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Editorial

New Perspectives in Photocatalytic Water Treatment

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This Special Issue, entitled "New Perspectives in Photocatalytic Water Treatment", was planned to cover all relevant topics related to photo-initiated oxidative processes in water treatment, with a special emphasis on pollutant abatement and microorganism inactivation, which were required for improving their practical uses. Articles presenting advances in these processes or showing a correlation between the synthesis, structure, and performance of photocatalytic systems were evaluated. On the basis of previous experience, the following topics were particularly followed: (i) water treatment and photocatalytic advanced oxidation processes; (ii) visible light active photocatalyst preparation, characterization, and applications; and (iii) inactivation of microorganisms, kinetics, and mechanism.

From a drinking water quality point of view, two main components are natural organic matter (NOM) and microorganisms (e.g., *E. coli*). Both of them are of prime importance from a public health safety point of view. NOM is known as the main surrogate organic group for the formation of harmful disinfection by-products. This important feature makes it necessary to be eliminated from natural waters. Besides conventional treatment methods (e.g., coagulation and flocculation), the application of advanced oxidation technologies (AOPs) has received widespread attention for decades. Furthermore, the abatement of both inorganic as well as organic pollutants should also be taken into consideration.

AOPs are basically dependent on the formation and reaction of reactive oxidation species (ROS) mostly generated by light-initiated reactions. Among AOPs, photocatalysis has also attracted the interest of researchers, and over the past 30 years, photocatalysis has been recognized for its potential in water treatment, even expressing complete mineralization as articulated by complete removal of dissolved organic carbon (DOC). By definition, in a photocatalytic transformation process, the activation of a chemical reaction or its rate is changed when a semiconductor photocatalyst adsorbs photons (in the ultraviolet or visible radiation range) with energy sufficiently high to generate an excited electron-hole redox pair. The redox pair interacts either directly with the contaminants or with O_2/H_2O-forming reaction intermediates, which can further lead to the formation of harmless or harmful products.

Based on this fundamental knowledge, and considering the huge research efforts focused on the use of TiO_2, the band gap energy of the semiconductor and respective effective wavelength limited the application area. Therefore, recent interest has been directed at the more effective utilization of solar energy. To achieve this goal, several approaches were followed, such as modifications by metal and non-metal doping of TiO_2, nanocomposite catalysts in which a phase consists of photocatalytic TiO_2, surface functionalization, nano-heterojunction, and/or morphological changes. Moreover, the development of novel non-TiO_2 photocatalyst specimens was also investigated. In this respect, non-TiO_2 semiconductor specimens were demonstrated as novel composite photocatalysts (e.g., conducting polymer-modified ZnO).

Several transition metal oxide materials were investigated as heterogeneous catalysts in water treatment. Among others, the use of zeolites, mixed oxides, pillared clays, etc., could be indicated. Although some of these catalysts were very active, their stability in the aqueous medium was often unsatisfactory due to metal leaching under the specified

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operational conditions. Perovskites, e.g., lanthanum orthoferrites, are a versatile class of catalysts. In particular, $LaFeO_3$ is stable in the pH range from 3 to 8. It has been proposed as a visible-light photocatalyst since 2007, although most of its photodegradation studies have been focused on organic dyes in aqueous solution, often combined with a Fenton-like reaction. Recently, $LaFeO_3$ was used for photocatalytic degradation of humic acids as a model compound of NOM [1]. Based on the findings presented therein, $LaFeO_3$ was used for the inactivation of *E. coli* under solar irradiation to simulate natural water conditions.

In this respect, two complementary studies were presented by Birben and colleagues covering the effect of NOM analog compounds [2,3]. Besides sole *E. coli* inactivation kinetics, characterization of the released organic matter was also presented by UV-vis, fluorescence, and FTIR spectroscopic techniques as well as mineralization extents. Furthermore, spectroscopic and mechanistic investigations of destructed cell-derived organics excitation-emission matrix (EEM) fluorescence spectra with parallel factor multiway analysis (PARAFAC) modeling were also employed. As indicators of cell lysis, leakage of potassium ions, protein, and carbohydrate components were presented along with *E. coli* destruction. A comprehensive evaluation covering all indicated aspects was presented.

The use of conducting polymers (CP) (e.g., polyaniline, polypyrrole, polythiophene, etc.) in cooperation with semiconductors (e.g., TiO_2, ZnO, etc.) has been investigated for the last two decades. PANI-modified ZnO was used for the degradation of methylene blue dye that was selected as a model compound [4]. The major dissolution disadvantage of ZnO was eliminated by employing an in situ chemical oxidation polymerization method under neutral conditions (PANI-ES), whereas in the hybridization method, physical blending was applied using an emeraldine base of polyaniline (PANI-EB). PANI-ZnO composites were prepared in various ratios of aniline (ANI) to ZnO, and alterations on the structural and morphological properties of PANI-ZnO composites were compared by various spectroscopic techniques, such as Fourier Transform Infrared (FT-IR), Raman Spectroscopy, X-ray Diffraction (XRD), and Scanning Electron Microscopy-Energy Dispersive X-ray Analysis Unit (SEM-EDAX) techniques. Photocatalytic performances of PANI-ZnO specimens were investigated by following the degradation of methylene blue, chosen as the model dye substrate in an aqueous medium under UVA irradiation. The hybridization method was found to be more efficient than the direct in situ chemical oxidation polymerization method, emphasizing the significance of the neutral medium.

The sensitization property of CPs, e.g., PANI, was also accompanied by the application of metallo-phthalocyanine-sensitized TiO_2 (MPc/TiO_2) nanocomposites for photocatalytic treatment of noxious Cr(VI) and an antibiotic amoxicillin (AMX) [5]. A novel synthesis method was employed using a non-ionic surfactant Triton X-100 to obtain a homogenous and mesa pore catalyst structure. The composite was characterized by FT-IR, XRD, and SEM to determine the crystal and surface structural properties. Light intensity dependence of photoreduction of Cr(VI) ions and photodegradation of AMX was presented.

Removal of emerging pollutants from natural waters as well as from treated wastewaters holds prime importance. In this respect, a comparative study was presented by Montazeri and colleagues [6]. Applied AOPs were UV-light-, zero-valent iron-(ZVI) and zero-valent aluminum(ZVA)-activated persulfate (PS) oxidation processes. Iprodione (IPR), a once frequently used but recently banned dicarboximide fungicide, was selected as a pollutant, and reactions were performed in simulated tertiary-treated urban wastewater. Degradation of IPR was also followed in pure water, providing baseline information. Complete IPR and a considerable degree of DOC removals were obtained with ZVI/PS treatment as the most effective oxidation process in simulated tertiary-treated urban wastewater.

These studies revealed significant information through in-depth investigation of semiconductor photocatalysis and AOPs, bringing novel perspectives to the attention of scientists interested in this innovative research area.

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