catalysts

MDPI

Editorial

Environmental Catalysis for Water Remediation—Preface to the Special Issue

Silvia Álvarez Torrellas * and Juan García Rodríguez

Group of Catalysis and Separation Processes (CyPS), Department of Chemical Engineering and Materials, Complutense University of Madrid, 28040 Madrid, Spain; jgarciar@ucm.es
* Correspondence: satorrellas@ucm.es

Water is a basic resource and is required by all living beings on our planet. However, the scarcity and contamination of aqueous media have led to millions of people in sub-developed countries having limited access to it. Water pollution most frequently occurs via the entrance of chemicals into water bodies as a result of various human activities. Any amount of chemical is able to pollutes the water, regardless of the harm it may pose to human health and the environment.

This Special Issue aimed to provide a scientific overview of the main concepts and current advances in the field of environmental catalysis, including the application of catalytic processes as alternative methods for the treatment of aquatic pollutants, such as pesticides, herbicides and numerous industrial chemicals, with regard to water remediation. Original research papers and short reviews addressing the synthesis and characterization of new catalysts, the influence of various operating parameters and types of reactors on the removal of pollutants, the reaction kinetics and mechanisms implicated, as well as the identification of intermediate compounds were invited for submission. Some of the papers comprising the Special Issue are presented below, along with a discussion of the various wastewater remediation technologies employed.

Contribution 1 studies the adsorption of arsenic (As(V)) onto eggshell biochar. The maximum adsorption capacity (q = 6.3 mg g^{-1}) measured at a contact time of 120 min, which corresponded to 96% of pollutant removal, was determined at the following operating conditions: a solution pH of 4.5, an initial arsenic concentration of 0.6 mg L^{-1}, and an adsorbent dose of 0.9 g L^{-1}. Some authors have attempted to obtain effective and stable photocatalysts based on Cu-Mo nanostructures that are doped with a carbon source and synthesized via a solvothermal preparation route. These catalysts have been utilized for the degradation of Yellow 5 dye under solar light. The catalyst prepared via pyrolysis under N_2 atmosphere showed the highest photoactivity, due to its enhanced textural properties. In addition, as expected, the reaction mechanism for the dye degradation involved successive attacks of •OH radicals (Contribution 2).

Contribution 3 addresses another topic of high concern in this Special Issue; this is the electrocatalytic oxidation process of the plasticizer Dibutyl phthalate (DBT) from water. The authors used an electrode based on iridium–tantalum/titanium (IrO_2-Ta_2O_5/Ti) as the anode and graphite as the cathode. The authors obtained high DBP and total organic carbon (TOC) removal efficiency values of 90 and 56%, respectively, under a voltage gradient of 10 V cm^{-1} for 60 min. Another study demonstrated the potential utility of keratin char-TiO_2 composite films for the degradation of Methylene Blue from water via a photocatalytic process (Contribution 4). The main active species in the process were identified as $^1O_2$ radicals. Density Functional Theory (DFT) calculations demonstrated that the high photocatalytic properties of the calcined keratin char-TiO_2 composites could be mainly ascribed to their rough surface, particular porous structure, high water contact angle, and high adsorption energy towards the organic pollutant.

check for updates

Citation: Álvarez Torrellas, S.; García Rodríguez, J. Environmental Catalysis for Water Remediation—Preface to the Special Issue. *Catalysts* **2024**, *14*, 178. https://doi.org/10.3390/catal14030178

