



Water Pollution and EPR

Hazardous organic waste, widely spread in water by industrial, military and domestic sources, is an existent and pervasive pollution issue. Advanced Oxidation Processes (AOPs) are efficient methods to remove these contaminants that are not biologically degradable. AOPs are based on the chemistry of hydroxyl radicals ($\bullet\text{OH}$), which are non-selective reactive oxygen species, able to oxidize water pollutants into inactivated end-products.

The design and optimization of AOPs depends on several parameters: reagent dosage, additional reactants, and reaction time. Optimal conditions must be determined in order to achieve the most effective treatment and reduce operating costs.

The hydroxyl radical is the most reactive species in AOPs and its interaction with the pollutants determines the efficiency of the oxidation process. Therefore, it is very important to increase the yield of hydroxyl radicals generated during AOPs.

Electron Paramagnetic Resonance (EPR) spectroscopy is the only technique for the direct and non-invasive detection of free radicals. By using EPR spin-trapping techniques, one can identify, quantify and monitor intrinsic generation of short-lived radicals such as hydroxyl radicals produced during AOPs. In spin trapping experiments unstable radicals are converted to stable radicals by reactions with spin-trapping agents and are detected by EPR.

Challenge: Reduction of operating costs and optimization of the free radical yield in Advanced Oxidation Processes (AOPs) to improve waste and ground water treatment technology.

Solution: The Magnettech ESR5000 benchtop EPR spectrometer package

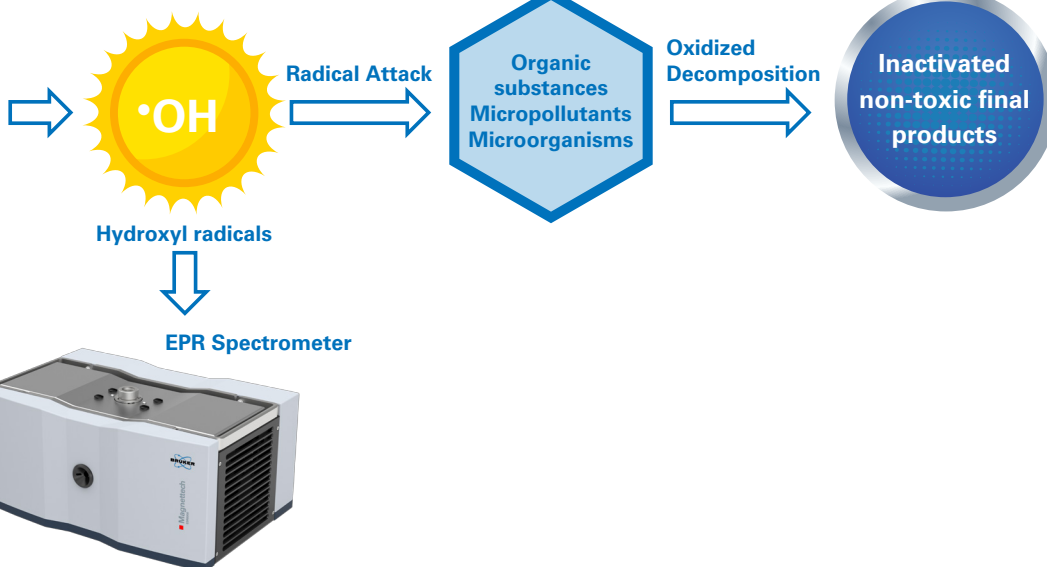
- Detects, identifies, and quantifies hydroxyl radicals and other reactive oxygen species involved in AOPs
- Determines the effectiveness and helps to optimize the AOPs
- Monitors radical reactions to further understand oxidation mechanisms and to determine the degradation efficiency

Magnettech ESR5000 key features:

- No prior EPR experience needed
- Accurate results
- Superior sensitivity
- Ease of use
- Full workflow for measuring, analyzing and quantifying impurities
- Compact foot print
- Low cost of ownership
- Seven resistant pharmaceutical agents (Diclofenac,

