

Editorial

Catalytic Processes for Water and Wastewater Treatment

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Water and wastewater treatment still face significant challenges today. Due to climate change, water shortages are already noticeable in many regions of the world. To overcome these problems, alternative water sources must be generated and used, for example, treated wastewater, rainwater, surface water, etc. Since the development of highly sensitive methods reveals the presence of hazardous compounds in low concentrations, these water sources must be treated before use. The detected compounds include pharmaceuticals, which have a serious influence on human health. Generally, the concentrations of these compounds is low. However, recent statistics have revealed that the per capita consumption of medicines within the European Union for the period of 2000–2014 has almost tripled, reflecting the excessive and perhaps reckless use of similar products. In particular, there are numerous different ways that remedies may permeate into surface recipients, such as landfill leachates, excessive consumption by people themselves, high volumes of organic hospital effluents, and the undeniably incorrect rejection of medicines that have expired or were not used. Due to the incomplete biodegradation of complex organic molecules in conventional wastewater treatment plants, the accumulation of organic pollutants on surface waters endangers biodiversity through its potential toxicity. Thus, these pollutants should be removed. Many processes have been proposed for their degradation/removal, including catalytic methods. These methods, in which catalysts are in a solid form in particular, exhibit significant advantages such as easy separation, better stability, higher activity, and a lower cost of the process. Catalytic oxidation or reduction processes are among the most efficient processes. These include photocatalysis and sulfate- and hydroxyl-radical-based advanced oxidation processes.

The application of a solid catalyst in a removal experiment combines not only the oxidation reaction but also the adsorption of the contaminant on the catalyst surface. The adsorption is a necessary step for the catalytic process, and hydrophilicity of the surface is required in such cases. By itself, adsorption very useful for removing heavy metal ions. Heavy metals are highly soluble in water and are toxic, carcinogenic, and non-degradable. In the study by Neelgund et al. [1], a nanocomposite CNTs-Ag₂S was prepared through the facile deposition of Ag₂S nanoparticles onto oxidized carbon nanotubes (CNTs), using the hydrothermal method. At first, the hydrophobic CNTs were treated with concentrated nitric and sulfuric acids under reflux. The modification increased the hydrophilic nature of the CNTs by introducing oxygen species onto the surface. The Ag₂S nanoparticles were then deposited onto the modified CNTs. The CNTs-Ag₂S is more efficient than CNTs and Ag₂S and can completely adsorb Cd (II) within 80 min. The adsorption follows pseudo-second-order kinetics, while intraparticle diffusion and the boundary layer effect contribute to the removal of Cd (II) [1]. The CNTs-Ag₂S can also act as a photocatalyst for the degradation of alizarin yellow R (AYR), a dye used in the textile industry. With the irradiation of the material with natural sunlight, complete degradation of AYR is achieved. The degradation follows pseudo-first-order kinetics. Different reactive species such as electrons, holes, hydrogen peroxide, and ROS are the active species for the degradation, and the CNTs-Ag₂S was found to be stable for three cycles [1].



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Photocatalysis is probably the most common method used for the degradation of organic compounds in water matrices, and titania-based materials are widely used as photocatalysts. In the study by Khan et al., [2] binary CdTiO₂ and ternary NiCdTiO₂ were compared with bare TiO₂ for the photocatalytic degradation of organic dyes such as methylene blue (MB) and methyl green (MG). It was found that the photocatalytic degradation of TiO₂, CdTiO₂, and NiCdTiO₂ for MB was 77, 82, and 86%, while for MG the binary and ternary materials were even better, achieving a degradation of 63.5, 88, and 97.5%, respectively. In all three materials, the TiO₂ was in the form of anatase, while the deposition of Cd and Ni caused a red shift in the absorbance spectra by coupling with Ni and Cd. This shift can be considered responsible for the enhanced photocatalytic activity.

Kong et. al. [3] used anatase TiO₂ to degrade Auramine O (AO) under 365 nm light irradiation. The titania nanoparticles had a mean diameter of 100nm. The degradation process followed a pseudo-first order reaction, with $k = 0.048 \pm 0.002 \text{ min}^{-1}$. This value is significantly lower than the corresponding value for the degradation of methylene blue ($0.173 \pm 0.019 \text{ min}^{-1}$); this is due to the nonplanar structure of AO. The higher photocatalytic efficiency was found to be 96%, and it decreased nonlinearly with an increase in the initial concentration and catalyst dosage. Finally, the authors confirmed the superiority of titania nanoparticles compared to the use of micro-sized powders.

The degradation process is more complicated when more than one dye is present in the solution; however, this scenario is also more realistic. Therefore, there are numerous studies in which binary or ternary solutions of dyes are used in photocatalytic degradation. In this recent review [4], the photocatalytic behavior of methylene, rhodamine B, and methyl orange in their binary or ternary solutions was summarized. In this review, the importance of diffusion was discussed. It was revealed that smaller dyes with a planar conformation are easier to degrade and dominate in photocatalytic degradation in their binary or ternary solutions.