Received: 21 February 2024
Accepted: 29 February 2024
Published: 3 March 2024

In Contribution 5, superparamagnetic Iron oxide nanoparticles for the degradation of tetracycline from wastewater via a photocatalytic process were synthesized. Photocatalytic degradation tests showed that approximately 40% of the tetracycline was degraded within 60 min of irradiation when using UV/vis light. It was also observed that the H_2O_2 generated in the photocatalytic reaction could lead to the development of heterogeneous photo-Fenton processes on the surface of the iron oxide nanoparticles. In this way, more hydroxyl and hydroperoxyl radicals were generated, promoting the photodegradation of tetracycline. Furthermore, in Contribution 6, commercial Mn_2O_3 nanoparticles were used for the efficient removal of bisphenol A (BPA) from wastewater via the activation of peroxymonosulfate (PMS) activation. A total of 15 transformation by-products were identified via the use of the LC/MS-MS technique during BPA degradation with the Mn_2O_3/PMS system, and three BPA degradation pathways were proposed. Compared to lab-made materials, it seems that commercial Mn_2O_3 catalysts led to a high TOC removal, low PMS consumption and a rapid BPA degradation rate.

In order to reduce the concentration levels of the anti-inflammatory compounds naproxen (NAP) and diclofenac (DCF) in different environmentally relevant aqueous matrices, several catalytic wet peroxide oxidation (CWPO) experiments using a magnetic catalyst, prepared with magnetite as a precursor, were assessed in Contribution 7. In this study, the optimization of the operating parameters was accomplished via the utilization of the Response Surface Methodology (RSM) coupled with the Box–Behnken design (BBD). The obtained removal percentages of the NAP and DCF were of 19 and 54%, respectively. In this case, the main NAP and DCF removal mechanism was based on the formation of •OH radicals. Drug degradation tests in real aqueous solutions (WWTP effluent, hospital wastewater) and disinfection tests were performed; it was then found that the magnetic catalyst has the potential to treat real effluents polluted with NAP and DCF. Contribution 8 studied the removal of the emerging contaminant Acetaminophen (ACE) from water via catalytic wet peroxide oxidation (CWPO) using metal-loaded mesoporous MCM-41 catalysts. The effect of the incorporation of Zn, Fe, Cu and Cr in the framework of MCM-41 solids and the reaction temperature (25–55 °C) on ACE removal were studied. The leaching results obtained with the Fe/MCM-41 catalyst were better than those previously reported in the literature, confirming the high stability of this material.

The effect of iron impurities in different activated carbons (ACs) of commercial and synthesized origin on the removal of phenols via CWPO was studied in Contribution 9. In this study, the activity of ROX 0.8 oxidized with the 673 K catalyst (lab prepared) was the highest among the tested materials, with phenol and TOC removal values of 92 and 57%, respectively, and an iron leaching concentration (0.67 mg L^{-1}) below the limits established by the European regulations. Moreover, the photocatalytic degradation of caffeine when using TiO_2 films immobilized on circular glass sheets as a catalyst under ultraviolet C irradiation was studied in Contribution 10. In this study, caffeine removal was found to increase as the irradiation time increased. In this way, the reactions kinetic were described well by the pseudo-first-order kinetic model. In addition, the caffeine removal efficiency using the TiO_2-coated glass sheets remained high (~100%) within 15 consecutive runs. Contribution 11 reported the degradation of cyanobacteria cylindrospermopsin (CYN) in water when utilizing an abundant mineral, pyrite, under solar light. This degradation system seems to be specifically efficient in the presence of relatively high amounts of natural organic matter because the uracil ring structure is broken down in the detoxification process of CYN.

Furthermore, Contribution 12 presents the preparation of a novel catalyst, $WO_3/MoCl_5$, via a thermal method. In this study, the degradation of two dyes in water, Crystal Violet (CV) and Rhodamine B (RB), was accomplished in normal and dark conditions. In addition, the reusability of the catalysts was studied within three cycles, maintaining 100% dye removal; the reactivation of the solids only involved their washing after the reaction. In another interesting work, Contribution 13 synthesizes NiMo catalysts through a simple co-reduction method; these catalysts are to be used in the catalytic degradation of hydrous

hydrazine at 70 °C, evaluating the production of hydrogen along the reaction. The support material-free nanocatalysts were highly efficient compared with bimetallic NiMo catalysts in terms of the hydrogen generation (TOF = 62, and 71.4 h^{-1}, for $Ni_9Mo_1(Pr_2O_3)_{0.375}$ and $Ni_4Mo@Cu_2O$, respectively). This study was the first to report the use of Pr-modified NiMo and core–shell $NiMo@Cu_2O$ catalysts for the production of H_2 from hydrous hydrazine.

