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Biogenic Wastes-Enabled Nanomaterial Synthesis

Applications in Environmental Sustainability

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Contents

A Review on Agricultural Wastes–Based Green Metal and Metal Oxide Nanoparticles

Sakshi Kabra Malpani, Renu Hada, and Deepti Goyal

1 Introduction

Nanoparticles are small-sized particles with at least one dimension in the nano range, that is, less than 100 nm. These particles have high specific surface area and exhibit size-dependent features such as high reactivity; strong sorption capacity; superparamagnetism; excellent mechanical, optical, and electrical properties; uniform porosity; surface functionalization; and superior attachment with functional groups (Khan et al., 2019). Owing to these unique properties, nanoparticles are extensively used in diverse fields of applications such as catalysis (Astruc, 2020), environmental remediation (Del Prado-Audelo et al., 2021), fuel cells, adsorption (Osagie et al., 2021), coatings, sensing, medicinal chemistry, drug delivery (Mitchell et al., 2020), and energy storage (Awad et al., 2021). These days nano metals, nano metal oxides, nano silica, and carbon nanoparticles are the most usual types of nanoparticles, which have been extensively synthesized (Joudeh & Linke, 2022). Especially nanoscale metals and metal oxides are potential candidates in the field of adsorption, catalysis, and pollution control and can easily substitute traditional adsorbents, catalysts such as activated carbon, silica, alumina, and polymers (Chavali & Nikolova, 2019). Nano metals and nano metal oxides are used as such in the form of powder or compressed as pellets for their larger scale use in many industrial applications. Depending upon the application of nanoparticles, their methods

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of synthesis may vary. Two approaches—top-down and bottom-up—are majorly used to synthesize nanoparticles. Many physical, mechanical, chemical, and biological methods are used within these two approaches to produce such nanoparticles. Ball milling, etching, mechanical alloying, reactive milling, and micromachining are common top-down synthesis methods. While, molecular self-assembly, sol-gel, electron/ion beams, chemical vapor deposition, inert gas condensation, electrodeposition, ultrasonic dispersion, vacuum arc deposition, etc., are conventional bottom-up synthesis procedures (Abid et al., 2022). Nanoparticles extracted from agricultural wastes possess some lucrative features such as smaller size, more stability, reduced toxicity levels, decreased environmental and health issues associated with their preparation, and, above all, they are highly cost-effective. Nowadays, metal and metal oxide nanoparticles synthesized by using these approaches are of tremendous therapeutic, chemical, eco-friendly, sustainable importance and can be efficiently used in real-life applications (Zamani et al., 2019). For example, silver and gold nanoparticles can be produced from biomolecules available in agricultural wastes (Thangadurai et al., 2021). Apart from metal nanoparticles, production of metal oxide nanoparticles has also gained a lot of attention. For example, silicon oxide or silica nanoparticles are extensively prepared from agricultural waste materials such as rice husk ash, sugarcane bagasse, and corncobs (Malpani & Goyal, 2022). These nanoparticles are chemically inert, stable at higher temperatures, can be modified easily, and thus they have numerous industrial applications such as drug delivery, furnace lining, catalysis, adsorption, and energy storage. Several types of important carbon nanoparticles can also be derived from agricultural and biomass waste materials (Thangadurai et al., 2021).

About 2.6 billion tons of solid waste will be generated across the globe by the end of 2030 (Peng et al., 2023). Out of this total solid waste, about 1300 million tons of waste has been generated from the agricultural sector (Amran et al., 2021). Agricultural or agro-wastes are results of agricultural practices right from crop cultivation, dairy farming, livestock rearing to the first processing of raw agricultural products. Approximately 30% of agricultural goods produced globally are discarded as agricultural wastes (El-Ramady et al., 2022). These agricultural wastes are rich sources of nutrients, organic material, and metal and metal oxide–based nanoparticles. They comprise husks from cereal and oil industries, fruit peels from beverage and juice industries, and tea and coffee wastes from their respective manufacturing units. In low- or middle-income countries, more than 50% of agricultural waste is either burnt or dumped as such. Such careless waste management practices are considerable reasons for environmental pollution and harmful diseases. Thus, there is a pressing need to develop useful and sustainable methods to utilize such wastes in a fruitful manner. Production of nanoparticles is one of the value-added methods to utilize or recycle agricultural wastes. It not only helps in attaining goals of circular economy, green chemistry, and sustainable development but also minimizes the negative footprint of ill management or disposal of agricultural wastes. It also adds up to the total income of local people and helps with their welfare.

