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Editorial

New Trends in Environmental Catalytic Technologies for Water Remediation

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Due to climate change, industrialization, and overpopulation, water resources management is becoming a crucial sector. Consequently, as the limits of legislation for effluents' reuse and recycling and use in crops or aquifers enrichment are becoming increasingly stringent, advanced wastewater treatment is becoming very demanding. Simultaneously, in recent years, a new generation of pollutants has emerged. The xenobiotic compounds present a disproportionately high degree of toxicity even though they are detected in minimal quantities, which is why they are called micro pollutants. This category contains many compounds belonging to different families, such as endocrine disruptors, pharmaceutical compounds, and personal care products.

One of the main problems of this new generation of pollutants is their extremely low biodegradation or their tendency to accumulate in the sludge of conventional biological wastewater treatment systems. On the other hand, in the scientific community and the environmental restoration industry, the search for the optimal solution for removing recalcitrant organic pollutants such as humic acid and inorganics such as heavy metals from environmental matrices continues at an intensive pace. In this light, the scientific interest has turned to a new generation of physicochemical methods called advanced oxidation processes (AOPs). These processes are based on the in situ generation of reactive oxygen species. AOPs include technologies such as photocatalysis, photo Fenton and Fenton-like reactions, activated persulfate, ozonation, wet air oxidation, UV/H_2O_2, hydrodynamic or acoustic (sonochemistry) cavitation, and others.

In this light, this special issue presents various advanced technologies for tackling these emerging environmental problems.

Most of these processes are heterogeneous and catalytic, and the reaction usually occurs at the liquid/solid interface. Therefore, the role of materials in performance is crucial. Many research teams have turned to the search for new photocatalytic materials. These semiconductors must have a high response to sunlight irradiation so that photocatalytic decomposition becomes an environmentally-friendly process. At the same time, preferably, these materials must have a large specific surface area to favor the adsorption of pollutants and mass transfer. Finally, they should be cheap, abundant in nature, nontoxic, and present photo-stability.

Plakas et al. [1] examined the combination of activated carbon fibers with the well-studied, "benchmark" catalytic material titanium dioxide to enhance photocatalytic efficiency. The study showed interesting results in terms of phenol decomposition resulting from the combination of photocatalysis with sorption. At the same time, the as-prepared materials showed significant stability and regeneration capacity. Therefore, attempting to couple photocatalysis with adsorption seems like an interesting strategy for future research. Konstas et al. [2] studied different photocatalytic materials, namely titanium dioxide (TiO_2)Aeroxide, graphitic carbon nitride (g-C_3N_4), and g-C_3N_4/$SrTiO_3$, for the photocatalytic destruction of pharmaceuticals in hospital effluent. Carbon nitride showed a

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higher or, in some cases, similar performance to the commercially available TiO_2 Aeroxide. The research team identified 11 transformation products during the photocatalytic oxidation using liquid chromatography high-resolution mass spectrometry. In the work of Petala et al. [3] Ag_2CO_3, a promising photocatalyst, was synthesized, characterized, and evaluated for the photocatalytic destruction of the endocrine disruptor ethyl paraben. Ag_2CO_3 showed high activity under both solar or visible irradiation, while in the presence of ions like chlorides or bicarbonates, the removal rate was enhanced. According to the results, the proposed material is competitive with well-studied materials like carbon nitride; however, future research is needed to determine the catalyst stability.

One of the most intractable environmental problems is soil pollution and remediation. The most used method to address this issue is soil washing, which transfers the problem to the aqueous phase, at which point further treatment is required. Zhan and Chen [4] prepared (i) biochar (BC) from maize straws and (ii) $ZnCl_2$ modified biochar (ZnBC) and examined the removal of heavy metals (Cd, Pb, Cu, and Zn) from $FeCl_3$ washing effluent. Indeed, the Zn-modified biochar showed higher removal than that of the unmodified biochar for all the heavy metals examined, possibly due to the significant enhancement of the surface area of the ZnBC or due to the ion exchange between Zn-OH and the metal ions. However, the removal remained relatively low, possibly due to acidic pH, and the efficiency of the process was lower compared to the well-known $Ca(OH)_2$ treatment. Unfortunately, according to the researchers, even the latter can achieve the limit stipulated by the legislation. Therefore, future research must turn towards sequential $Ca(OH)_2$ treatment and adsorption.

