

Photocatalytic Oxidation/Ozonation Processes

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Diffuse pollution and the presence in waters of so-called emerging pollutants, among others, represent a major global environmental problem. Often, the technologies implemented in conventional treatment plants fail to effectively solve this problem [1].

Deepening the study of already known processes (e.g., membranes, adsorption, and chemical oxidation) and some of their variants, or other innovative technologies, could improve water quality indices. Among these technologies are advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals with high oxidizing capacity. These short-lived species can completely eliminate pollutants and form CO₂ and H₂O, unlike classic tertiary processes such as membrane filtration and adsorption, which only transfer contaminants from one phase (water) to another (membrane concentrates, adsorbents, etc.) and do not destroy them.

Ozonation in the presence of homogeneous metallic catalysts (e.g., iron or manganese), hydrogen peroxide, and ultraviolet radiation are widely studied AOPs. Their effectiveness and ease of application make them very attractive for removing pollutants from water.

More innovative are AOPs in which light radiation electronically activates a semiconductor material (catalyst), generating charge carriers (holes and electrons) that eventually form hydroxyl radicals. Works carried out in the laboratory indicate that the process is efficient with UV light as the radiation source and TiO₂ in powder form as the catalyst. However, its implementation in a water treatment plant presents a series of problems, such as the source of UV radiation or the use of powdered TiO₂ (whose separation from treated water is difficult and expensive). Furthermore, the high recombination of charge carriers, which inhibit the oxidation process, is another problem that must be solved. Accordingly, new research focuses on cheap and environmentally sustainable sources of radiation (e.g., sunlight and LEDs) and on the development of efficient catalysts that are easy to use and handle in water treatment plants (e.g., doped TiO₂, supported photocatalysts, photocatalysts with magnetic properties, etc.).

The synergy between ozonation and photocatalytic oxidation (photocatalytic ozonation) constitutes another AOP with application potential due to its various methods of hydroxyl radical formation to enhance the effect of the direct ozonation of pollutants.

This Special Issue focuses on the synthesis and characterization of supported or magnetic photocatalysts and their application in reactions with water pollutants in the presence of visible light (solar or simulated) or radiation from UVA-visible LEDs, with and without the presence of ozone. Additionally, this issue deals with ozone processes in water that involve the simultaneous application of ozone with homogeneous catalysts (e.g., iron and manganese), UV radiation (without catalysts), hydrogen peroxide, etc., which are called ozone advanced oxidation processes. The aim is to highlight conditions that improve photocatalytic oxidation performance and ozone advanced oxidation processes.

The contributions to this issue are summarized below:

Peng et al. [2] synthesized and applied Ag/ZnO nanocomposites in the photocatalytic ozonation of phenol. Their crystal, textural, morphological, optical, and electrochemical properties were investigated in detail using XRD, Raman, SEM, TEM, UV-vis diffuse



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reflectance spectroscopy (DRS), X-ray photoemission spectroscopy (XPS), and photoluminescence (PL) techniques. The results indicated that silver nanoparticles were well dispersed on the surface of porous ZnO and that intimate contacts were formed at the Ag/ZnO interfaces. This prominently favored the separation and transfer of photoinduced electrons from ZnO to Ag nanoparticles for the activation of ozone to produce hydroxyl and superoxide ion radicals. As a result, significant enhancement in the photocatalytic ozonation of phenol was achieved over Ag/ZnO catalysts. The results also showed a synergistic effect between photocatalysis and ozonation.

Due to the rising threat to aquatic environments, the removal of methyl *tert*-butyl ether (MTBE) is necessary. This pollutant, even at very low concentrations, makes water undrinkable; therefore, an effective treatment must be developed. Šihor et al. [3] carried out photocatalytic oxidation of MTBE in the presence of various TiO₂ photocatalysts with different phase composition prepared using different methods. The authors confirmed that the phase composition of TiO₂ had the most significant influence on the photocatalytic degradation of MTBE. The rutile phase more easily reduced oxygen adsorbed by photo-generated electrons to superoxide radicals, supporting the separation of charge carriers. About 40% of total organic carbon was removed after 1 h of irradiation in the presence of TiO₂-ISOP-C/800 photocatalysts composed of anatase and rutile phase.

Zhang et al. [4] prepared hexagon-shaped potassium ferrite (K₂Fe₄O₇) crystals of different sizes using the hydrothermal method. The crystals showed a narrow band gap of 1.44 eV, revealed via UV-visible diffuse reflectance spectroscopy; they were thus used as a heterogeneous Fenton catalyst to degrade methylene blue and crystal violet in the presence of green oxidant H₂O₂ under visible-light irradiation. Among the investigated crystals, the as-prepared one with an average size of 20 μm exhibited better photocatalytic activity due to its high surface area. When this catalyst was used in a photo-Fenton process, 100% methylene blue and 92% crystal violet were degraded within 35 min. Moreover, the catalyst maintained high photocatalytic activity and was stable after four continuous cycles. Trapping experiments showed that the active hydroxyl radical (OH) was dominant in the photo-Fenton reaction. Therefore, this new photo-Fenton catalyst has great potential for the photocatalytic degradation of dye contaminants in water.