Nanoparticles synthesized by conventional methods are highly expensive and could turn out to be toxic also, thus can pose health, legal, and environmental threats. If agricultural wastes are used as raw materials for preparing nanoparticles, then by using green or clean manufacturing processes such wastes can be converted into value-added materials. Such solid wastes can be practically recycled, embark on the economic value of the final products, and deploy mass-scale manufacturing. This chapter provides a perception about various solid agricultural wastes that are generally used for bulk-scale production of metal and metal oxide nanoparticles. Results of characterization techniques, which give a clear vision about features of nanoparticles, are also summarized here. Then, several research works about synthesis of metal and metal oxide nanoparticles from these agricultural wastes are discussed. In the end, general applications of these nanoparticles are discussed briefly. Prospects and concerns are elucidated. This chapter also sketches that production of clean, safe metal and metal-oxide nanoparticles from solid agricultural wastes can become a golden chance in terms of research in areas of nanotechnology, solid waste management, mass-scale production of green nanoparticles, and concurrently also divulged in solving the issues of circular economy and sustainable growth.

2 Agricultural Wastes and Their Types

The agriculture sector plays a vital role in the social and economic development of India, but simultaneously, a huge amount (approximately 350 MTons) of agricultural wastes is generated every year. As per the data released by Ministry of New and Renewable Energy, these wastes can be utilized to generate about 18,000 MW of power every year (Mohite et al., 2022). Agricultural wastes, such as rice husk, wheat husk, rice straw, sugarcane bagasse, bamboo leaves, empty seed shells, and fruit and vegetable wastes, are the most common examples which have been produced worldwide (FAO, 2000; Mohite et al., 2022). If these wastes are released into the environment without applying proper disposal procedures, it may cause environment pollution and create threat to the mankind and animals as well (da Luz Corrêa et al., 2020; Lopes et al., 2021).

The agricultural waste materials mainly contain organic and inorganic components. The organic components can be oxidized easily, and the inorganic component consists of various minerals applicable for manufacturing various metal nanoparticles such as silver and gold nanoparticles and metal oxide nanoparticles such as silica nanoparticles. Agricultural wastes are classified into two different types, that is, agro-wastes and agro-industrial wastes. Agro-wastes can be further divided into field wastes and process wastes. Field wastes are wastes that are present in the field after the process of crop harvesting. These wastes consist of stalks, stems, leaves, and seed pods, whereas the process wastes are wastes present after the produced crop is being processed. These wastes consist of husk, bagasse, seeds, peels, roots, etc. The process waste and the field waste are commonly used for animal food, fertilizing soil, manufacturing, and other processes (Sadh et al., 2018). The agro-industrial wastes involve farm products and the wastes generated every year through the food processing industries such as juice, fruits, chips, and meat industries (Rudra et al., 2015). These wastes are schematically presented in Fig. 1.

2.1 Straw

Straw falls in the category of agricultural waste, and it contains dry stalks of cereal plants without grain. It consists about half of the yield of cereal crops such as wheat, barley, and rice (FAO, 2000). They can be used as energy sources, additives of concrete materials, and nanoparticles production. They mainly consist of cellulose, hemicellulose, lignin, lipids, and protein. Wheat straw and rice straw are rich in mineral content and poor in nitrogen. They show high carbon to nitrogen ratio, which leads to lower biodegradability as compared to other agricultural residues. Most of the quantity of straws are being utilized traditionally in major developing countries where they are produced largely (Álvarez et al., 2021; Belewu & Babalola, 2009).