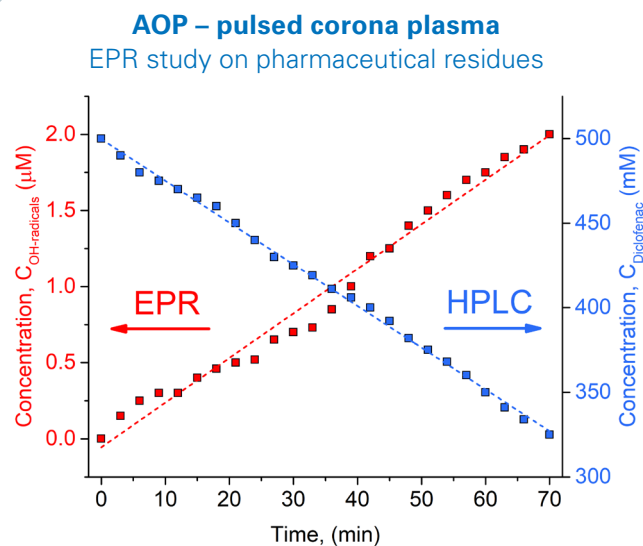
AOPs

- Fenton ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$)
- Ozonation (O_3)
- Electrolysis (electrodes + current)
- Sonolysis (ultrasound)
- Photolysis ($\text{UV} + \text{H}_2\text{O}_2$)
- Photocatalysis ($\text{UV} + \text{catalyst}$)
- Photo-Fenton ($\text{UV} + \text{Fenton}$)

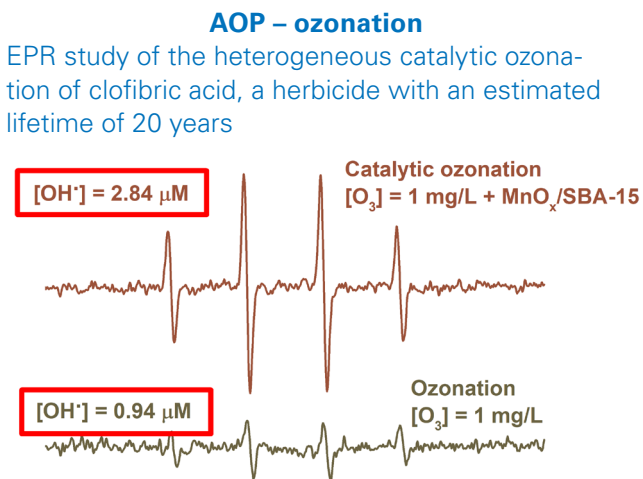


Ibuprofen, Diazepam, etc.) are decomposed by pulsed corona plasma generated in water.

- The degradation of Diclofenac measured by HPLC is directly correlated to the increase in hydroxyl radical concentration over time.
- Hydroxyl radicals detected by EPR are responsible for the decomposition of pharmaceutical compounds.
- EPR measurement of hydroxyl radical concentration aids in optimizing the decontamination process.

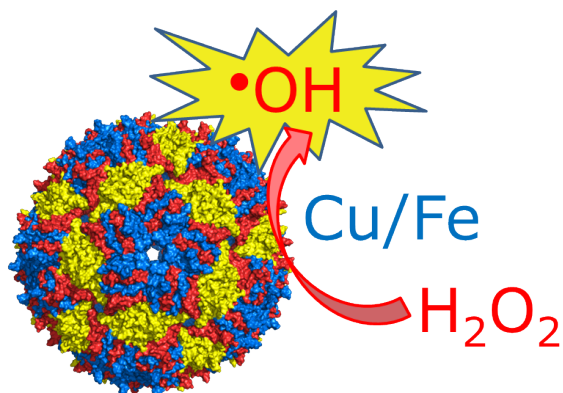


- EPR monitors the catalytic performance of manganese oxides (MnO_x) in mesoporous silica as an effective catalyst for clofibric acid degradation.
- EPR detects, identifies, and quantifies the formation of hydroxyl radicals to access catalytic quality.
- An increased hydroxyl radical concentration after using the catalyst leads to an enhanced degradation of clofibric acid.

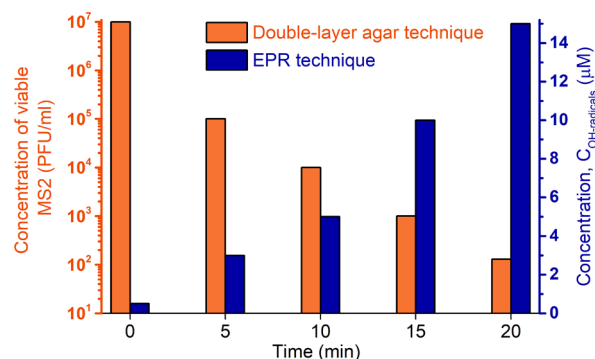


AOP – Fenton system

Inactivation of bacteriophages by iron- and copper-catalyzed systems during water treatment: role of EPR



Virus inactivation by Cu- or Fe-catalysis



- EPR detects and quantifies the production of hydroxyl radicals that are necessary to inactivate coliphage MS2 (bacteriophage):



- EPR monitors and aids in the optimization of the rate of hydroxyl radical production, which strongly depends on the concentration of peroxides, transition metals, pH, light exposure.