Contribution 14 also explored the effect of the surface chemistry of a TiO_2 catalyst on the photocatalytic degradation of Bisphenol A. In this study, a correlation between the % exposure of the (001) facets of the TiO_2 solid and its catalytic activity could be established. Thus, it could be observed that the mineralization of BPA decreased as the exposure of the anatase (001) facets of the catalyst increased. Finally, Contribution 15 analyzed the potential application of the catalytic wet peroxide oxidation (CWPO) process for the efficient removal of the anti-inflammatory drug naproxen (NAP) from wastewater using magnetite/multi-walled carbon nanotubes (Fe_3O_4/MWCNTs) as a catalyst. In this study, the effect of the operation parameters, e.g., pH, temperature, and H_2O_2 dosage, on the CWPO process efficiency was evaluated. The versatility of the catalyst's applications was evidenced when different environmentally relevant effluents were efficiently treated.

The scientific contributions that comprise this Special Issue have shed significant light on the state of the art in emerging catalysis-based wastewater treatment technologies that could be incorporated into the industrial sectors.

We would like to express our gratitude to MDPI Editorial through and the *Catalysts* journal for the opportunity to serve as Guest Editors, contributing to the current state of the art in environmental catalysis for water remediation, as well as to the Assistant Editor, Ms. Janine Li, who worked hard with us to publish this Special Issue. In addition, we would like to thank all the authors who shared their research and the referees for their invaluable contributions.

Acknowledgments: S.A.T and J.G.R. thank the Spanish MICINN through the CATAD3.0 Project PID2020-116478RB-I00. In addition, the authors acknowledge the support of the Comunidad de Madrid (Spain) through the Industrial Doctorate Project IND2019/AMB-17114, and the Research Network REMTAVARES (S2018/EMT-4341).

Conflicts of Interest: The authors declare no conflicts of interest.

List of Contributions:

1. Akram, A.; Muzammal, S.; Shakoor, M.B.; Ahmad, S.R.; Jilani, A.; Iqbal, J.; Al-Sehemi, A.G.; Kalam, A.; Aboushoushah, S.F.O. Synthesis and Application of Egg Shell Biochar for As(V) Removal from Aqueous Solutions. *Catalysts* **2022**, *12*, 431. https://doi.org/10.3390/catal12040431.
2. Muñoz-Flores, P.; Poon, P.S.; Sepulveda, C.; Ania, C.O.; Matos, J. Photocatalytic Performance of Carbon-Containing CuMo-Based Catalysts under Sunlight Illumination. *Catalysts* **2022**, *12*, 46. https://doi.org/10.3390/catal12010046.
3. Xu, J.-M.; Chou, S.-H.; Zhang, Y.; Kumar, M.; Shen, S.-Y. Degradation of Dibutyl Phthalate Plasticizer in Water by High-Performance Iro_2-Ta_2O_5/Ti Electrocatalytic Electrode. *Catalysts* **2021**, *11*, 1368. https://doi.org/10.3390/catal11111368.
4. Zhang, J.; Zhang, H.; Li, W.; Yang, L.; Wu, H.; Mao, N. Photocatalytic Properties of a Novel Keratin char-TiO_2 Composite Films Made through the Calcination of Wool Keratin Coatings Containing TiO_2 Precursors. *Catalysts* **2021**, *11*, 1366. https://doi.org/10.3390/catal11111366.
5. Olusegun, S.J.; Larrea, G.; Osial, M.; Jackowska, K.; Krysinski, P. Photocatalytic Degradation of Antibiotics by Superparamagnetic Iron Oxide Nanoparticles. Tetracycline Case. *Catalysts* **2021**, *11*, 1243. https://doi.org/10.3390/catal11101243.
6. Chen, L.; Fu, W.; Hou, C.; Yang, Y.; Zhang, X. A Comprehensive Assessment of Catalytic Performances of Mn_2O_3 Nanoparticles for Peroxymonosulfate Activation during Bisphenol A Degradation. *Catalysts* **2021**, *11*, 993. https://doi.org/10.3390/catal11080993.
7. Huaccallo-Aguilar, Y.; Álvarez-Torrellas, S.; Martínez-Nieves, J.; Delgado-Adámez, J.; Gil, M.V.; Ovejero, G.; García, J. Magnetite-Based Catalyst in the Catalytic Wet Peroxide Oxidation for Different Aqueous Matrices Spiked with Naproxen–Diclofenac Mixture. *Catalysts* **2021**, *11*, 514. https://doi.org/10.3390/catal11040514.

