

Editorial

Photoactive Materials for the Catalytic Decomposition of Water Pollutants

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The use of UV and Vis light (in the form of solar energy) in the presence of semiconductor nanostructured materials as photocatalysts is effective for the adequate removal of a wide spectrum of pollutants (resistant to other degradation techniques) in various types of wastewater, which are important elements of the development of science related to photocatalysis. The following is a brief overview of several papers included in the special issue on points to the practical aspects of this type of research. The use of photolysis processes in organic matter degradation not only has practical applications in wastewater treatment but is also of major importance in the pretreatment of samples prior to the trace analysis of numerous analytes. A special, very interesting application is the preparation of a sample before speciation analysis. Particularly, speciation analysis is currently the most important environmental challenge in the case of toxicity of xenobiotic in water systems. For example, As and Tl speciation in water polluted with surfactance require the degradation of them before HPLC separation of species and electrochemical analysis or ICP MS determination. The heterogeneous degradation is simple to implement prior to ultra-traces determination and is the only one allowed before the speciation analysis. In the trace analysis of water, organic compounds are the principal interfering compounds reducing the quality of the obtained results or even preventing the determination of the examined analytes altogether. The oxidation can be performed using homogenous photolysis (UV mineralization with hydrogen peroxide addition), while heterogenous photolysis using semiconductors helps to increase the removal efficiency of interferents dissolved in water. Utilizing semiconductor nanostructured materials as photocatalysts has been shown to be effective for the adequate removal of a wide spectrum of pollutants in water. Several semiconductor systems are used in the degradation of organic compounds, e.g., TiO_2 , Fe_3O_4 , WO_3 , Fe_2O_3 , ZnO , and mixtures of these oxides enriched with various precious metals, such as silver or gold. The review included in the special issue presents state-of-the-art of photocatalysis as a simple and effective technique for sample pretreatment in ultra-trace and speciation analysis. However, the paper also includes unpublished data about hierarchical systems with an Fe_2O_3 layer between WO_3 layers. The operation of such systems depends on the arrangement of the layers and the operating pH. This allows them to be adapted to the simplification of organic matter before total content analysis (pH 2) or before speciation analysis (pH 6). An interesting part of the study is dedicated to the equilibrium of chromium ions under homogeneous and heterogeneous photolysis conditions [1].

Access to clean water is limited and liquid waste is a serious threat to many ecosystems. Therefore, water purification is an important environmental issue. For example, this issue is a presence of phenol and its derivatives are present in effluents from several industrial processes, such as petroleum refinement (produced water) and the pharmaceutical industry. These components are highly toxic. The photocatalyst was prepared by a simple method from the ammonium oxalate of niobium and nickel nitrate, resulting in heterostructures (NiNb/Pt catalyst). The efficiency was proved by the degradation of phenol in a seawater matrix and distilled water. The tests were conducted in the presence and absence of UV-C light (germicidal, $\lambda = 254 \text{ nm}$), and with varying solutions containing a variety of Pt



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content and diverse pH. The reuse of the catalyst was also studied, and the photocatalytic mechanism was investigated by tests with scavenger agents and terephthalic acid. It should be pointed that the study showed that photodegradation using the NiNb/Pt catalyst achieved 65% phenol removal in seawater and about 57% removal in distilled water [2].

A number of photocatalysts are proposed for the decomposition of various compounds in an aqueous environment. One of these examples is a work in which Ag_2CO_3 (micro-sized particles with a rectangular shape) was used. The photocatalytic activity of the catalyst was evaluated in the degradation of 4-tert-butylphenol under simulated solar light irradiation. The effects of 4-tert-butylphenol initial concentration (ppm), catalyst dosage ($\text{X}00 \text{ mg L}^{-1}$), different types of lamp sources, and the water matrix were investigated. Complete degradation was achieved after 60 min in the presence of $200 \text{ mg of L}^{-1} \text{ Ag}_2\text{CO}_3$. Furthermore, the effect of anions such as CO_3^{2-} , HCO_3^- , NO_3^- , and Cl^- in the concentration range of $100\text{--}300 \text{ mg L}^{-1}$ was also studied. Carbonates promoted the photocatalytic degradation process, while hydrogen carbonates and nitrates exhibited an inhibition effect, which was marked with increasing hydrogen carbonate and nitrate concentrations. The presence of chlorides at the concentration increased the degradation, but concentrations higher than 100 mg L^{-1} inhibited the photocatalytic reaction. Cyclic experiments showed that the catalyst practically retained its catalytic activity after three successive experimental runs [3].

