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Advanced Oxidation Processes for Wastewater Treatment

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1. Introduction

The modern way of life, the development of industry, and the production of new products and by-products have led to an increase in the volume of liquid waste and significant changes in its characteristics. As a result, water and wastewater treatment face significant challenges in efficiently and economically removing numerous contaminants from water matrices.

In this regard, in recent years, there has been an ever-increasing interest in Advanced Oxidation Processes (AOPs), as they constitute an environmentally friendly way to destroy organic and inorganic pollutants found in water resources [Dewil *et al.*, 2017]. The term AOPs defines the technologies that are based on the creation of strong oxidizing chemical species (Reactive oxygen species, ROS), with the main ones being hydroxyl radicals (•OH), which are characterized by high oxidation potential (2.8 V vs NHE, pH~6). Heterogeneous Photocatalysis, Fenton reagent and photo-Fenton (homogeneous photocatalysis), ozonation (O_3, O_3/UV, O_3/H_2O_2), liquid oxidation, electrochemical oxidation, use of ultrasound and persulfate oxidation are some characteristic examples of AOPs. However, usually the high energy requirement, the formation of toxic by-products, the challenges in scaling up etc. [Petala *et al.*, 2021, Bampos *et al.*, 2022], preventing their integration into industrial applications.

In this context, this Special Issue presents various AOPs for addressing these emerging environmental issues.

2. Summary of this Special issue

In the field of Photocatalysis, scientists' main concerns in the last decade include the development of visible-light active materials and the demonstration of the process under more realistic conditions. Towards this direction, six papers were included in this Special Issue. In specific, trying to improve the optical properties of TiO_2, which is the most popular photocatalytic material, S. Mergenbayeva et al. [Mergenbayeva *et al.*, 2023] deposited molybdenum (Mo) oxy species on its surface and the as-prepared photocatalytic materials was further modified with another metal ion M^{2+} (M: Co, Cu, Zn). Their photocatalytic activity was evaluated towards sulfamethoxazole degradation in water under simulated solar irradiation. It was found that the deposition of Mo has a detrimental effect on the activity of TiO_2 , while the deposition of Zn or Cu can improve

the activity of the ternary system. H. Kanwal and his coworkers [Kanwal *et al.*, 2023] proposed a green synthesis of TiO_2 photocatalyst. In particular, they prepared TiO_2 nanoparticles with *Mangifera indica* leaves extract as the organic source and tested their photocatalytic efficiency for methylene blue degradation in water under ultraviolet irradiation. The effect of several experimental parameters, such as pH and photocatalyst dosage, was studied using response surface methodology, providing useful information for the effective design of similar degradation systems.

P.L. Hariani et al. [Hariani *et al.*, 2023] synthesized a series of core-shell-shell $Fe_3O_4/SiO_2/NiO$ composites with magnetic properties. They tested their photocatalytic efficiency for methylene blue degradation under ultraviolet irradiation. A high degradation rate was achieved under basic conditions, with the catalytic materials showing high reusability and stability. Another core-shell configuration was also proposed by M.N. Anjum et al. [Anjum *et al.*, 2023], who synthesized conducting poly(o-toluidine) (POT)/titanium dioxide (TiO_2) nanocomposites by in situ chemical oxidation polymerization of o-toluidine in the presence of TiO_2 nanoparticles and studied their photocatalytic properties towards violet 1 removal in water under ultraviolet irradiation.The as modified samples possessed superior photocatalytic efficiency than the parent TiO_2 material.

From another point of view, H. Kamani et al. [Kamani *et al.*, 2023] paid special attention to the effect of the water matrix on the efficiency of a photocatalytic process. For this, they studied the degradation of coliform and fecal coliform from real hospital wastewater effluent instead of ultrapure water using commercially available nitrogen-doped TiO_2 under UV light. Their results showed that the N-TiO_2/UV system is a very promising technology for inactivating all coliform and fecal coliforms in hospital effluents in very short periods.

Another important issue in Photocatalysis is the design of proper reactor configurations allowing the operation of such systems under continuous flow conditions. Towards this direction, S. Ragunath et al. [Ragunath *et al.*, 2023], used a submerged photocatalytic membrane reactor (SPMR) for Apocynin photocatalytic degradation from effluent water, utilized with suspended and immobilized Sr-$LaNiO_3$ under gamma irradiation, either with or without H_2O_2. They confirmed the beneficial role of H_2O_2 and the higher removal efficiencies in the case of suspended photocatalytic nanoparticles than the immobilized ones.

