



Study of Advanced Oxidation Processes, Mechanisms and applicability

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Abstract : Hazardous organic waste, widely spread in water by industrial, military and domestic sources, is an emerging issue. Advanced Oxidation Processes (AOPs) are efficient methods to remove organic contamination not degradable by means of biological processes. AOPs are a set of processes involving the production of very reactive oxygen species able to destroy a wide

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range of organic compounds. AOPs are driven by external energy sources such as electric power, ultraviolet radiation (UV) or solar light, so these processes are often more expensive than conventional biological wastewater treatment. Moreover, AOPs can be applied for the disinfection of water, air and for remediation of contaminated soils.

Introduction

Advanced Oxidation Processes (AOPs) refer to a set of oxidative water treatments that can be used to treat toxic effluents at industrial level, hospitals and wastewater treatment plants. AOPs are successful to transform toxic organic compounds (e.g. drugs, pesticides, endocrine disruptors etc.) into biodegradable substances. AOPs in general are cheap to install but involve high operating costs due to the input of chemicals and energy required (COMINELIS et al. 2008). To limit the costs, AOPs are often used as pre-treatment combined with biologic treatment (PULGARIN et al. 1999). Advanced oxidation was recently also used as quaternary treatment or a polishing step to remove micro-pollutants from the effluents of municipal wastewater treatment plants and for the disinfection of water. The combination of several AOPs is an efficient way to increase pollutant removal and reduce costs.

Examples of AOPs

Many methods are classified under the broad definition of AOPs. The table shows some of the most studied processes. Advanced oxidation generally uses strong oxidising agents like hydrogen

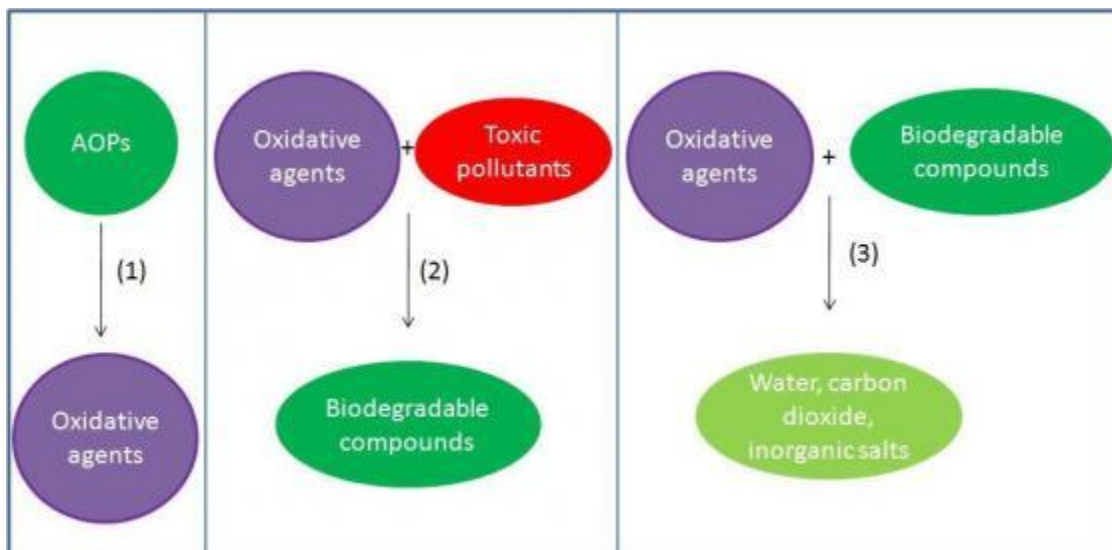


peroxide (H₂O₂) or ozone (O₃), catalysts (iron ions, electrodes, metal oxides) and irradiation (UV light, solar light, ultrasounds) separately or in combination under mild conditions (low temperature and pressure). Among different available AOPs, those driven by light seem to be the most popular technologies for wastewater treatment as shown by the large amount of data available in the literature (STASINAKIS 2008). Solar AOPs are particularly attractive due to the abundance of solar light in regions where water scarcity is high and due to their relatively low costs and high efficiencies.

AOP Mechanism

Advanced oxidation involves several steps schematised in the figure below and explained as follows:

- Formation of strong oxidants (e.g. hydroxyl radicals).
- Reaction of these oxidants with organic compounds in the water (KOMMINENI et al. 2008) producing biodegradable intermediates.
- Reaction of biodegradable intermediates with oxidants referred to as mineralisation (i.e. production of water, carbon dioxide and inorganic salts).