Although titania is likely the better photocatalyst, it has some limitations, among which is its limited optical adsorption in the visible light spectrum. Many methods have been used to further expand the optical UV–Vis absorption region of TiO₂ and to enhance the efficient light-induced charge separation. The best option reported is to combine TiO₂ with typical narrow-bandgap quantum dots (QDs) of different semiconductors and carbon quantum dots (CQDs). In the work of Rawal et. al., [5] nitrogen (N) and sulfur (S) co-doped graphene quantum dots (GQDs) were used. This material has a narrowed E_g value that improves photogenerated electron transfer due to π -conjugation. The activity was found to be 2.3–3 times higher than that of TiO₂. The photocatalyst was stable for at least three cycles, and the formation of C–O–Ti bonds provided a charge transfer pathway.

BaTiO₃ is another promising material, especially when it is combined with the double-hole coupling of anion–anion combinations. Barium titanate has a perovskite structure and large band gap of 3.0–3.3 eV; it has the appropriate band positions to split water into hydrogen and oxygen, although the band gap should be regulated in lower values to provide the ability to absorb more visible light. It has also been reported that by substituting a metal dopant at a Ba or Ti site, a direct effect on the band gap energy (E_g), the stability, and the formation of oxygen vacancies can be achieved. On this basis, the electronic properties and optical absorption characteristics of BaTiO₃, with the double-hole coupling of anion–anion combinations using first-principles methods, were studied. It was found that the N–N co-doped BaTiO₃ exhibited a more favorable formation energy under an O-poor condition, and all the co-doping configurations reduced the value of E_g . The tuning of the E_g makes the photocatalyst a promising candidate for visible-light water splitting [6].

Due to the importance of photocatalysis, as it is one of the most innovative advanced oxidation techniques used, many materials have been tested for their photocatalytic activity. A photocatalytic process should present a high efficiency, low cost, and avoid the production of intermediate products with a high toxicity. The selection of a photocatalyst is very important, as it must be cheap, stable, environmentally friendly, and have high activity. Usually, a photocatalyst is a semiconductor with a high degree of absorption of light, prefer-

ably solar light, and high rate of photogenerated charge carriers. One review summarized the application of CuS as a photocatalyst [7]. CuS is a p-type semiconductor with different nanostructures, such as nanoparticles and quantum dots or heterojunctions with carbon materials, organic materials, or metal oxides. The recent developments in organic pollutant photodegradation with a CuS as catalyst are discussed on the basis of different synthesis parameters (Cu:S molar ratios, surfactant concentration etc.) and properties (particle size, morphology, bandgap energy, and surface properties)

In the study by Le Pivert et. al., [8], ZnO nanoparticles were synthesized onto Zn and used as roof for the photocatalytic removal of organic contaminants in rainwater. The authors prepared the ZnO nanoparticles on the Zn roof with a hydrothermal growth method in 2 h. The presence of Zn (II) ions and the native oxide film on the Zn surface acted as active sites for the growth of ZnO nanoparticles. The photocatalytic activity was determined using Methylene Blue under UV irradiation and Acid Red 14 with solar light.

The removal of Methyl Tert Butyl Ether (MTBE) using $\text{Fe}_2\text{O}_3/\text{MgO}$ as a catalyst was studied in the presence of arsenic under UV irradiation [9]. The catalyst contained 33.06% Fe_2O_3 and 45.06% MgO . The main parameters of the degradation process, including the effect of arsenic and MTBE concentrations, catalyst mass, pH, etc., were studied. It was found that the concentration of MTBE influenced the most the photocatalytic process. The higher performance in the removal of MTBE was achieved at pH = 5 and an initial concentration of MTBE equal to 37.5 mg/L, with a catalyst dose of 1.58 mg/L without the presence of As. The presence of arsenic decreased the removal efficiency remarkably. Therefore, pretreatment for the removal of arsenic and more details of this interference effect are suggested.

Psychiatric drugs, including amisulpride, a typical antipsychotic drug, are a class of pharmaceuticals that are often prescribed and used in a wide range of mental health problems. Their use is increasing worldwide. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) can be used as photocatalyst for the degradation of this type of drug. In the work of Antonopoulou et. al. [10], the application of $\text{g-C}_3\text{N}_4$ catalysts for the degradation of amisulpride was studied. Particularly, in the degradation process of amisulpride under UV-A irradiation with the application of $\text{g-C}_3\text{N}_4$, the transformation products and the ecotoxicological assessment were investigated. It was found that the degradation pathways of amisulpride included mainly oxidation, dealkylation, and the cleavage of the methoxy group. The main reactive species were found to be h^+ and $\text{O}_2^{\bullet-}$. In ultrapure water, the transformation products had a low toxicity, while an increased toxicity was observed when wastewater was used as a matrix, especially at the beginning of the process.

