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Novel Zr(IV) and Hf(IV) – Schiff base complexes as white light photocatalysts for the degradation of methylene blue

Lilachjini S., Adhikari A. A. D. M., Amnah M. H. F., and Hettiarachchi C. V.*

Department of Chemistry, Faculty of Science, University of Peradeniya, Sri Lanka.

** champikav@sci.pdn.ac.lk*

Untreated dyes found in industrial effluent damage aquatic habitats and diminish biodiversity. Therefore, dye-containing hazardous substances must be treated before being disposed of. Nowadays, TiO_2, ZnO, metal niobates and titanates, as well as other semiconductors with a large band gap, serve as the foundation for extensively used UV photocatalytic materials with high performance. To produce novel photocatalysts with excellent efficiency under white light, zirconium(IV) and hafnium(IV) Schiff base complexes were synthesized and studied to determine their potential as photocatalysts for the degradation of methylene blue (MB) dye. The Schiff base, $H_2(Sal)_2$(hexamethylenediamine) (SB) ligand, a yellow crystalline solid (m. p. 65 ^{0}C, 18.45%) was synthesized by the condensation of salicylaldehyde and hexamethylenediamine. Coordination complexes of Zr(IV) and Hf(IV) were synthesized by mixing M : SB in 1:2 ratio to obtain light yellow and orange solids with yields of 58.8% and 6.5%, respectively, and both exhibit high thermal stability with melting points above 300 ^{0}C. The characterization of both complexes was conducted through Fourier-transform infrared spectroscopy (FTIR). The three-dimensional structures of the complexes were predicted using sophisticated computer modeling. Additionally, the ORCA 5.0 code, the hybrid B3LYP functional, and the def2-TZVP basis set were used for calculations in the aqueous phase. The catalytic efficacy of the Zr(IV) and Hf(IV) Schiff base complexes for the degradation of methylene blue (MB) was systematically examined under white light irradiation for varying durations (30, 60, 90, 120, and 150 minutes) using UV-Vis spectroscopy. The study was conducted both in the absence and presence of different volumes of 30% H_2O_2 (0.1, 0.15, and 0.2 mL) to investigate the role of H_2O_2 in enhancing the catalytic performance. The complexes' strong metal-ligand interactions, excellent thermal stability, and favorable electronic characteristics contribute to their increased activity. Overall, this study demonstrates that the synthesized metal complexes act as excellent photocatalysts in the presence of H_2O_2 for organic dye degradation, offering an environmentally benign method of wastewater treatment. In conclusion, Zr(IV) and Hf(IV) Schiff base complexes showed the highest degradation percentage of methylene blue after 150 minutes with 0.2 mL of 30% hydrogen peroxide, 73% and 82%, respectively. Further research into understanding mechanistic pathways may improve their practical applicability in industrial wastewater treatment.

Keywords:
Zirconium; Hafnium; Schiff base ligand; photocatalysis

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