Abstract of the doctoral dissertation by MSc. Patrycja Wilczewska, entitled: Synthesis, characterization, and application of bismuth-based semiconductors for photocatalytic removal of micropollutants from the water phase

Bismuth halides (BiOX, X = F, Cl, Br, I) are non-toxic, chemically and photochemically stable layered materials. In this work solvents: water, aqueous mannitol solutions, mixtures of ethylene glycol and anhydrous ethanol, and glycerin were used in solwo/hydrothermal synthesis. The solvents interacted with: free ions Bi^{3+} and X^-, forming BiOX crystallites, and atoms in (110) and (102) planes affecting the crystallographic properties, morphology, states of bismuth atoms, band structure, and light absorption capacity. Mono- and polyhydroxy alcohols used in the synthesis of BiOX acted as structure-directing compounds influencing the photooxidizing and photoreducting properties of the obtained semiconductors. The photocatalytic activity was evaluated based on the removal rate of the rhodamine B dye, the reduction of Cr(VI) in the form of $Cr_2O_7^{2-}$ ions, and the removal of the three anticancer drugs 5-fluorouracil (5-FU), imatinib (IMA), and cyclophosphamide (CF). The research showed the materials synthesized from mannitol solutions had the highest photooxidizing and photoreducing properties.

The introduction of the second type of halogen to the BiOCl crystal lattice contributed to the increased photocatalytic activity in relation to 5-FU, IMA, and CF, while in the case of $Bi_4O_5Br_2$, IMA and CF were removed more effectively. Additionally, the use of imidazolium ionic liquids (bmimX) as a precursor of halogens changed the morphology and increased the ability to mineralize organic micropollutants of the obtained materials. In the synthesis, bmimX acted as a source of X^- ions, template, and structure-directing agent during the formation of nanostructures. The conducted research showed that the optimal Cl: Br ratio in the synthesis introduced with KCl and KBr was 1.3: 0.7.

Antineoplastic pharmaceuticals are biologically active substances, with carcinogenic, mutagenic, and teratogenic properties. In addition, they are resistant to the conventional wastewater treatment and thus, they can be introduced and accumulated in the environment. The presented work showed the photocatalytic degradation of anticancer drugs present in single solutions and mixtures in the presence of photocatalysts from the group of bismuth oxyhalides (BiOX (X = Cl, Br, I), BiOClBr and $BiOCl_nBr_m/Bi_4O_5Br_2$) was effective under simulated environmental conditions.

Anions and cations naturally present in waters and biologically treated sewage caused inhibition (SO_4^{2-}, NO_3^-, Cl^-), acceleration (HCO_3^-, Fe^{3+}, Ag^+) or did not affect (Ca^{2+}) the removal of 5-fluorouracil under the irradiation of simulated sunlight and visible light in the presence of the $BiOCl_nBr_m/Bi_4O_5Br_2$ composite. Biologically active micropollutants may form more toxic mixtures during decomposition. The conducted experiments proved that obtaining a mixture of imatinib decomposition products by bismuth oxyhalides shows 3.3 times lower ecotoxicity than the stock solution, and in the case of 5-fluorouracil, the ecotoxicity to *Chlorella vulgaris* was low. The degradation mechanism of cytostatics depends on their chemical structure. In the presence of BiOClBr, 5-FU was mainly decomposed by (h^+), IMA in reaction with $^{\bullet}O_2^-$ and CF by (e^-), (h^+), and $^{\bullet}O_2^-$. The tested materials successfully removed low biodegradable anticancer drugs due to the effective production of $^{\bullet}O_2^-$ and a large number of active sites.

Keywords heterogeneous photocatalysis, bismuth oxyhalides, BiOX, anticancer pharmaceuticals, degradation of water micropollutants