

ABSTRACT

Water pollution and the scarcity of quality drinking water are critical ecological issues worldwide, significantly affecting natural ecosystems and living organisms. Rapid industrialization and the soaring human population have greatly increased the demand for water resources, leading to an extensive amount of wastewater being produced globally. Many countries are currently grappling with the challenge of treating effluents contaminated with harmful organic dyes. Recent advancements in industrial processes and improved living standards have led to the emergence of various water contaminants, with dyes being a primary concern. Organic dyes are extensively utilized in the production of textiles, leather, and paper, contributing significantly to water pollution. Several countries are currently facing the formidable task of addressing effluents with harmful organic dyes. According to data from the World Bank, textile dyeing and finishing processes contribute to an estimated 15–20% of industrial wastewater production. In India alone, the dyestuff industry contributes around 60,000 metric tons, representing approximately 6.6% of the global colorant consumption. Notably, Methylene Blue (MB) dye holds significant importance in the textile sector. Its complex molecular structure with resistance to light, temperature, chemicals, and water, thereby intensifying environmental pollution.

To address this issue, numerous methods have been proposed, including biodegradation (aerobic and anaerobic degradation), electrochemical treatment, adsorption, ozonation, coagulation and flocculation, filtration, ion exchange, and photodegradation. Among these, photocatalytic degradation in aqueous environments emerges as a straightforward and effective approach for dye reduction.

In the present study, TiO_2 was chosen as the primary photocatalyst, and its photocatalytic efficiency was enhanced through the doping of Lanthanum (La) and iodine (I) and co-

doping La-I. The synthesis of the photocatalysts was achieved using the solution-combustion technique. The photocatalytic activity of the synthesized photocatalysts was evaluated through kinetic studies of dye degradation conducted in a UV-photochemical reactor. In the UV-photochemical reactor, photodegradation reactions were carried out using quartz tube. Additionally, following dye degradation, the used photocatalysts were regenerated for further use in the dye degradation process. A phytotoxicity study was conducted to examine the harmful effects of MB dye on germination of mung bean (*Vigna Radiata*) seeds. The results suggest that its harmful effects can be reduced drastically by degrading the MB dye and transforming wastewater into less toxic. The germination test of "*Vigna Radiata*" was done to determine phytotoxicity as part of the investigation into the potential use of photocatalytically treated water in irrigation.

The Undoped TiO₂, La-doped TiO₂, [Ti_{1-x}La_xO₂ (x = 0.00, 0.005, 0.01, 0.015, 0.02 and 0.025)], I-doped TiO₂ [Ti_{1-x}I_xO₂ (x = 0.01, 0.02, 0.03, 0.04 and 0.05)] and La-I co-doped [Ti_{1-x-y}La_xI_yO₂, where x = 0.00 – 0.05, y = 0.00 – 0.005] TiO₂ photocatalysts with enhanced photocatalytic activity were synthesized using a citric-acid-assisted solution-combustion method. The characterization of synthesized photocatalysts were done using XRD, DRS, FTIR, XPS, and FE-SEM analysis. XRD analysis confirmed the presence of the anatase phase of TiO₂ in all synthesized photocatalysts (undoped TiO₂, La-doped TiO₂, I-doped TiO₂ and La-I co-doped TiO₂). The average crystallite size of undoped TiO₂, 1.5% La-doped TiO₂, 3% I-doped TiO₂ and 2% La- 3% I co-doped TiO₂ was found to be 30.16, 19.90 nm, 15.20 nm, and 13.76 nm, respectively. DRS analysis indicated that doping of La and I and co-doping of La-I in TiO₂ reduced its band-gap energy from 3.2 to 2.7 eV, 3.2 to 1.95 eV and 3.2 to 2.68 eV for 1.5% La-doped, 3% I-doped and 2% La-3% I co-doped TiO₂ respectively. FTIR spectra revealed the presence of hydroxyl and chemisorbed water groups in the photocatalysts. XPS spectra showed the presence of all

expected elements in their respective oxidation states. FE-SEM analysis indicated that all synthesized photocatalysts exhibited a spherical shape.

The dye degradation kinetic studies were done with all photocatalysts in UV-Photochemical reactor. It demonstrated that 1.5% La-doped, 3% I-doped and 2% La-3% I co-doped TiO₂ exhibited the highest photocatalytic activity, surpassing that of Aeroxide P-25. The degradation kinetics of MB with all the catalysts was found to be pseudo-first-order. With 98% MB dye degradation, it was found that the 2% La-3% I co-doped TiO₂ was the best catalyst out of all the best ones (1.5% La-doped, 3% I-doped and 2% La-3% I co-doped TiO₂). These photocatalysts were reused after regeneration for five times to degrade MB dye; the reuse makes photodegradation process more economical. The results of the photodegradation indicate that the photocatalyst's performance diminishes with the number of reuses. After fifth cycle a loss of 7.85%, 10.13% and 11.67% of activity was there for 1.5% La-doped, 3% I-doped and 2% La-3% I co-doped TiO₂ respectively.

In phytotoxicity study when mung bean seeds were treated with MB solution, their root and shoot lengths were shorter than those treated with distilled water and degraded MB solution. The toxicity of the MB dye was substantially diminished when it was subjected to photocatalytic degradation. After 7 days of incubation, the root and shoot lengths of mung beans irrigated with the degraded dye were significantly greater than those of irrigated with untreated MB solution (30 ppm). These results suggest that its harmful effects can be reduced drastically by degrading the MB dye.