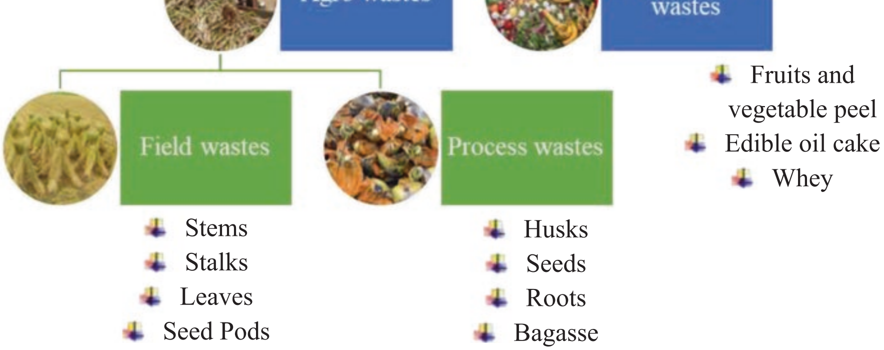


Fig. 1 Schematic classification and major sources of agricultural wastes

2.2 *Rice Husk and Rice Husk Ash*

Rice husks are the hard protecting covers of rice grains, which are considered as a waste during rice grain processing. They consist of mainly cellulose, lignin, and minerals (Das et al., 2020; Esra et al., 2013). The mineral quantity in rice husks varies from 15% to 20% by weight of rice husks. Due to high silica content in rice husks, it burns with difficultly under natural conditions, and biodegradation of rice husk is quite difficult and can also create environmental and ecological issues. Rice husk has high calorific value, approximately 17,000 KJ/Kg, due which it is mainly used in energy production through direct burning. This inappropriate combustion of rice husk generates another waste known as rice husk ash, which again causes environmental and disposal problem (Hossain et al., 2018). Being rich in silica, it also acts as a source for producing silica nanoparticles.

2.3 *Sugarcane Bagasse*

Sugarcane bagasse is an abundantly available biomass, obtained after sugarcane processing. It is majorly found in tropical countries (Ajala et al., 2021; Vaibhav et al., 2015). Due to its abundance in nature, it is harnessed for numerous applications such as energy and environment sustainability; paper industries; and feedstock for various products such as biopolymers, biochemicals, and biofuels (Hernández-Salas et al., 2009; Loh et al., 2013; Mahmud & Anannya, 2021; Toscano Miranda et al., 2021). It is typically rich in cellulose (44%) (Karp et al., 2013), which can be easily extracted and further utilized in paper and fiber production. The fibrous part may also be used in the textile and civil engineering sectors. Other than that, the bagasse can also be a feedstock for producing nanoparticles, for example, cellulose nanocrystals and starch-fiber nanocomposites (Gilfillan et al., 2012; Slavutsky & Bertuzzi, 2014).

2.4 *Corncob*

Corn is one of the most commonly planted and consumed crops round the globe. At the time of corn processing stems, leaves, husks, and corncobs remain as waste. Corncob is essential inedible residue generated in large amount after the removal of corn kernels and considered as an agricultural waste. Approximately 18 kg corncob waste is generated from 100 Kg of corn grain production (Tsai et al., 2001). Corncob has low density; fibrous, porous sponge like structures; and excellent adsorbing capacity. It is rich biomass resource that contains cellulose, hemicelluloses, and lignin. Some agricultural wastes can be treated as feed or compost, but it is difficult to treat corncob in the similar manner; hence, a large amount of corncob remains untreated. Since corncob contains wood like fibrous components, it is suitable as a building material, and it can also be used as mild abrasives to clean building surfaces. Most of their properties such as macrostructure, microstructure, chemical composition, water absorption, fire resistance, and thermal insulation capacities are found to be comparable with extruded polystyrene and expanded polystyrene (Berber-villamar et al., 2018; Choi et al., 2022). It also acts as an excellent source of producing silica and carbon nanoparticles.