The Fenton reagent is frequently regarded as the precursor of AOPs as it is possibly the first discovered. It is a simple and effective process that can be combined with irradiation (photo-Fenton). However, its widespread industrial application is hindered by the requirements of acidic conditions, sludge generation, and iron extraction from the effluent. In this Special Issue, K. Umiejewska et al. [Umiejewska *et al.*, 2023] compared the effectiveness of the coagulation process and Fenton reagent towards organics degradation contained in real wastewater from plastic lens production. In the case of aluminum coagulants, COD reduction reached 55%, while the maximum COD reduction after the Fenton process was 50.7%. However, proper tuning of the

reaction parameters could alter the obtained results in both cases. In addition, photo-Fenton, was studied by M. Mohan et al. [Mohan *et al.*, 2023] for landfill leachates treatment. They compared the efficiency of the process by using three different light sources (solar, UV, and LED). Moreover, Taguchi statistical experimental method in Minitab software was used to examine the effect of different experimental parameters. It was found that higher removal efficiency was achieved in the case of the solar photo Fenton process.

Another AOP technology successfully used to eliminate pollutants of emerging concern is catalytic wet peroxide oxidation (CWPO). In particular, in the study of N.M.C. Guari et al. [Guari *et al.*, 2023], paracetamol degradation was investigated using cobalt ferrite carbon-coated nanoparticles as catalysts. The authors noted the low amounts of iron leaching in the liquid phase and the high stability of the catalysts. Moreover, they proposed an empirical kinetic model composed of a second-order and an autocatalytic expression that can describe the decomposition of H_2O_2 and paracetamol. Peroxide oxidation was also the research topic of M.S. Kalmakhanova et al. [Kalmakhanova *et al.*, 2023]. This work proposed using natural clays in synthesizing low-cost pillared clays for application as catalysts in oxidation technologies for wastewater treatment. In their study, the oxidation of 4-nitrophenol was reported. They observed that pillared clay materials showed higher catalytic activity than the pristine materials with the best results obtained after the simultaneous modification with Fe/Cu/Zr cations.

Plastic pollution was studied utilizing Ozonation by the research group of N. Lekše et al. [Lekše *et al.*, 2023]. In specific, considering the fact that one of the most significant sources of microplastics (MPs) are wastewater treatment plants (WWTPs), they tried to evaluate the impact of ozonation as pretreatment of Polyvinylchloride (PVC) contaminated waste aerobic sludge on biogas and methane production. They concluded that ozonation could inhibit or increase CH_4 yield, depending on ozone dose and treatment time, thus pointing out the need for further analysis to understand the impact of MPs on biogas production and CH_4 yield.

In recent years, sulfate radicals-based AOPs have gained significant attention as an alternative method for eliminating refractory organic contaminants from wastewater. Towards this direction, the research group of M. Nowakowski et al. [Nowakowski *et al.*, 2023] investigated anthracene and phenanthrene degradation in water by potassium peroxydisulfate activated by UV light. They paid particular attention to the formation of nitro-, oxy- and hydroxy-PAHs as by-products of the degradation process, as well as on the impact of the addition of nitrogen-containing compounds (NH_4OH, NO_2, NO_3), for the formation of nitro-PAHs.

Ultrasound is another group of AOPs based on the *in-situ* production of reactive species and can degrade persistent contaminants to less toxic substances or even carbon dioxide. In this Special Issue, Sonocatalytic process was employed by H. Kamani et al. [Kamani *et al.*, 2023], who studied the degradation of catechols from aqueous solutions in the presence of magnesium oxide nanoparticles. They paid special attention to the

effect of pH, MgO and catechol concentration, as well as the applied frequency. Based on the results, it was concluded that ultrasound is an easy, practical, and cost-effective method for water treatment.

One step further, G. Dogdu et al. [Dogdu *et al.*, 2023], investigated the efficiency of a hybrid ultrasound and photocatalytic system for treating poultry slaughterhouse wastewater. In specific, they investigated COD and oil and grease removal under different operating conditions such as catalyst type (TiO_2 and ZnO), irradiation type (UVA and UVC), catalyst dosage (0.5-2.5 g/L), and pH (2–10). They concluded that the synergy index value for the combined US/UVC/ZnO process was equal to 1.42 and showed higher oxidation performance than the ones. Moreover, the catalyst type and the pH were the most crucial factors in the efficiency of the hybrid process.

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