Editorial

Special Issue on “Green Catalysts: Application to Waste and Groundwater Treatment”

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Water and soil pollution are among the most critical global problems due to population growth, industrial development, and associated resource consumption. According to sustainability criteria, this context requires solutions based on efficient, economic, and low-environmental impact processes, in line with the European Green Deal. Some of the significant advances in the treatment of polluted waters have been focused on catalytic processes, and therefore, the interest in the development of green catalysts has dramatically increased. Green catalysts are eco-friendly, inexpensive, reusable, and/or recyclable materials that reduce or eliminate the use or generation of hazardous substances.

This Special Issue gives an overview of the state of the art in the use of green materials for the treatment of polluted waters and soils by several processes, mainly advanced oxidation processes (AOPs), with different degrees of sophistication, including eleven research papers [1–11] and two bibliographic reviews [12,13].

Some of these works are based on the Fenton process (the catalytic decomposition of hydrogen peroxide, \( \text{H}_2\text{O}_2 \), by iron salts to generate hydroxyl and hydroperoxyl radicals, able to mineralize recalcitrant organic compounds), but introducing substantial improvements, mainly from the point of view of the catalyst. In the catalytic wet peroxide oxidation (CWPO) process, the iron salts are replaced by solid catalysts with redox properties to generate radical species from \( \text{H}_2\text{O}_2 \) decomposition. This modification allows one to work on a broader pH range than the homogeneous process (limited to pH = 3–3.5) and favors catalyst reuse. In this sense, the performance of iron-functionalized activated carbon (AC) catalysts was successfully evaluated on the CWPO of phenol in synthetic and real water matrices [7]. The functionalization of the commercial activated carbons with nitric acid, sulfuric acid, and ethylenediamine induced the modification of the AC surface functional groups and the interaction with iron, increasing the catalysts stability and allowing their reusability. The use of non-expensive and naturally occurring iron materials, such as magnetite [8] and goethite [6], has been explored, as green catalysts in the CWPO and CWPO intensified by visible LED of a highly toxic cyanotoxin (cylindrospermopsin) and a chlorinated organic compound (1,2,4-trichlorobenzene), respectively. The use of magnetite, combined with \( \text{H}_2\text{O}_2 \), was shown to be highly effective in the removal of the cyanotoxin, achieving up to 80% pollutant conversion under optimized conditions. Moreover, the catalytic system showed high stability with limited iron leaching [8]. In the case of goethite, Lorenzo et al. (2021) proved that this green catalyst intensified by VIS monochromatic LED light (470 nm) was effective for the CWPO of chlorinated organic pollutants at neutral pHs [6]. The light lamp promotes the reduction of Fe(III) in the goethite surface to Fe(II), yielding hydroxyl radicals faster than Fe(III). Costamagna et al. (2020) performed a valuable study focused on the environmental impacts generated by the heterogeneous photo-Fenton processes (CWPO-light) using bisphenol A as a target contaminant [3]. A life-cycle assessment (LCA) methodology was applied to identify the hotspots of using magnetite particles covered with humic acids (HAs) as a green heterogeneous photo-Fenton catalyst for water remediation. The introduction of HAs improved the efficacy and stability of the catalyst without
significant environmental impacts, whereas working at circumneutral pH would effectively limit the environmental impacts.

The application of mineral Fe-based natural materials (ilmenite, pyrite, chromite and chalcopyrite) as effective and available catalysts for the degradation of refractory contaminants, such as the antibiotic cefazolin, by heterogeneous electro-Fenton, was demonstrated [4]. The stability and reusability experiments showed a negligible decrease in the catalytic activity of chalcopyrite after five consecutive runs. In addition to economic evaluation, the empirical assessment confirmed that iron-based mineral catalysts could be an appropriate and cost-effective alternative catalyst for this process due to the high catalytic activity, availability, eco-friendly nature and low energy consumption, compared to other synthesized catalysts. The use of heterogeneous electro-Fenton as “Green” technology for pharmaceutical contaminants removal from aquatic environments was reviewed in detail [13]. The main challenges facing this process revolve around enhancing performance, catalysts’ stability for long-term use, life-cycle analysis considerations and cost-effectiveness. The efficiency of the treatment significantly improved; however, ongoing research efforts need to deliver economic viability at a larger scale due to the high operating costs, primarily related to energy consumption [13].

On the other hand, the remediation of soils contaminated with persistent organic pollutants by the chelate-modified Fenton process was reviewed by Checa-Fernandez et al. (2021) [12]. This review provides a general overview of the application of organic and inorganic chelating agents to enhance the Fenton process for the remediation of soils polluted with the most common organic contaminants, especially for a deep understanding of the activation mechanisms and influential factors. The existing shortcomings and research needs were highlighted. Future research perspectives on the use of non-toxic and biodegradable chelating agents for the Fenton process were provided.

The use of new or modified materials in photocatalysis, which uses a renewable source of energy, is also remarkable. A promising nanocomposite (TiO$_2$ doped with activated carbon and clinoptilolite) has been tested as a sustainable catalyst for the adsorption–photocatalytic hybrid process of bromophenol blue dye under UV-irradiation of a wavelength of 400 nm [5]. The development of mathematical models, able to predict the degradation of pollutants based on the different operational variables, and the determination of the oxidation routes is decisive for applying this process. In line with this, the photocatalytic degradation of triclosan, an antimicrobial and antifungal pollutant was studied and optimized, paying particular attention to reaction products and kinetics [11]. Moreover, a kinetic model for the degradation of S-metolachlor in a heterogeneous photocatalytic system was developed, allowing for the process design and scale-up of LED–photocatalytic reactors [10].

Novel heterogeneous materials were also used to activate other oxidants such as persulfate (PS) or as adsorbents. Thus, lanthanum nickel oxide was shown to be a very effective activator of PS for the degradation of micropollutants present in surface waters, such as sulfamethoxazole, piroxicam and methylparaben, exhibiting good stability under consecutive experimental runs [9], whereas a natural bionanocomposite of eggshell/Ag-Fe was successfully employed as an efficient adsorbent material for the removal of lead, arsenic, and mercury from water [1]. The search for new materials and the optimization of processes to make them more efficient and sustainable also shows innovation in the field of the absorption of pollutants from gaseous streams and their subsequent treatment. In line with this, the removal of perchloroethylene from gaseous streams using two types of absorption devices (jet absorber and absorption column) connected with electrolyzers was studied [2].

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