1309.	10.1021/jz200396h
2	Serpone, N.; Emeline, A. V. Semiconductor Photocatalysis — Past, Present and Future Outlook. <i>J. Phys. Chem. Lett.</i> 2012 , 3, 673–677.	10.1021/jz300071j
3	Teoh, W. Y.; Scott, J. A.; Amal, R. Progress in Heterogeneous Photocatalysis: From Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors. <i>J. Phys. Chem. Lett.</i> 2012 , 3, 629–639.	10.1021/jz300064e
4	Ng, Y. N.; Lightcap, I. V.; Goodwin, K.; Matsumura, M.; Kamat, P. V. To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO ₂ Nanostructured Films? <i>J. Phys. Chem. Lett.</i> 2010 , 1, 2222–2227.	10.1021/jz100728z

requirement of UV light and low quantum yields. These limitations have spurred the development of a variety of visible-light-activated (VLA) materials, sensitized processes, and semiconductor composites. VLA TiO₂ processes appear to involve more selective oxidative species but may not be as effective for general water purification processes.

The basis for the use of AOPs for the remediation of organic and inorganic toxins lies in the fundamental reactions of reactive oxygen species. While kinetic parameters and reaction pathways have been determined for the aqueous-based free-radical-mediated destruction of numerous problematic pollutants, even simple organic compounds can involve complex reaction pathways and product mixtures. The generation of hydroxyl radical by various homogeneous and heterogeneous AOPs can also involve different reaction dynamics and lead to significantly different reaction pathways. A more complete understanding of structure–reactivity relationships for classes or groups of compounds for individual treatment processes, based on kinetic data and measured product distributions, is critical for the identification of an appropriate AOP. In addition to these fundamental aspects, the influences of water quality and economic factors need to be considered for the implementation of a process with specific treatment objectives. Major challenges for the broader application of AOPs include further development of the fundamental understanding of the reaction pathways and dynamics and engineering advancements in the materials and equipment to make these processes more energy-sustainable.

Note: We provide a very broad overview of the topic with a limited number of references to recent examples of relevant contributions. Many important topics and contributors have been left out or are condensed due to space constraints.

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