$\text{g-C}_3\text{N}_4$ is an interesting material with a graphene-like structure, chemical and thermal stability, and a low cost. Is a good visible light absorber and can be used in a wide variety of photocatalytic applications. It has a narrow band gap of ~2.7 eV, but it exhibits a high recombination process and thus limited activity. This drawback can be overcome with the combination of $\text{g-C}_3\text{N}_4$ and MoS_2 , since heterostructuring can decrease the recombination effects between electrons and holes. The photocatalytic removal of psychiatric drugs in secondary effluents of hospital wastewater with $\text{g-C}_3\text{N}_4$ or 1% $\text{MoS}_2/\text{g-C}_3\text{N}_4$ was studied [11] in a laboratory-scale pilot plant and in a solar simulator apparatus. The results showed that the 1% $\text{MoS}_2/\text{g-C}_3\text{N}_4$ was more active than the $\text{g-C}_3\text{N}_4$, with 54% and 30% removal, respectively. The degradation followed first order kinetics, and six transformation products were generated during degradation; these were totally degraded at the end of the treatment.

As previously noted, research on new materials is always challenging. These materials should be active, selective, and of a low cost. It is also desirable that they are ecofriendly, and, if possible, they should originate from the valorization of waste. Biochar is such a materials. It can be produced from any kind of biomass through a pyrolysis process under a limited- or no-oxygen atmosphere. Generally, biochar has a moderate or high specific surface area, a hierarchical pore structure, and active surface groups. The utilization of biochar and biochar-based nanocomposites for dye removal from wastewater was

reviewed [12]. The removal of dyes from wastewater via natural and modified biochar follows numerous mechanisms, such as precipitation, surface complexation, ion exchange, cation– π interactions, and electrostatic attraction. The preparation parameters and the post treatment of biochar can alter the surface speciation, and the modified biochar can exhibit better performance in the removal of dyes. A framework for artificial neural networking and machine learning to model the dye removal efficiency of biochar from wastewater was also proposed.

In addition to the excellent adsorption properties of the biochar, it can also act as a catalyst for the activation of persulfate ions and the oxidation of organic compounds. Biochar from lemon stalks, pyrolyzed at 850 °C under a limited oxygen atmosphere, produced a highly active and selective biochar for the oxidation of sulfamethoxazole (SMX), using sodium persulfate as oxidant [13]. The biochar had a significant amount of carbonates and could completely degrade 0.5 mg L⁻¹ SMX within 20 min using 500 mg L⁻¹ sodium persulfate (SPS) and 100 mg L⁻¹ biochar in ultrapure water (UPW). The degradation process is favored at a low pH and in the presence of chlorides. The complexity of the water matrices usually has a negative impact on the degradation. The mechanism follows radicals with hydroxyl radicals as the main active species and non-radical pathways; electron transfer pathway was proven with electrochemical characterization. The biochar from lemon stalks is stable and active.

The combination of more than one advanced oxidation process often leads to synergistic effects and has proved to be a more efficient strategy. In this respect, the degradation of SMX was studied using a CuOx–BiVO₄ catalyst as either a photocatalyst or persulfate (sodium persulfate, SPS) activator [14]. This hybrid process (catalyst/SPS/Solar System) was found to be synergistic for copper-promoted BiVO₄ photocatalysts. Specifically, different loadings of CuOx (0.75–10% wt.) were deposited on BiVO₄ and tested under solar irradiation for the degradation of SMX. The most active catalyst was found to be the 0.75 CuOx–BiVO₄, while a higher loading of CuOx delayed the degradation process. The complexity of the water matrix (from ultrapure to bottled, BW, and wastewater, WW) also has a negative effect on the degradation process. The addition of SPS is beneficial for the degradation process, and the two processes exhibit a synergistic effect. Specifically, in a BW matrix, the application of SPS results in complete elimination after 60 min, while in the absence of SPS, an SMX degradation of only 40% took place in 120 min under solar light. For the WW, ~37%, 45%, and 66% degrees of symmetry were determined using 0.75, 3.0, and 10.0 CuOx–BiVO₄, respectively.

Catalytic processes for water and wastewater treatment are a promising approach to improving the quality of the water. Although photocatalysis is the most popular and attractive process due to its simplicity and utilization of the abundant solar light, the combination of other advanced oxidation processes can lead to effective systems. Interestingly, the presented experimental results highlight that it is difficult to decide which catalyst or process is better, and the determination of the activity must be performed in a wide window of operating parameters.

Conflicts of Interest: The author declares no conflict of interest.

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