8. Hachemaoui, M.; Molina, C.B.; Belver, C.; Bedia, J.; Mokhtar, A.; Hamacha, R.; Boukoussa, B. Metal-Loaded Mesoporous MCM-41 for the Catalytic Wet Peroxide Oxidation (CWPO) of Acetaminophen. *Catalysts* **2021**, *11*, 219. https://doi.org/10.3390/catal11020219.
9. Pinho, M.T.; Ribeiro, R.S.; Gomes, H.T.; Faria, J.L.; Silva, A.M.T. Screening of Activated Carbons for the Treatment of Highly Concentrated Phenol Solutions Using Catalytic Wet Peroxide Oxidation: The Effect of Iron Impurities on the Catalytic Activity. *Catalysts* **2020**, *10*, 1318. https://doi.org/10.3390/catal10111318.
10. Muangmora, R.; Kemacheevakul, P.; Punyapalakul, P.; Chuangchote, S. Enhanced Photocatalytic Degradation of Caffeine Using Titanium Dioxide Photocatalyst Immobilized on Circular Glass Sheets under Ultraviolet C Irradiation. *Catalysts* **2020**, *10*, 964. https://doi.org/10.3390/catal10090964.
11. Wang, S.; Chen, Y.; Jiao, Y.; Li, Z. Detoxification of Cylindrospermopsin by Pyrite in Water. *Catalysts* **2019**, *9*, 699. https://doi.org/10.3390/catal9090699.
12. Kim, D.; Kim, G.; Bae, H.; Kim, E.; Moon, B.; Cheon, D.; Tarte, N.H. An External Energy Independent $WO_3/MoCl_5$ Nano-Sized Catalyst for the Superior Degradation of Crystal Violet and Rhodamine B Dye. *Catalysts* **2019**, *9*, 642. https://doi.org/10.3390/catal9080642.
13. Liu, Y.; Zhang, H.; Ma, C.; Sun, N. Modified Nimo Nanoparticles for Efficient Catalytic Hydrogen Generation from Hydrous Hydrazine. *Catalysts* **2019**, *9*, 596. https://doi.org/10.3390/catal9070596.
14. Žerjav, G.; Pintar, A.; Ferentz, M.; Landau, M.; Haimovich, A.; Goldbourt, A.; Herskowitz, M. Effect of Surface Chemistry and Crystallographic Parameters of TiO_2 Anatase Nanocrystals on Photocatalytic Degradation of Bisphenol A. *Catalysts* **2019**, *9*, 447. https://doi.org/10.3390/catal9050447.
15. Huaccallo-Aguilar, Y.; Álvarez-Torrellas, S.; Larriba, M.; Águeda, V.I.; Delgado, J.A.; Ovejero, G.; García, J. Optimization Parameters, Kinetics, and Mechanism of Naproxen Removal by Catalytic Wet Peroxide Oxidation with a Hybrid Iron-Based Magnetic Catalyst. *Catalysts* **2019**, *9*, 287. https://doi.org/10.3390/catal9030287.