

Green Synthesis of MnO₂ Nanoparticles Using *Bunium persicum* Extract and Their Catalytic and Biological Applications

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Abstract- An eco-friendly and sustainable approach for the synthesis of manganese dioxide (MnO₂) nanoparticles was developed using *Bunium persicum* seed extract as a natural reducing and stabilizing agent. The green-synthesized MnO₂ nanoparticles were characterized using UV-Vis spectroscopy, FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDX), confirming their crystalline nature, nanoscale dimensions, and high purity. The catalytic efficiency of the prepared MnO₂ nanoparticles was evaluated in organic transformation reactions, where they exhibited excellent activity under mild conditions. In addition, preliminary biological studies demonstrated notable antimicrobial activity against selected bacterial strains. The results highlight the dual catalytic and biological potential of biosynthesized MnO₂ nanoparticles and emphasize the advantages of plant-mediated nanomaterial synthesis in green chemistry and sustainable nanotechnology.

Keywords: Green synthesis, MnO₂ nanoparticles, *Bunium persicum*, heterogeneous catalysis, antimicrobial activity.

I. INTRODUCTION

Conventional methods commonly used for the synthesis of metal and metal oxide nanoparticles are frequently associated with significant toxicological drawbacks, which has stimulated growing interest within the scientific community to develop safer and more sustainable alternatives. Traditional synthetic routes often generate hazardous byproducts and involve toxic reagents, thereby necessitating a transition toward environmentally responsible methodologies. In this regard, plant-derived extracts obtained from leaves, seeds, flowers, and other botanical sources have emerged as effective green alternatives, as they contain bioactive constituents capable of chelating metal ions and promoting nanoparticle formation in a cleaner and eco-friendly manner. These natural systems facilitate nanoparticle synthesis through biologically mediated reduction and stabilization processes, offering an environmentally compatible pathway aligned with sustainable chemistry principles.

Green chemistry plays a crucial role in this approach by enabling controlled surface functionalization, which significantly affects the physical, chemical, electrical, and optical properties of nanoparticles [1–2]. The adoption of green chemistry strategies allows

fine-tuning of nanoparticle surfaces, thereby enhancing their performance and suitability for a wide range of applications. This methodology has gained considerable attention, particularly for the synthesis of biocompatible metal nanoparticles, which are increasingly preferred in biomedical applications due to their reduced toxicity and improved compatibility with biological systems.

The incorporation of green chemistry concepts into nanotechnology has thus become a fundamental aspect of modern nanoscience research, reinforcing sustainability while fostering technological progress. The increasing emphasis on green nanoparticle synthesis has intensified the demand for environmentally benign production methods that minimize adverse effects, especially in medicinal applications where safety considerations are critical [3]. As nanotechnology continues to advance, it spans a broad range of disciplines, extending from fundamental investigations of material properties to practical applications in consumer products such as cosmetics and personal care formulations [4–5]. This interdisciplinary expansion reflects the versatility of nanoparticles, which have enabled innovative developments, including targeted drug delivery systems that enhance therapeutic efficiency through site-specific action.

Nanoparticles are of particular scientific interest due to their ability to bridge the gap between bulk materials and atomic or molecular dimensions [6]. This transitional scale imparts unique and often enhanced properties, including nanoscale size, uniform dispersion, and diverse morphologies, distinguishing them from their bulk counterparts. Consequently, nanomaterials have found widespread use in everyday products such as sunscreens, toothpaste, antimicrobial coatings, and food-related applications, underscoring their functional importance and the necessity for safe and sustainable synthesis strategies [7].

As a result, there is a growing demand for eco-friendly approaches to synthesize noble metal nanoparticles—including gold, silver, and platinum—which are widely used in products that come into direct contact with the human body and therefore require stringent safety measures [8–9]. Beyond commercial relevance, inorganic nanoparticles have also demonstrated significant biological activities, such as scavenging oxygen-derived free radicals that contribute to oxidative stress and cellular damage [10]. Among these materials, manganese dioxide nanoparticles (MnO₂-NP) have attracted particular attention owing to their distinctive physicochemical characteristics and broad applicability in biochemical research and plant biotechnology [11]. Notably, MnO₂-NP at concentrations below 10 mg L⁻¹ have been reported to enhance growth parameters in tomato plants, highlighting their potential agricultural benefits.

Motivated by these observations, the present study aims to synthesize MnO₂ nanoparticles using *Bunium persicum*, a plant rich in phytochemicals, and to evaluate their antibacterial activity as a representative application of green nanotechnology. The synthesis strategy employs *Bunium persicum* as a natural reducing and stabilizing agent to achieve environmentally sustainable nanoparticle production. In addition, the catalytic efficiency of the biosynthesized MnO₂ nanoparticles was examined through their application in the synthesis of quinoxaline derivatives—heterocyclic compounds formed via nucleophilic and electrophilic interactions—thereby demonstrating their

multifunctional utility. This investigation highlights the potential of green nanotechnology to integrate environmental responsibility with advanced applications in both biological and catalytic domains.

II. EXPERIMENTAL SECTION

Materials

All chemicals used were of analytical grade and employed without further purification. *Bunium persicum* seeds were procured from a local source and authenticated before use.

Preparation of *Bunium persicum* Extract

The dried seeds were finely powdered and refluxed in distilled water. The resulting extract was filtered and stored at 4 °C for subsequent nanoparticle synthesis.