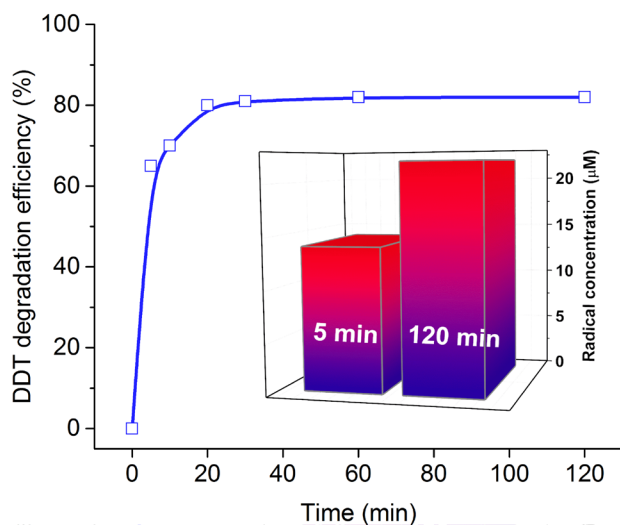
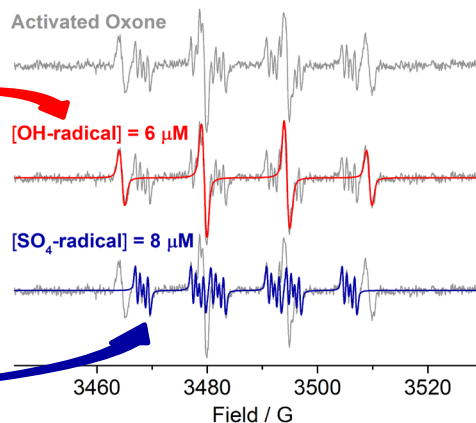
- Increasing the OH production correlates with a decrease of the virus's activity.
- EPR quantification of radicals offers direct process control for optimization of the decontamination reaction.



AOP – sulfate radical generation

EPR study on DDT, one of the most persistent pesticides with half-life of 2–15 years

- EPR directly detects the reactive species involved in DDT degradation catalyzed by the commercial decontaminant Oxone (potassium peroxymonosulfate - $\text{KHSO}_5 \bullet 1/2\text{KHSO}_4 \bullet 1/2\text{K}_2\text{SO}_4$) in the presence of transition metals
- Two radicals are identified: the sulfate radical ($\text{SO}_4^{\bullet-}$) and the hydroxyl radical ($\bullet\text{OH}$)
- $\text{SO}_4^{\bullet-}$ is longer-lived and selectively degrades contaminants:



- DDT degradation efficiency as measured by GC-MS is directly correlated with the radical concentration as measured by EPR. Control and optimization of the radical concentration results in improved degradation efficiency.

Summary:

Advanced Oxidation Processes decontaminate water through the destruction of organic pollutants, the neutralization of transition metals, and the inactivation of bacteria and viruses by radical production. The Magnettech ESR5000 characterizes and monitors radical formation during AOPs resulting in their improved efficacy.

Further Reading

1. Banaschik R. et al., Degradation and intermediates of Diclofenac as instructive example for decomposition of recalcitrant pharmaceuticals by hydroxyl radicals generated with pulsed corona plasma, *J. Hazard Mater.* (2018) 342 651
2. Sun Q. et al., Mechanism for enhanced degradation of clofibric acid in aqueous by catalytic ozonation over $\text{MnOx}/\text{SBA-15}$, *J. Hazard Mater.* (2015) 286 276
3. Nieto-Juarez J.I. et al., Inactivation of MS2 coliphage in Fenton and Fenton-like systems: role of transition metals, hydrogen peroxide and sunlight, *Environ. Sci. Technol.* (2010) 44 3351
4. Qin W. et al., Efficient transformation of DDT by peroxymonosulfate activated with cobalt in aqueous systems: kinetics, products, and reactive species identification, *Chemosphere* (2016) 148 68