Green synthesis of some novel nanocomposite materials and their photocatalytic activity

Abstract of

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Abstract

The primary objective of the present research work is to synthesized some novel nanocomposite materials through the utilization of diverse plant extracts and subsequently evaluate of their photocatalytic efficacy in the degradation of harmful organic pollutants.

Chapter 1 deals the introductory section, dealing nanomaterials, their fundamental principles, classification, synthetic methodologies, and an extensive review of relevant literature. It also elucidates the influence of various physical parameters and concepts on the size and shape of synthesized nanomaterials. Scope drawn from exhaustive literature review, this chapter outlines the research objectives and potential outcomes.

Chapter 2 focuses on the principles, operation, and applications of various instrumental techniques, such as UV-Visible spectroscopy, FTIR spectroscopy, XRD, SEM@EDAX, FESEM, TEM, and XPS, employed for characterizing the produced nanomaterials. Additionally, it covers experimental methods, including photocurrent response measurement, COD analysis, and LC-MS, which are employed to assess the photosensitivity of the nanomaterials, the mineralization of dyes, and the identification of intermediates formed during the degradation process.

This thesis focuses on research related to the synthesis and characterization of nanocomposites. These nanocomposites include Ni@ZnO/MoO_3/g-C_3N_4, SA@Ag@IONCs, ZnO/MoO_3/g-C_3N_4, and Ag@MoO_3/$BiVO_4$, all of which were synthesized using aqueous leaf extracts obtained from *Curcuma longa*, *Saraca asoca*, *Moringa oleifera*, and *Cymbopogon citratus*. The engineered nanocomposites characterized using a variety of analytical techniques, including UV-visible spectroscopy, XRD, FTIR spectroscopy, SEM@EDAX, FESEM, TEM, XPS, and photocurrent response analyses. The primary focus of this research was to assess the photo-assisted catalytic properties of the fabricated nanocomposites in terms of their effectiveness in degrading toxic dyes. This degradation process was further analysed through mineralization studies using LC-MS and COD analysis.

The optical and electronic properties of the synthesized nanocomposites were examined using UV-Visible spectra. The presence of phytochemical capping on the surface of the nanocomposites was confirmed via FTIR analysis. XRD analysis was

utilized to determine the phase purity of the fabricated materials and calculate crystallite sizes using the Debye-Scherrer equation. The nanomaterials' shape, size, and morphology were confirmed through SEM, FESEM, and TEM analysis. EDAX and elemental mapping analysis were performed to validate the elemental composition of the fabricated materials. SAED patterns were examined to understand the crystalline nature and phase purity of the synthesized materials. XPS analysis confirmed the chemical states of elements within the fabricated metal oxide nanocomposites.

To evaluate the light sensitivity of the materials, photocurrent responses of the engineered nanocomposites were analysed. The mineralization of toxic pollutants was investigated through LC-MS analysis and chemical oxygen demand (COD) measurements. Furthermore, radical scavenging experiments were conducted to evaluate the involvement of reactive radical species in photocatalytic processes. The recyclability of the synthesized materials was also assessed. The photo-assisted catalytic activities of the synthesized metal-metal oxide nanocomposites were investigated in the degradation of Azure B and Malachite green under solar radiation. Various reaction parameters such as catalyst dosage and pH of the medium were also explored in this research.

Chapter 3 describes the formation of z-scheme type structures comprising Ni@ZnO/MoO_3 supported on g-C_3N_4 nanosheet by the sonochemically assisted biogenic method using *Curcuma longa* leaf extract. Structural, morphological, and surface topographies were investigated using X-ray diffraction (XRD), FTIR, UV-Visible, SEM/EDX, HR-TEM, XPS, and BET for surface analysis. Results reveals that MoO_3 nanoplates and Ni@ZnO nanorods are beautifully oriented and interconnected, and these two crystalline materials are wrapped with a stacked layer of g-C_3N_4 which facilitating efficient charge transfer and significantly enhancing the photocatalytic performance of the composite. Additionally, ternary composite has a large surface area as well as pore volume which automatically increased active site on the surface which enhanced photoactivity. In comparison to the g-C_3N_4 and Ni@ZnO/MoO_3 composite, the Ni@ZnO/MoO_3/g-C_3N_4 ternary nanocomposite displayed superior photocatalytic efficiency for the degradation of Azure B (AzB). Furthermore, the recyclability study demonstrated its extended reusability. Under optimized conditions, the photodegradation of AzB by the ternary composite followed pseudo-first-order

kinetics, with a rate constant value of 0.074 min^{-1}. Our findings indicated that $^{\bullet}O_2^-$ and h^+ were the active species responsible for the photodegradation of AzB.