Sugiyama et al. [5] investigated which active oxygen species affect the oxidative dehydrogenation of methane by employing photo-catalysts such as TiO₂ and WO₃, which generate active oxygen from UV-LED irradiation conditions under oxygen flow. These photo-catalysts were studied in combination with Sm₂O₃, which is a methane oxidation coupling catalyst. Their constructed reaction system directly irradiated UV-LED to form a solid catalyst via a normal fixed-bed continuous-flow reactor operating under atmospheric pressure. UV-LED irradiation clearly improved the partial oxidation from methane to CO and/or slightly improved the oxidative coupling route from methane to ethylene when binary catalysts consisting of Sm₂O₃ and TiO₂ were used, while negligible UV-LED effects were detected when using individual Sm₂O₃ and WO₃. The authors concluded that Sm₂O₃-TiO₂ coupling catalysts and UV-LED irradiation generated the active oxygen of O₂[−], thus contributing to the oxidative dehydrogenation of methane, while the active oxygen of H₂O₂ from WO₃ under the same conditions afforded only negligible effects on the activation of methane.

Aguilar-Melo et al. [6] evaluated naproxen degradation efficiency via ozonation using nickel oxide films as a catalyst. The nickel oxide films were synthesized via chemical vapor deposition and characterized via X-ray diffraction, scanning electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. Naproxen degradation was conducted for 5 min using 10 films of nickel oxide. The results were compared to those from 100 mg/L nickel oxide powder ozonation and conventional ozonation. Total organic carbon analysis demonstrated mineralization degrees of 12, 35, and 22% with conventional ozonation, nickel oxide powder, and nickel oxide film ozonation, respectively, after 60 min of reaction. The films of nickel oxide were used sequentially four times in ozonation, demonstrating the stability and properties of the synthesized material as a catalyst for ozonation. A proposed modeling strategy using robust parametric identification

techniques allows for comparison of the pseudo-monomolecular reaction rates of naproxen decomposition.

Shurbaji et al. [7] conducted a review of visible light photocatalysis for the decomposition of ciprofloxacin, norfloxacin, tetracycline, and sulfonamide antibiotics in wastewater. This review summarized recent studies regarding semiconducting material modifications for antibiotic degradation using visible light irradiation. Antibiotics are chemical compounds that are used to kill bacteria or prevent their growth. They are used in fields such as medicine, agriculture, and veterinary medicine. The removal of antibiotics from wastewater is necessary since they develop antibacterial resistance. Conventional elimination methods are limited due to the high costs and effort involved, as well as their incomplete elimination. Semiconductor-assisted photocatalysis is an effective elimination method for different organic wastes including antibiotics, and various semiconducting materials have been tested to eliminate antibiotics from wastewater; nevertheless, research is still ongoing due to some limitations.

Beltrán et al. [8] analyzed the role of catalytic ozonation processes in the elimination of disinfection byproducts (DBPs) and their precursors in drinking water treatment. Special attention has always been paid to the formation of DBPs in drinking water treatment because of pathogen removal in the preparation of safe water. DBPs are formed by oxidant-disinfectant chemicals (mainly chlorine derivatives such as chlorine, hypochlorous acid, and chloramines), which react with natural organic matter (mainly humic substances). DBPs are usually refractory to oxidation, mainly due to the presence of halogen compounds, so advanced oxidation processes are recommended to deal with their removal. This work reviewed the application of catalytic ozonation processes (with and without the simultaneous presence of radiation), which are moderately recent advanced oxidation processes, for the removal of humic substances (also called DBP precursors) and DBPs themselves. First, a short history of the use of disinfectants in drinking water treatment, DBP formation discovery, and alternative oxidants used is presented. The following sections are dedicated to the application of conventional advanced oxidation processes to remove DBPs and their precursors. Finally, a description is given of the principal research achievements found in the literature regarding the application of catalytic ozonation processes. In this sense, the authors review aspects such as operating conditions, the reactors used, the radiation sources applied, kinetics, and mechanisms.

One of the difficulties in establishing the intrinsic kinetics of photocatalytic oxidation processes is the complexity of the mathematical formula used to determine the rate of photon absorption. To solve this problem, some models have been proposed and checked, such as the six-flux model (SFM) confirmed for central-lamp photoreactors. External-lamp photoreactors are also one of the most-used configurations for studying the photocatalytic oxidation of contaminants in water, and complex mathematical solutions have been reported to solve the rate of photon absorption. Beltrán et al. [9] adapted the SFM equations already reported for the central lamp photoreactor to determine the rate of photon absorption in an external four-lamp photoreactor. The results obtained showed slight differences compared to those of the Monte Carlo method. Additionally, once the rate of photon absorption was validated, the authors determined the intrinsic rate constant and scavenging factor of the photocatalytic oxidation of some contaminant compounds from the already-published results.

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