Green Synthesis of MnO₂ Nanoparticles

An aqueous solution of manganese precursor was mixed with the plant extract under controlled conditions. The reaction mixture was stirred until a color change indicated nanoparticle formation. The resulting MnO₂ nanoparticles were collected by centrifugation, washed repeatedly with distilled water and ethanol, and dried for further analysis.

Characterization Techniques

The synthesized MnO₂ nanoparticles were characterized by UV-Vis spectroscopy, FT-IR, XRD, SEM, and EDX to determine their optical properties, functional groups, crystallinity, morphology, and elemental composition.

Catalytic Activity Studies

The catalytic efficiency of MnO₂ nanoparticles was evaluated in selected organic reactions under optimized conditions. Reaction progress and product formation were monitored using standard analytical techniques.

Antimicrobial Activity

The antimicrobial potential of the synthesized nanoparticles was assessed against selected Gram-positive and Gram-negative bacterial strains using standard in vitro methods.

3. Results and Discussion

The foundational aspects of this study are summarized through a systematic experimental design that outlines the initial reaction conditions and key parameters. This stage focuses on evaluating the catalytic role of various fluoride anions in promoting the condensation reaction between diamines (1a) and diketones (2a), a crucial step in heterocycle formation. These reactants were selected due to their established importance as precursors for quinoxaline derivatives, which possess broad relevance in medicinal and materials chemistry.

A clear representation of the reaction sequence illustrates how fluoride anions influence the interaction between diamines and diketones to facilitate cyclization. Complementary experimental data compile reaction conditions and product yields, enabling systematic comparison of catalytic efficiencies. Together, these elements establish a robust framework for interpreting early experimental outcomes and guiding further optimization.

Fluoride anions were investigated for their ability to activate reactants and lower activation barriers during condensation. The reaction proceeds via nucleophilic attack of the diamine nitrogen atoms on the electrophilic carbonyl carbons of the diketone, ultimately forming a cyclic quinoxaline scaffold. Variations among fluoride salts—arising from differences in solubility, counterions, and basicity—were expected to influence reaction kinetics and selectivity. Accordingly, different fluoride sources were screened to identify optimal catalytic performance.

All reactions were initially conducted in ethanol at ambient temperature, chosen for its polarity, hydrogen-bonding ability, and alignment with green chemistry principles. Ethanol effectively solubilized reactants and stabilized transition states, enabling efficient reactions without external heating. The diamine 1a (*o*-phenylenediamine) and diketone 2a (benzil) functioned synergistically under these conditions to generate quinoxaline derivatives through fluoride-assisted cyclization.

Experimental evaluation revealed that inorganic fluoride salts such as NaF, KF, and CsF promoted quinoxaline formation but afforded only moderate yields. Notably, increasing the temperature and solubility of NaF significantly improved yields, highlighting the importance of thermal activation and catalyst dispersion. In contrast, tetrabutylammonium salts provided limited improvement.

A dramatic enhancement was observed upon employing manganese dioxide nanoparticles (MnO₂-NPs) as catalysts, which afforded quinoxaline products in excellent yields, far outperforming bulk MnO₂. This superior activity is attributed to the high surface area and enhanced reactivity of MnO₂-NPs. Structural confirmation of products was achieved using ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry analyses.

Further optimization studies examined solvent effects, catalyst loading, and reaction time. Polar solvents such as acetonitrile, methanol, and ethanol facilitated rapid reactions with high yields, while ethanol was selected as the optimal solvent due to its low toxicity, affordability, and sustainability. Deviations from the optimal MnO₂-NP loading resulted in longer reaction times and reduced yields. Substrate scope evaluation demonstrated that electron-donating substituents on either the diamine or diketone accelerated reactions and improved yields, whereas electron-withdrawing groups—particularly nitro substituents—reduced yields and required higher temperatures and longer reaction times. Aliphatic diketones also reacted efficiently, confirming the versatility of the catalytic system.

Mechanistic considerations suggest that fluoride ions enhance diamine nucleophilicity through deprotonation, while transient hydrogen fluoride formation may increase carbonyl electrophilicity. The reaction is proposed to proceed via imine formation, followed by cyclization through nucleophilic substitution and final aromatization. While the exact mechanistic details remain under investigation, this model aligns well with the observed experimental trends.

Extended applications of the manganese dioxide-catalyzed system demonstrated the successful synthesis of complex fused heterocycles, including phenazine-linked and biquinoxaline derivatives, obtained in good to excellent yields. These results highlight the adaptability of both MnO₂ and MnO₂-NPs in constructing multifunctional heterocyclic frameworks.

Competitive experiments further established that diketones react preferentially over α -bromoketones in the presence of MnO₂, yielding predominantly 2,3-disubstituted quinoxalines. This selectivity arises from the presence of dual carbonyl functionalities, which enable rapid double condensation, whereas α -bromoketones proceed through slower substitution-based pathways.

These findings provide a comprehensive understanding of catalyst effects, solvent influence, substituent electronics, and mechanistic pathways governing quinoxaline synthesis. The study establishes manganese dioxide nanoparticles as highly efficient and versatile catalysts and offers a reliable platform for designing structurally diverse quinoxaline derivatives under environmentally sustainable conditions.

IV. CONCLUSION

A sustainable and green approach for the synthesis of MnO₂ nanoparticles using Bunium persicum seed extract was successfully developed. The synthesized nanoparticles displayed excellent catalytic efficiency and promising antimicrobial activity, highlighting their multifunctional potential. This study demonstrates that plant-mediated synthesis is a viable strategy for producing value-added nanomaterials and opens new avenues for their application in catalysis and biomedical research.

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