Humic acids are macromolecules derived from the decomposition of organic matter and are persistent against further biodegradation. In the work of Salvestrini et al. [5], electrochemical oxidation using platinum electrodes was examined for the fast destruction of humic acid. Depending on the presence or absence of a large concentration of chlorides, two distinct paths were suggested. The first was based on oxidation through hydroxyl radicals and the second on the production of active chlorine species. The researcher proposed a model that can adequately simulate the system. On the other hand, in Oulego et al. [6] the catalytic wet oxidation for the removal of humic acid was investigated. Under the circular economy and valorization perspective, the authors synthesized novel catalytic materials based on iron or copper deposition on calcined eggshells. The use of eggshells as the supporting material with 15% wt. copper showed encouraging results, with almost 75% of the Chemical Oxygen Demand (COD) removed after three hours. Interestingly, despite the moderate COD reduction, the use of calcined eggshells without metal ions showed a promising improvement of biodegradability expressed as the Biochemical Oxygen Demand (BOD)/COD ratio; therefore, further research is needed in this direction.

The Fenton reaction, discovered in the 1984, is maybe the oldest advanced oxidation process and is often considered the origin of advanced oxidation processes. Although it is a simple and effective process and can combine with artificial or solar irradiation (photo or solar Fenton), the need for acidic conditions, sludge production, and iron separation from the effluent prevent its wide industrial application. Sarmento et al. [7] investigated the addition of Mn^{+2} to enhance the efficiency of the Fenton reaction in the degradation of the antibiotics sulfamethoxazole (SMX) and trimethoprim (TMP). It was found that the addition of Mn^{+2} did not improve efficiency compared to the conventional Fenton reaction. The latter in optimized conditions achieved almost complete mineralization of the antibiotic trimethoprim in less than 90 min of treatment. The use of heterogeneous catalysts is an interesting proposal to overcome the problems of the homogeneous Fenton process. In this light, Haneef et al. [8] examined the decomposition of polycyclic aromatic hydrocarbons (PAHs) from real wastewaters using a zero-valent iron catalyst and hydrogen peroxide as the oxidant. The authors used a factorial design methodology and a central composite design to investigate the effect of operating parameters, namely, treatment

time, catalyst concentration, hydrogen peroxide, and pH. After optimization, the heterogeneous process showed promising results: the PAHs removal and COD reaction were 87.4% and 73.5%, respectively.

Another approach to enhance the efficiency of AOPs is the simultaneous application of different processes. To reduce the energy footprint, Stathoulopoulos et al. [9] proposed the simultaneous activation of persulfates by heat and (solar or LED-UVA) radiation for the destruction of the non-steroidal anti-inflammatory drug (NSAID) piroxicam. According to the results, the combined activation by heat and irradiation showed a significant enhancement of piroxicam in different synthetic and real water matrices. In conclusion, the researchers suggested further research into coupling/combining technologies to improve efficiency and, at the same time, reduce the energy footprint of processes.

Future Trends

In contrast to industry, a unique feature of environmental systems is that the composition and supply of wastewater vary significantly. Therefore, each case may be different, and technologies that seem to prevail in some cases are impossible to implement or are inefficient in specific applications. Therefore, the development of a single technology that will address the problem of environmental pollution holistically seems unlikely. New trends in environmental remediation are (i) the correlation of the properties of catalytic materials with the performance of processes in real conditions and the development of new materials with specific properties that can work on an industrial scale and in real systems, (ii) the effort to increase efficiency through a combination of processes and therefore reduce the energy and environmental footprint, and finally (iii) the effort to develop holistic processes that will utilize agro-industrial residues (valorization) for the restoration of the environment in the context of the circular economy

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