In chapter 4 the sonochemical-assisted fabrication of silver-supported α-Fe_2O_3 nanocomposite (SA@Ag@IONCs) by using *Saraca asoca* leaves extract has been reported. For structural, optical, morphological, and surface topographies were investigated using X-ray diffraction (XRD), FTIR, UV-Visible, Photoluminescence SEM/EDX, HR-TEM, XPS, VSM, and BET for surface analysis etc. The XRD, electron microscopy, reveals that small size well crystalline, SA@Ag@IONCs particles have spherical structures. Absorption edge in UV-visible spectra appears to migrate towards a higher wavelength for the SA@Ag@IONCs composite, causing a change in bandgap energy. In the case of sonication-assisted composite bandgap energy is 2.1 eV, making it easier for an electron transfer from the valance band to the conduction band. The decoration of ultrasmall silver onto the surfaces of α-Fe_2O_3 nanocomposite, which considerably increases the capacity to absorb sunlight and enhances the efficiency of charge carrier separation, inhibits the electron holes recombination rate which is confirmed by the reduced PL intensity, responsible for the excellent photocatalytic degradation performance. Outcomes show SA@Ag@IONCs exhibits a high photodegradation rate as well as high-rate constant value at an optimized condition that is pH 9 with 0.5 gL^{-1} dose of nanocomposite and pH 9, photodegradation rate of Azure B ~ 94 %. Trap experiment results indicated that $^{\bullet}O_2^-$ and h^+ are the active species responsible for the photodegradation of AzB.

In next chapter, we present the fabrication of ZnO/MoO_3/Bi_2O_3 by using a sonochemical assisted biochemical (leaf extract of *Moringa oleifera*) method. The structural, morphological, and surface characteristics of the resulting composite were comprehensively examined using a range of techniques including X-ray diffraction (XRD), FTIR, UV–Visible spectroscopy, SEM/EDX analysis, HR-TEM imaging, XPS for chemical composition analysis, and BET surface area analysis. Our findings reveal that the ZnO nanorods and MoO_3 nanoplates are exquisitely aligned and interconnected within the structure. These two crystalline components are decorated with Bi_2O_3 sheets which can be attributed to the efficient prevention of photoinduced electron-hole pair recombination, achieved through the vectorial transfer of electrons and holes between ZnO/MoO_3 and Bi_2O_3. This configuration significantly enhances the photo-assisted

catalytic performance of the composite. Moreover, the ternary composite possesses a substantial surface area and pore volume, thereby increasing the number of active sites on its surface and consequently enhancing its photoactivity. In contrast to both Bi_2O_3 and ZnO/MoO_3, the $ZnO/MoO_3/Bi_2O_3$ composite exhibited an impressive 98.8% degradation efficiency of Malachite green (MG) dye within 48 minutes under direct sunlight radiation, under optimized conditions (pH 13, 75 mg photocatalyst dose). The photocatalytic degradation process followed pseudo-first-order kinetics with rate constant 0.090 min^{-1}. Additionally, inhibitor studies allowed us to propose a mechanism that highlights the significant contributions of h^+ (holes) and $^{\bullet}O_2^-$ in the photocatalytic process.

Chapter 6 reports one pot green synthesis of (leaf extract of *Cymbopogon citratus*) ternary nanocompositeAg@MoO_3/$BiVO_4$ followed by sonochemical method. The structural, morphological, and surface characteristics of the resulting composite were comprehensively examined using a range of techniques including X-ray diffraction (XRD), FTIR, UV–Visible spectroscopy, SEM/EDX analysis, HR-TEM imaging, XPS for chemical composition analysis, and BET surface area analysis. Our findings reveal that the Ag nanoparticle decorated on nanorods of MoO_3 are exquisitely aligned and interconnected within the structure. These two crystalline components are interconnected with $BiVO_4$ nanoflakes/nanoplates, which can be attributed to the efficient prevention of photoinduced electron-hole pair recombination, achieved through the vectorial transfer of electrons and holes between and Ag@MoO_3 and $BiVO_4$ and Ag@MoO_3.

This configuration significantly enhances the photo-assisted catalytic performance of the composite. Moreover, the ternary composite possesses a substantial surface area and pore volume, thereby increasing the number of active sites on its surface and consequently enhancing its photoactivity. In contrast to both Ag@MoO_3 and $BiVO_4$, the Ag@MoO_3/$BiVO_4$ composite exhibited an impressive 99.8% degradation efficiency of malachite green (MG) dye within 60 minutes under direct sunlight radiation, under optimized conditions (pH 13, 55 mg photocatalyst dose). The photocatalytic degradation process followed pseudo-first-order kinetics with rate constant 0.094 min^{-1}. Additionally, inhibitor studies allowed us to propose a mechanism

that highlights the significant contributions of $^{\bullet}OH$, $^{\bullet}O_2^-$ and h^+ (holes) in the photocatalytic process.

In the last chapter-7 brief summary of the research work performed and scope of further research work have been presented.