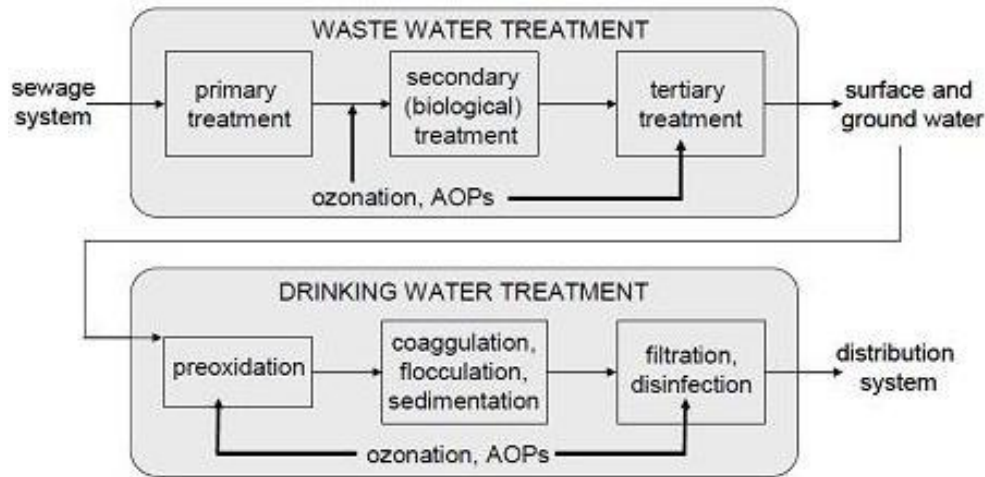
Main *steps* involved in an AOPs treatment of *wastewater* containing toxic organic compounds. Source: MAZILLE (2011)



Strategies to Implement AOPs

The costs of AOPs are relatively high and directly related to the efficiency and operational time of the processes. It is therefore worth optimising implementation of AOPs at the right place to limit costs. Several strategies were found to achieve this:

- Simultaneous application of different AOPs promotes the rates of organics oxidation. Typical examples include UV/H₂O₂, UV/H₂O₂/TiO₂, UV/Fenton and Ultrasound/UV/TiO₂, among others. These types of combinations may lead to synergetic effects when treatment efficiencies are greater than the sum of efficiencies that could be achieved by the individual treatments alone.
- Sequential application of various AOPs can treat effluents containing a mixture of organics. This approach is useful when the compounds in the mixture present different levels of reactivity towards different AOPs.
- Application of separation treatment prior to AOP treatment to transfer pollutants to another phase so that they can be treated more easily. Such separation treatment includes stripping, coagulation-flocculation, sedimentation, filtration, adsorption etc.
- AOPs can be applied in pre-treatment stage to enhance biodegradability and to reduce toxicity followed by biological post-treatment. This approach is based on the fact that biological treatment is perhaps less costly and more environmentally friendly than other destructive treatments and that complete mineralisation by AOPs incurs excessive treatment costs.



Possible applications of ozonation and AOPs in wastewater and drinking water treatment.

Source: PETROVIC et al. (2011)

AOPs can be installed at different stages of waste (and also drinking) water treatment plants depending on influent composition and desired effluent quality. AOPs can be installed either as tertiary treatment after the biological (secondary) treatment of wastewater, or as pre-treatment stage in order to enhance the biodegradability of trace organic contaminants (PETROVIC et al. 2011).

Applicability

AOPs have a wide range of applications such as air (odour elimination, purification), soil (remediation) and water decontamination. In water, these processes have the ability to destroy organic pollutants but they can also be adapted to the removal of inorganic metals. Furthermore AOPs are successful to inactivate bacteria, viruses etc. Different kinds of water are therefore suitable for an AOP treatment: for example industrial wastewater containing toxic compounds can be treated by solar photo-Fenton; surface or ground water can be disinfected by means of improved solar water disinfection by adding H₂O₂ (see also H₂O₂ and SODIS); both bacteria in drinking water plants or micro-pollutants in sewage systems can be degraded using ozonation; Dissolved arsenic can be removed from water by co-precipitation by means of simple methods (GENORI et al. 2009) in presence of iron (see also arsenic removal technologies).



Advantages

- Destroys toxic organic compounds without pollution transfer to another phase
- Very efficient to treat almost all organic pollutants and remove some toxic metals
- Works also for water disinfection
- Cheap to install
- Adaptable to small scales in developing countries

Disadvantages

- Relatively high operation costs due to chemicals and/or energy input
- Formation of oxidation intermediates potentially toxic
- Engineers are required for the design and often also for operation
- Emerging technologies (still a lot of research is required)

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The Limitations Of Crystal Field Theory

A scientist named Bethe proposed crystal field theory to explain the bonding nature in ionic crystals. Later on this theory was applied by other scientists to account the magnetic properties of transition metal ions and their complexes. Crystal field theory received considerable support from the coordination chemists and hence it replaced the valence bond theory. Crystal field theory is based on the assumption that the interaction between the metal ions and the ligands is purely electrostatic in nature. When the ligands approach the central metal atom or ion, the five degenerate d-orbitals of the central atom become differential that is they split into different energy levels under the influence of electrostatic field of ligands.

The crystal field theory is highly useful and more significant as compared to the valence bond theory. Even after such useful properties, it has many limitations. The following points will clearly state the limitations of crystal field theory:

The assumption that the interaction between metal-ligand is purely electrostatic cannot be said to be very realistic.

This theory takes only d-orbitals of central atom into account. The s and p orbits are not considered for study.

The theory fails to explain the behavior of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H₂O is a stronger ligand as compared to OH⁻.

The theory rules out the possibility of having p bonding. This is a serious drawback because p bonding is found in many complexes.

The theory gives no significance to the orbits of the ligands. Therefore it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals.