

Agrowaste Derived Bimetallic Nanoparticles for Environmental Remediation: A Short Review

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ABSTRACT

Environmental pollutants emanated from industrialization and anthropogenic activities have become a matter of great concern nowadays due to their persistent nature that adversely affects water, soil, and air. The treatment of these pollutants by using conventional methods is challenging and, therefore, various sustainable alternatives are being explored. Bimetallic nanoparticles represent one such alternative because of synergistic effects among metals and higher catalytic activity, stability, and selectivity. Green synthesis, using agricultural waste as reducing and capping agents, has shown to be a proficient and cost-effective approach for nanoparticles' production. Agricultural waste is a potential source of phytochemicals, including polyphenolics, flavonoids, proteins, terpenes, and sugars. These phytoconstituents present in plant waste can be effectively utilized for the synthesis of bimetallic nanoparticles. The present review focuses on agro-waste-derived bimetallic nanoparticles, including the mechanism of their synthesis, and factors affecting their physicochemical properties. The article discusses how agricultural waste plays a key role in the green synthesis process. The review includes information about the application of agro-waste-derived bimetallic nanoparticles (AW-bimetallic NPs) for remediation of organic dyes, heavy metals, and other pollutants. Current research trends, challenges and future prospects of using agricultural waste in bimetallic nanoparticle synthesis are also discussed.

Keywords: Agrowaste, Bimetallic Nanomaterials, Environmental Remediation, Environmental Pollutants, Green Synthesis.

Introduction

Environmental pollutants are substances that are dangerous to human health and have entered the environment as a result of human activity. By contaminating the soil, water, and air, human activity introduces pollutants. A country's growth is aided by industrialization, but it also releases numerous harmful pollutants into the environment [1]. Public concern over the effects of the large-scale chemical discharge and ensuing pollution on the environment and human health has been growing. Unintentional exposure to various pollutants, including organic chemicals, air pollutants, and heavy metals, can have a variety of harmful effects on human bodies, leading to the development and progression of various diseases [2]. Due to issues with selectivity, efficiency, and flexibility, conventional water and wastewater treatment techniques frequently fail to sufficiently eliminate these persistent pollutants. Nanotechnology has emerged as a novel and efficient way to remove contaminants as depicted in Figure 1 [3].

If a material's size or one of its dimensions falls between 1 and 100 nm, it is referred to as a nanomaterial. Studies in recent years have demonstrated the potential of nanostructured materials, also known as nanomaterials, in applications related to water treatment and sanitation, health and well-being, and responsible resource production and consumption. Because of their exceptional properties, such as their greater surface area, surface energy, and chemical reactivity when compared to macroscopic materials, metal-based nanostructures have been used in wide range of applications such as drug delivery systems, electronics, gene therapy, sensors, bioactive materials and environmental remediation [4-8]. Two types of NPs are produced: monometallic and bimetallic NPs, depending on how many metals are used in their structure [9]. In particular, bimetallic nanoparticles (BMNPs) have garnered interest recently because of their superior optical and catalytic characteristics when compared to monometallic nanostructures. Because of their synergistic qualities, they have a diverse range of applications, including chemical and physical applications in optics and catalysis, biological applications in medicine and agriculture, and environmental applications in water treatment and the removal of harmful contaminants [10]. Currently, the primary techniques for the large-scale synthesis of nanomaterials are chemical and physical, but these processes are costly, have negative environmental and health effects, and require more energy. One promising and eco-friendly method for creating materials with unique properties is the green synthesis of nanoparticles.



Figure 1. Applications of traditional and green synthesized BMNPs related to SDG 6: clean water and sanitation [3].

The green synthesis of nanomaterials reduces the carbon footprint of the process by using natural reagents like bacteria, fungi, plant extract, and agricultural waste in place of dangerous chemicals. Compared to conventional techniques, green synthesis of nanomaterials is very advantageous because it is inexpensive, produces very little pollution, and is safe for both human health and the environment [11]. Among the various renewable resources used in green synthesis. Plant-mediated synthesis of nanoparticles offers a sustainable alternative to conventional chemical methods by eliminating toxic reagents, reducing energy input, and utilizing renewable biomolecules as natural reducing and stabilizing agents. This eco-friendly route not only minimizes environmental burden but also enhances biocompatibility, aligning with principles of green chemistry and circular economy [12]. Agricultural waste can be effectively used to create a variety of value-added nanoparticles and is a rich source of different phytochemicals. Agricultural wastes, also known as agro-wastes, are the leftovers from cultivating crops and/or from the initial processing of raw agricultural products. Crop waste, fruit or food waste, plant waste, and industrial waste are among the various agricultural wastes that are widely utilized in the production of NPs [13]. It has been demonstrated that plant metabolites, including proteins, alkaloids, terpenoids, polyphenols, sugars, and phenolic acids, are essential for the reduction of metal ions into nanoparticles. Plant extracts are used as potential reducing and capping agents in green nanoparticle synthesis. Plant leaves, stems, seeds, pulp, and bagasse are among the resources used in the top-down and bottom-up synthesis of sustainable nanoparticles [14]. Bimetallic nanoparticle catalysts demonstrate superior catalytic performance compared to their corresponding monometallic counterparts and possess broad industrial application potential. As the name suggests, the two metallic elements are generally present as alloys or as a mixture of particles. The distinctive synergistic interaction between the two metal components imparts exceptional catalytic properties to bimetallic nanoparticles, resulting in enhanced activity, stability, and selectivity. Because of the synergistic effects of the combined metals, the biosynthesized bimetallic Ag–Au or Ag–Cu NPs from food waste extract exhibit significantly higher antimicrobial and catalytic properties than monometallic performance [15]. This review provides a comprehensive overview of agro waste derived bimetallic nanoparticles for environmental remediation. It discusses the role of agricultural waste as a sustainable source of reducing and capping agents, the green synthesis strategies employed for the fabrication of bimetallic nanoparticles, and the influence of phytochemicals on nanoparticles formation. Furthermore, the review highlights recent application of these nanoparticles in the removal of environmental pollutants, along with the associated challenges and future prospects.

Green synthesis of Agrowaste Derived Bimetallic Nanoparticles

In every part of the world, agriculture is the main source of energy, food, waste, and greenhouse gas emissions. Because of their activities, agriculturally based enterprises generate a lot of waste. Agro-waste is the term used to describe plant parts that are not edible. The farming sector produces billions of tonnes of waste from the cultivation and processing of different crops. The crops that generate the most residues include rice, maize, soybean, sugarcane, potato, tomato, and cucumber, along with certain fruits, primarily bananas, oranges, grapes, and apples [16].

Plant extracts are rich in bioactive compounds that possess notable anti-oxidant properties. These bioactive substances are referred to as phytochemicals. These substances encompass alkaloids, phenolic acids, flavonoids, steroids, terpenoids, isoprenoids, tannins, glycosides, saponins, and quinones. Phytochemicals play a crucial role in stabilizing, preventing agglomeration, and regulating the size and morphology of metal oxide nanoparticles. It has been confirmed that, in the eco-friendly synthesis of nanoparticles, phytochemicals act as reducing and stabilizing agents [17]. BMNPs can be produced in an eco-friendly manner using a green chemistry method that includes at least three elements: the employment of non-toxic capping agents, safer reducing agents, and the choice of environmentally safe solvents. Consequently, utilizing these green chemistry principles in nanomaterial synthesis facilitated the rise of the green nanotechnology domain [18]. Fruit-peel-mediated synthesis has produced alloyed, core-shell, heterostructured, and nanocomposite-like BMNPs (Figure 2), yet many reports infer these structures from indirect evidence rather than rigorous structural analysis [19]. The diverse functional capabilities of green-synthesized BimNPs have prompted their investigation in various application fields, including environmental cleanup, biomedical diagnostics, and catalysis (Figure 3).

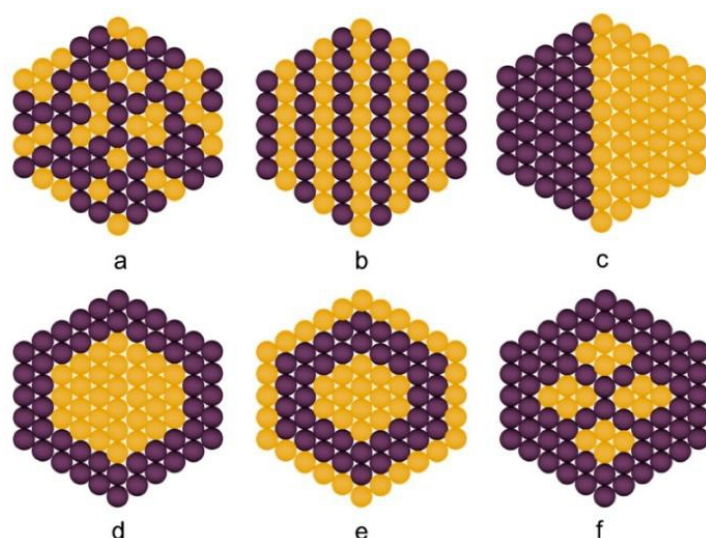


Figure 2. Types of bimetallic nanoparticles: (a) alloyed, (b) intermetallic, (c) subclusters, (d) core-shell, (e) multi-shell core-shell, and (f) multiple core materials coated by a single shell material. Yellow and purple spheres represent two different kinds of metal atoms [19].

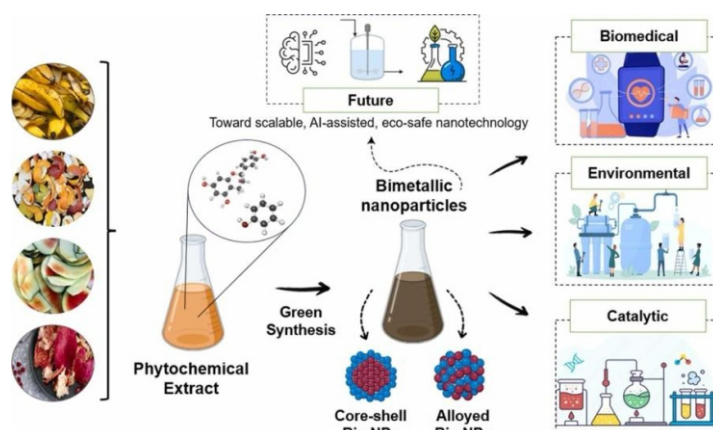


Figure 3. Synthesis of Bimetallic NPs using phytochemical-rich fruit peels as sustainable, low-cost reducing and stabilizing agents [20].

The creation of green-synthesized nanoparticles is affected by various factors that can impact their size, shape, and overall quality (**Figure 4**). For example, the pH level can alter the charge and function of biomolecules, subsequently affecting how the particles assemble and remain stable. The length of the reaction is important as extended periods typically enable greater development and enhancement of the nanoparticles. The kind of plant extract utilized is essential because it includes phytochemicals such as flavonoids and phenols that aid in reducing and stabilizing the particles. The levels of both the extract and the metal salt influence the rate and efficiency at which nanoparticles are generated. Moreover, the solvent influences the solubility and interactions of substances, while surfactants can assist in preventing particle aggregation. Ultimately, the type and quantity of precursor materials employed directly influence the formation and development of the nanoparticles [21].

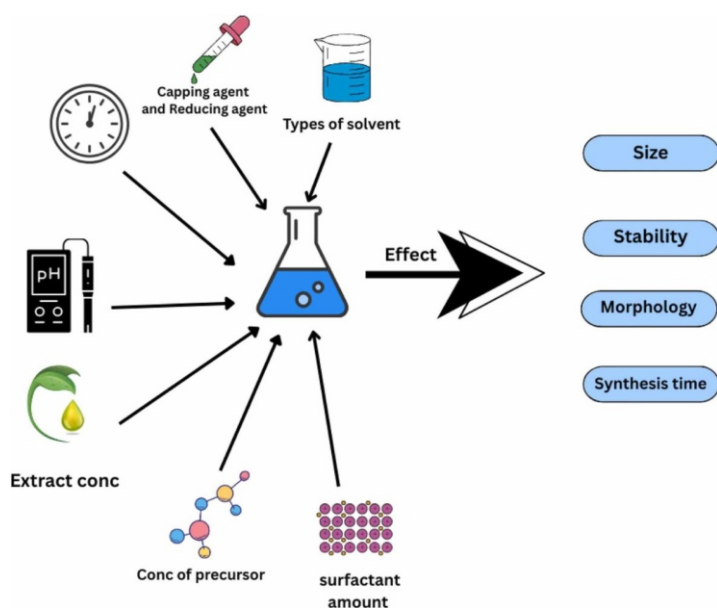


Figure 4. Schematic representation of factors affecting morphology, synthesis time, size, and stability [21].

Environmental Remediation Application

Bimetallic nanoparticles have a low band gap, excellent semiconducting behaviour, remarkable stability, smooth charge separation, and reduced charge recombination likelihood due to their synergistic effects. As a result, they make significant contributions in areas where dangerous contaminants are degraded by photocatalysis.

Dye degradation, water purification, antibiotic and pesticide degradation, and the transformation of hazardous chemicals into innocuous byproducts are significant photocatalytic uses of bimetallic nanoparticles. Bimetallic nanoparticles can aid in converting hazardous metals such as chromium, arsenic, and mercury into safer forms. Out of the multitude of pollutants that significantly endanger the environment, pharmaceuticals and personal care products (PPCPs) raise particular alarm due to their ability to bioaccumulate and biomagnify in aquatic life [22]. Well-designed BMNPs are becoming increasingly popular for eliminating emerging organic and inorganic pollutants in water and air via adsorption and photocatalytic/redox processes. BMNPs like Bi-Mg and Fe-Cu are efficient in eliminating cadmium, lead, zinc, and various other heavy metals from wastewater. Utilisation of plant-based synthesis technique to create Bi-Mg BMNPs for the uptake of cadmium, lead, and zinc from wastewater. The incorporation of agricultural byproducts like orange peels illustrates the application of the circular economy. Additional research shows the application of Pd-Au, Pd-Ag, and others for the efficient breakdown of halogenated organic compounds, dyes, pesticides, pharmaceutical and personal care items, as well as dyes in wastewater. Utilizing BMNPs for water and environmental remediation supports the circular economy by promoting green synthesis methods, reducing waste, recovering resources, enhancing reusability, and ensuring sustainability [23]. Nano-biosensors are designed to track NPs, plant fractions, soil, water, and nanotubes, nanowires, or nanocrystals within the agro ecosystem. By leveraging the physico-chemical properties of NMs, NBSs offer a potent tool in contrast to existing analytical sensors and biosensors that combine biological element detection with chemical or physical principles. Biological data is converted by a transducer into a signal that can be generated by an electrical component. With this skill, an agronomist can precisely and swiftly track the crops' water and nutritional requirements as well as any early indications of illness [24]. It has been discovered that bimetallic nanoparticles are highly effective at supplying nutrients to soil, which directly improves plant development and large-scale crop production. For instance, bimetallic nanoparticles made of Ag-Fe or Mn-Fe can function as nanofertilizers; bimetallic nanoparticles made of Ag-Au, Ag-Cu, or Ag-Zn combinations offer biocide qualities because of their possible antibacterial and antimicrobial properties; and bimetallic nanoparticles made of Cu-Fe can be excellent nutrients that can improve plant growth [25]. **Table 1** collects some of the BMNPs synthesis using various agro-waste materials recently. Some of the reports have also proposed the mechanism of photodegradation of dyes through the excitation of electrons from the surface after absorbance of photons and the released electron then initiate the systematic pathway for the degradation of dye molecules as depicted in Figure 5.

Table 1: Valorisation of agro-waste for bimetallic nanoparticle synthesis

Sr. No.	Agro-waste	Metal	Size (nm)	Morphology	Application	Ref.
1	Lemon pomace + leaves	Fe -Zn	126	Spherical, agglomerated	Fenton like degradation of Reactive Red 2	[26]
2	Pomegranate peel	Fe - Pd	20 - 60	Mostly spherical; Pd coating around Fe	Removal/degradation of tetracycline	[27]
3	Waste tea leaves	Ag -Au	~ 20	Spherical	Degradation of conga red and 4 - Nitrophenol	[28]
4	Waste banana peel	Ag - Cu	~ 19	Spherical	Antimicrobial/Corrosion inhibition associated with oilfield environmental protection	[29]
5	Cabbage peel	Ag - Fe ₂ O ₃	22.3	Spherical/Core-shell	Degradation of methylene red and phenol red	[30]
6	Sugarcane pulp bagasse	Cu - Ni	~ 40	Fish-net-like porous biochar	Degradation of Malachite green, methylene blue & methyl orange	[31]
7	Passion fruit peel	Au - Pd	15.9 ± 2.4	Spherical Core-shell	Rhodamine B & methyl orange degradation	[32]
8	Kiwi Fruit peel	Ag-Zn	272	Spherical and irregular	Methyl red, Phenol Red, Eosin Yellow	[33]
9	Cornulaca monacantha stem	Zn-Fe	14	Spherical and irregular	Remediation of noxious organic pollutants, naphthalene (NPN) and 2-naphthol (2-NP)	[34]

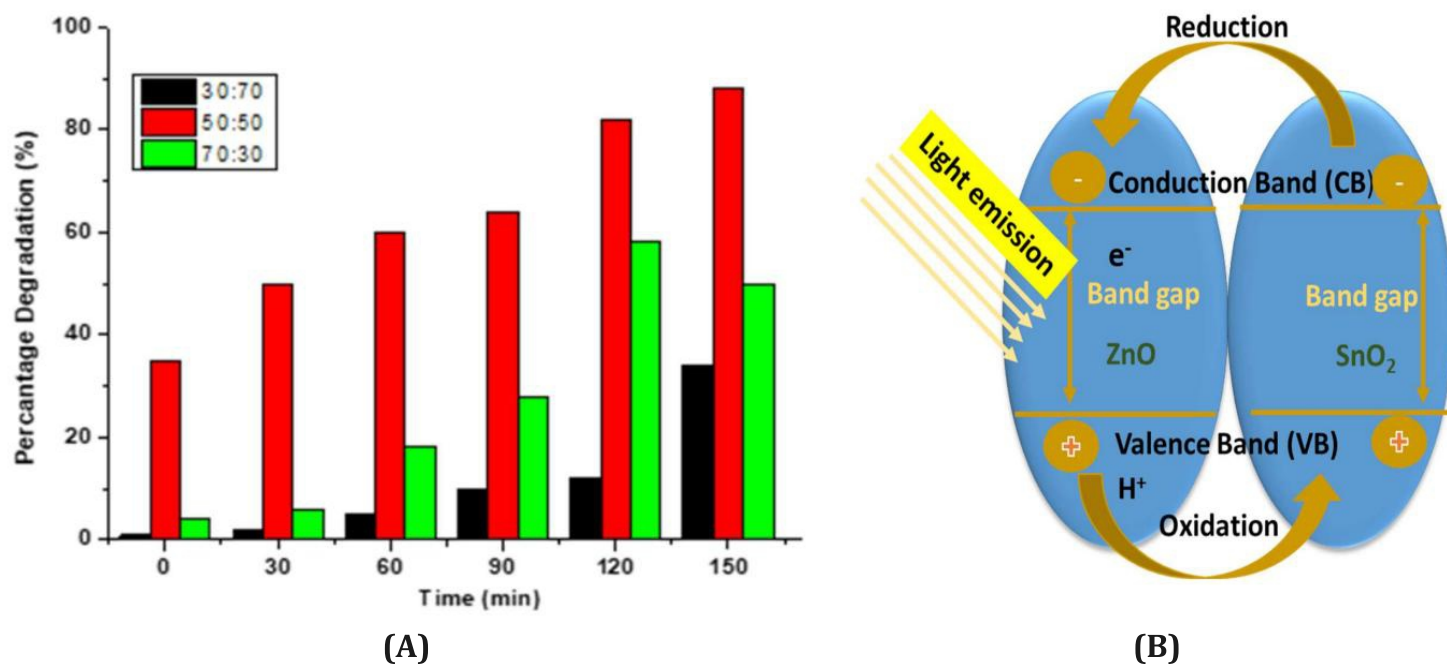


Figure 5. (A) Photocatalytic degradation of methylene blue dye, and (B) Mechanism of degradation for ZnO-SnO₂ nanoparticles.

Challenges

Utilising waste-derived nanoparticles is an effective method of environmental clean-up. We are unable to use these nanoparticles in practical applications due to certain issues. The fact that the trash used to create these nanoparticles is not always the same is a major problem. The kind of plant, its age, and the season in which it is grown. The nanoparticles are influenced by how it is treated. This implies that the nanoparticles may differ in size and form and may not be effective at cleaning up the environment. All of these factors have an impact on waste-derived bimetallic nanoparticles, or BMNPs. Another significant issue is the lack of options for creating green synthesis methods. Changes in the quantity of extract used, the pH level, the temperature, the duration of the reaction, the amount of precursor, and the conditions of heat treatment can all alter the characteristics of the BMNPs. Due to this, clear and consistent methods are required for production. Despite being made from bimetallic nanoparticles derived from agro-waste, these materials face several challenges. Variations in the composition of agro-waste can affect the size, shape, and overall performance of the nanoparticles. There is also a lack of a clear method to produce them, making it difficult to repeat the process consistently. Scaling up production, recovering the nanoparticles after use, and doing so in an affordable manner remain significant hurdles. Moreover, most studies are conducted in laboratory settings, and there is a lack of information on how these nanoparticles perform over time, their behaviour in the environment, and their safety. Future research should focus on developing standardized green synthesis methods, creating scalable production techniques, and testing the nanoparticles in real-world scenarios such as contaminated wastewater and polluted soil. Combining these nanoparticles with materials like biochar, chitosan, or polymers could enhance their effectiveness and durability. Recovery methods using magnets to make them reusable, examining their entire lifecycle, assessing their safety, and conducting field tests will be crucial for developing safe, cost-effective, and environmentally friendly solutions for pollution control.

Future perspective

Future research should focus on developing standardized and scalable green synthesis methods to produce bimetallic nanoparticles in a more cost-effective manner. Additional studies are needed that utilize wastewater and contaminated soil. These studies should also examine the stability of the nanoparticles over time, their potential toxicity, ease of recovery, and how frequently they can be reused. Combining bimetallic nanoparticles with materials such as biochar or chitosan, along with conducting lifecycle and large-scale field studies, could result in more effective and eco-friendly methods for environmental clean-up. We need to understand how these materials behave in real-world conditions. This requires testing them in the actual environments where they will be applied. Future research should focus on developing materials that are kind to the environment and produce minimal waste. This approach will help support economic growth. The circular economy is a system that encourages the reuse of resources. Our goal is to apply the knowledge gained in the lab to create technologies that are beneficial for the environment and safe for people. These technologies should also aid in cleaning up the environment. It is important to ensure that environmental remediation technologies are both practical and safe. Environmental remediation technologies are designed to clean up polluted areas.

Conclusion

An important turning point in nanotechnology is the green synthesis of nanomaterials from agricultural waste, which effectively bridges the gap between sophisticated material science and waste management. This biogenic approach provides a highly sustainable, economical, and environmentally acceptable substitute for conventional chemical and physical manufacturing processes by using agro-industrial residues—such as fruit peels, crop husks, leaves, and straws—as natural precursors. Agro-waste's natural abundance of bioactive compounds, such as proteins, carbohydrates, polyphenols, and flavonoids, has two functions: it effectively acts as a stabilizing and reducing agent.

This successfully removes the need for dangerous chemicals, lowers energy use, and minimizes harmful by-products all of which are in complete harmony with the tenets of green chemistry. Additionally, by converting environmental liabilities into valuable functional materials, this technique promotes trash valorization and makes a substantial contribution to the circular economy. The resulting biogenic nanoparticles function exceptionally well in a variety of industries. They have great biocompatibility as nano-fertilizers in sustainable agriculture, strong antibacterial and antioxidant qualities in biomedical and food packaging applications, and high catalytic efficiency in environmental remediation (such as wastewater treatment and dye degradation). However, key barriers must be removed in order to move this technique from laboratory success to industrial-scale manufacturing. In order to combat the inherent heterogeneity of agro-waste, future research must concentrate on standardizing extraction procedures, fine-tuning reaction settings for exact control over nanoparticle morphology, and carefully assessing the materials' long-term ecotoxicological effects. By overcoming these obstacles, commercial-scale, waste-free biorefineries that can create the upcoming generation of sustainable nanomaterials will become possible.

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