

From the Editor's Desk**Persistent Organic Pollutants in Water and Wastewater and their treatment by Advanced Oxidation Processes****Taicheng An**

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Water is vital for life. Ideally, it should be clear, colourless and well aerated, with no unpalatable taste or odour and should not contain suspended matter and harmful chemical substances. But it becomes very dangerous when it is contaminated by toxic organic substances.

Among the organic pollutants, persistent organic pollutants (POPs) are one kind of the refractory organic pollutants. POPs are chemical substances which persist in the environment, remain intact in the environment for long periods and become widely distributed geographically. They can bioaccumulate in the fatty tissue of living organisms through the food chain and pose a risk of causing adverse effects to human health and the environment. The safe drinking water is now globally one of the most serious challenges, one reason is that increasing public attention has been paid to the potential health and environmental problems of POPs in water; another is that water is becoming more critical commodity and recourse around the world.

It is well known that certain bacterium or bacterial consortiums are able to consume organic pollutants. Many of the microbial species have been investigated to degrade organic pollutants. With recent advances in biomolecular engineering, the bioremediation of organic pollutants using genetically modified microorganisms has become a rapidly growing area of research for environmental protection. Phytoremediation is a newly evolving field of science and technology that uses plants to clean-up polluted water. It is the use of plants to extract, sequester, and/or detoxify pollutants. The important aspect of this technology is that it can completely mineralize organic pollutants into relatively non-toxic constituents, such as carbon dioxide, nitrate, chlorine and ammonia. But one of the important drawbacks is that biological technology requires long residence times.

The destruction of toxic biologically recalcitrant pollutants also uses other conventional non biological technologies. These technologies

consist mainly of phase separation techniques (adsorption processes, stripping techniques). Obviously these methods based on phase separation techniques, do not give complete solution to the problem of pollutant abatement, in that phase separation is realised with the consequent pollution problem of the final disposal.

In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional detoxification processes. Large research efforts were focused on alternative remediation strategies that can effectively clean water and wastewater contaminated by POPs. Among the technologies available, a special class of oxidation techniques defined as advanced oxidation processes (AOPs) which usually operate at or near ambient temperature and pressure is the most promising technology and has been given special attention in the last decade. AOPs are processes that rely on the generation of highly reactive hydroxyl radical (OH^\bullet) as the main oxidative species for the potential of completely destroying and converting organic contaminants to harmless substances. The hydroxyl radical can be formed by a number of methods in aqueous systems:

H_2O_2 is a strong oxidant and its application in the treatment of various organic pollutants is well established. Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds, because of low rates of reaction at reasonable H_2O_2 concentrations. Thus, it must be combined with UV light, salts of particular metals or ozone to produce the desired degradation results.

$\text{UV}/\text{H}_2\text{O}_2$ is a process where the hydrogen peroxide is directly photolyzed with UV light having wavelengths smaller than 280 nm to the formation of OH^\bullet . It has been successfully used for the destruction of many refractory organic compounds. But the major drawback of this process is the small molar extinction coefficient of H_2O_2 , only a relative small fraction of incident light is therefore exploited in

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particular in the cases where organic substrates will act as inner filters.

Among the various known AOPs, the Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is particularly attractive for the degradation of highly toxic and/or nonbiodegradable compounds. This reaction is based on an electron transfer between H_2O_2 and a metal acting as a homogeneous catalyst. By far, the most common of these ones is iron. This process uses a combination of H_2O_2 and ferrous ions (Fe^{2+}). It causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants. The process may reduce the toxicity, improve biodegradability of the organics, or remove odour and colour. What is more, it can frequently lead to complete mineralization of the pollutant.

Ozone is a powerful oxidant with a standard redox potential of 2.07 V and it can react with many kinds of organic molecules in solution both directly and indirectly via its aqueous-phase degradation products such as the hydroperoxyl and hydroxyl radicals. However, many studies showed that some sorts of refractory compounds, such as TNT, are resistant to direct reaction with molecular ozone. Therefore, the combination technologies between ozone with other methods were proposed in order to enhance organic compound mineralization with respect to the ozone process alone.

UV/ O_3 process is an advanced water treatment method for the effective destruction of POPs in water. This oxidation process is more complex than the other ones, since hydroxyl radical is produced through different reaction pathway. Basically, ozone readily absorbs UV radiation at 254 nm wavelength producing H_2O_2 as an intermediate, which then decomposes to OH. The system has the chemical behaviour of both $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{UV}$ systems.

Ultrasonic treatment of water is based on the use of ultrasound at low to medium frequency and high-energy to destruct organic pollutants. The chemical effects of ultrasound have been explained in terms of reactions occurring inside at the interface, or at some distance away from cavitating gas bubbles. In the interior of a collapsing bubble, extreme but transient conditions are known to exist. The consequences of these extreme conditions are the cleavage of dioxygen and water molecules to produce active

species capable of attacking the organic compounds in water.

Photocatalysis is the photo-excitation of a semiconductor as a result of the absorption of UV radiation, often, but not exclusively, in the near UV spectrum. Under near UV irradiation a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes. These charge carriers are able to induce reduction or oxidation respectively. In this category, TiO_2 is almost, exclusively used as photocatalyst, due to its low photocorrosion.

There are many inherent problems in using the TiO_2 particle suspensions for toxic organic degradation. These include the difficulty of separating the photocatalyst from the water; the overall reaction was limited by the availability of oxygen; the quantum efficiency of TiO_2 is very low due to the rapid recombination of photoelectrons and photoholes.

In an effort to increase the photocatalytic efficiency of semiconductor for degrading undesirable organics in aqueous solution, the concept of the potential bias is also extended to nanoparticle semiconductor photocatalysis and a great deal of effort has simultaneously been devoted to develop the technology of photoelectrochemical decontamination for organic wastewater. Photoelectrochemical technology with anode bias appears to be a newly emerging research front of photocatalytic degradation of organic pollutants and many academic interests have been focused in this area to decontaminate various toxic organic contaminants in wastewater because the applied cell voltage can greatly accelerate the separation and suppress the recombination of photogenerated electrons and holes. In addition, the dependence of overall photooxidation rate on the reduction rate of the electron acceptor (e.g. O_2) is eliminated. The most significant advantage of this technology is that photocurrent/charge obtained from photoelectrocatalysis process can be directly used to quantify the kinetic, thermodynamic and the degree/extent of degradation. Recent studies have repeatedly confirmed that the external electric field could greatly enhance photocatalytic efficiency, which is well known as an electric field enhancement effect.

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