2.5 Plant Leaves

Leaves of many plants, for example, papaya, mango, cereal, and bamboo find application in nanoparticle synthesis. Bamboo is one of the abundant and fast-growing renewable bio-resources. Bamboo leaves obtained from bamboo are commonly used (Silviana & Bayu, 2018) for making papers, handicrafts, and medicines. Apart from cellulose, hemicelluloses, and lignin, bamboo leaves are also rich in a variety of bioactive components such as flavonoids, polysaccharides, phenolic acids, and amino acids, thereby exhibiting multiple pharmacological activities (Cheng et al., 2023; Shen et al., 2022; Wang et al., 2015b). Bamboo leaf extracts containing bioactive components have been found to have significant effects as anti-virus, anti-oxidants, anti-fatigue, and anti-inflammatory based on modern nano pharmacological research (Kimura et al., 2022). Bamboo leaves are also used as a source for nanoparticle synthesis such as spherical silica nanoparticles with average size of 25 nm that are synthesized by thermal combustion and alkaline extraction method (Rangaraj & Venkatachalam, 2017).

2.6 Fruit and Vegetable Peels

Peel is an outer protective layer of a fruit or vegetable, which can be peeled and separated out. Their chemical composition shows the presence of proteins, lipids, fibers, and carbohydrates as well as minerals of zinc, iron, calcium, and manganese (Dibanda Romelle et al., 2016). Peel is renewable, green, nontoxic material like most of other agricultural waste materials. Potato peels are used for the synthesis of various nanoparticles such as silver, copper (Idhayadhulla et al., 2021), and zinc oxide (Bhuvaneswari, 2017). They contain starch, non-starch polysaccharide, vitamins, protein, lipids, acid soluble/insoluble lignin, and ash (Bhuvaneswari, 2017). Lemon peel and orange peel are also used for green synthesis of silver nanoparticles, and the method used was clean, safe, and eco-friendly; thus, obtained silver nanoparticles showed efficient antibacterial activity toward *Escherichia coli* (Niluxsshun et al., 2021).

3 Synthesis of Metal/Metal Oxide Nanoparticles

Metal and metal oxide nanoparticles possess distinctive properties due to their high surface-to-volume ratio. Owing to their unique properties resulting from the exceptionally high surface-to-volume ratio, metal/metal oxide nanoparticles (NPs) have attracted much attention in the field of science as well as in different technologies. The conventional chemical methods for the synthesis of these metal/metal oxide nanoparticles consume hazardous chemicals as precursors or as reducing agents, which can lead to severe environmental issues (Gutiérrez-Wing et al., 2012). In addition, these methods are quite expensive and time-consuming. To overcome these issues, scientists are exploring the greener route for the synthesis of these nanoparticles. For this purpose, several plant-based materials have been successively utilized as a raw material (Kulkarni & Muddapur, 2014). Different parts of a plant or crop such as leaves, stem, fruit, and roots can be used for this purpose (Suman et al., 2013). The size and shape of the synthesized nanoparticles can be altered by optimizing the reaction conditions such as time, temperature, and pH of the solution (Kharissova et al., 2013). In the recent scenario, for the further improvement and cost-cutting of synthesis process of nanoparticles, agricultural wastes have been utilized in place of plant-based materials (Saha & Kim, 2022).

Below are some green approaches adopted for synthesis of some metal and metal oxide nanoparticles from agricultural wastes.

3.1 Synthesis of Silver Nanoparticles

Silver nanoparticles are the most widely utilized nanoparticles in the area of food, medicine, and health care due to their extraordinary antibacterial and antifungal activities. Every year an estimated amount of 500 tons of silver nanoparticles are produced globally. Nowadays, several environmental benign methods are being developed to produce these silver nanoparticles by the use of agricultural wastes.

Wheat straw extracted lignin has been utilized to synthesize silver nanoparticles under optimized reaction conditions. Lignin was successfully used as reducing, capping, and stabilizing agent. Thus, prepared silver nanoparticles possessed face cubic centered (FCC) crystal structure with the average particle size of 15–20 nm. Silver nanoparticles showed excellent antimicrobial and antioxidant activities (Saratale et al., 2019).