Doping ZnO with appropriate foreign metal and/or non-metal ions is one of the most promising ways to improve both the extension of ZnO photosensitization to the visible region and the separation of charge carriers. Herein, Mn-doped ZnO nanoparticles were synthesized using a precipitation method. The effect of the Mn amount on the physico-chemical properties of these nanomaterials was investigated. The photocatalytic properties of the synthesized nanomaterials were assessed through methyl orange under visible light. The obtained results showed that the properties of the synthesized Mn-ZnO nanomaterials depended greatly on the Mn amount and it was found that Zn(II) is substituted by Mn(II)/Mn(III). The photocatalytic experiments revealed that even the discoloration reached 96%, while the chemical oxygen demand reached only 1% after 820 min of visible illumination. The enhanced photocatalytic activity was attributed to the efficient separation of charge carriers. The active species quenching experiments showed that the holes are the main active species in methyl orange degradation under visible light in the presence of 10% Mn-ZnO [4].

An interesting aspect of research is the creation of complex systems with high specificity and efficiency. The hydrothermal sol-gel method was used to synthesize hexagonal Bi@PMOS and Ce@PMOS. These PMOS provided an opportunity for bismuth and cerium to retain a hexagonal configuration alongside their traditional crystalline phases (tetragonal and cubic) in Bi_2O_3 and CeO_2 nanosheets. All produced materials were found to be dynamic under sunlight irradiation for the degradation of methylene blue and methyl orange. However, the Bi_2O_3 and CeO_2 nanosheets showed better potential and photocatalytic performances than Bi@PMOS and Ce@PMOS due to the presence of the unique blend of crystalline phases. These showed characteristic vibrations of successfully loaded bismuth and cerium with hexagonal symmetry. The optical response and detection of reactive species were carried out by photoluminescence and showed emissions at 700 nm. A UV-vis spectrophotometer scanned the photocatalytic competences of the synthesized nanomaterials through the degradation of methylene blue and methyl orange dyes. The Bi_2O_3 and CeO_2 photocatalysts were regenerated and their photodegradation results were also recovered. Bi_2O_3 and CeO_2 showed only 10% and 8% (for methylene blue), and 8% and 10% (for methyl orange) decline in catalytic efficiency, respectively, even after four consecutive recycles. These results demonstrate that these materials are dynamic, long-lasting photocatalysts for the rapid degradation of azo dyes in contaminated water [5].

The use of waste, e.g., biomass produced during the production on a macro scale, e.g., palm oil, is not only scientifically valuable, but also accommodates the sustainable development of the economy and science. Photocatalytic biomass valorization has proven to be a valuable approach for sustainably constructing value—added products from waste

materials. The present study aimed to investigate Bismuth ferrite (BiFeO_3) nanoparticles combined into carboxymethyl cellulose (CMC) obtained from oil palm empty-fruit-bunch waste and used it as a catalyst composite for the degradation of anionic dyes, specifically on methyl orange and congo red. The parameter that affects the formation of carboxymethyl cellulose from wastes, such as the degree of substitution, depends upon the alkalization reaction time and NaOH concentrations. The highest degree of substitution was obtained at 1.562 and found at 60% NaOH with 9 h of alkalization, very close to the degree of substitution value of the commercial carboxymethyl cellulose. The comparative study on photocatalytic degradation of methyl orange and congo red using the CMC from wastes and the commercial CMC reinforced with 0.8% BiFeO_3 showed a minor difference in removal percentage. Nevertheless, it is interesting that the carboxymethyl cellulose from wastes film exhibited remarkable stability with an improvement in terms of tensile strength and stayed more intact than that of commercial carboxymethyl cellulose [6].

Research related to the application of photoactive materials for the catalytic degradation /simplification/decomposition of water pollutants has high application potential and should be continued. The creation of simple and well-known systems for the hereto catalytic decomposition of organic compounds should be carried out at the basic level of as well as in application research.

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

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