Francisco et al. have reported the synthesis of silver nanoparticles from safflower waste (*Carthamus tinctorius* L.) (Figs. 2 and 3). As-synthesized silver nanoparticles were characterized using SEM and TEM techniques, and the results showed that the synthesized nanoparticles were uniform and spherical with the average particle diameter of 8.67 ± 4.7 nm. The prepared silver nanoparticles showed excellent antibacterial activity toward *Staphylococcus aureus* (Gram positive) and *Pseudomonas fluorescens* (Gram negative) bacteria (Rodríguez-Félix et al., 2021).

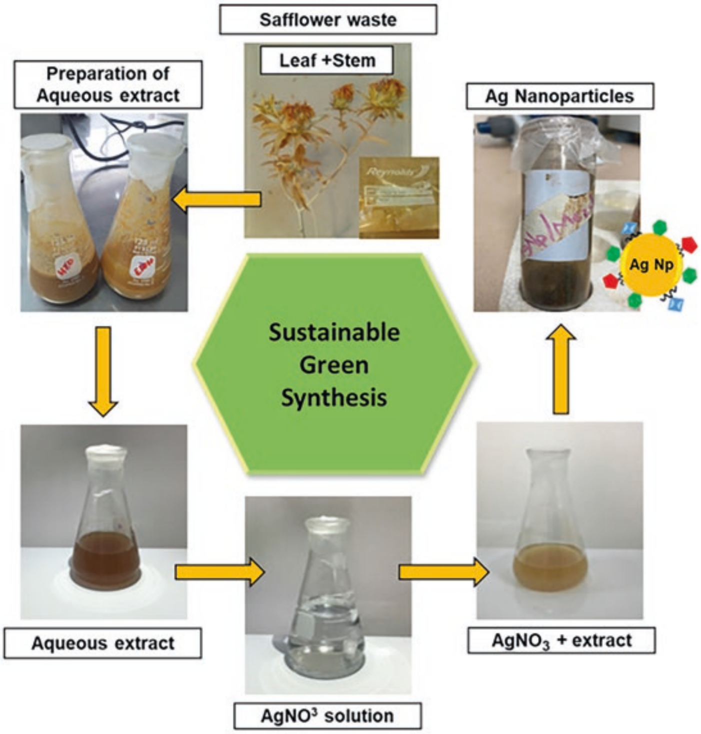


Fig. 2 Schematic representation of obtaining silver nanoparticles from aqueous extract of safflower waste. (Rodríguez-Félix et al., 2021)

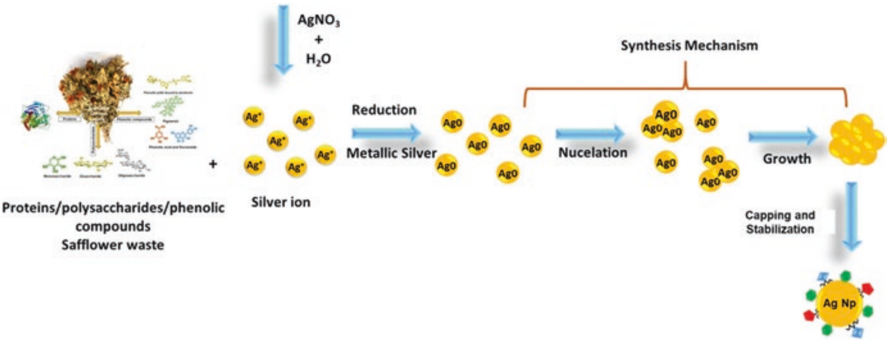


Fig. 3 Possible macromolecules and phenolic compounds present in the safflower waste aqueous extract

In two separate studies, silver nanoparticles were synthesized using the same material, that is, pomegranate fruit peel extracts. In the first study, authors reported that the use of ellagic acid present in the peel extract as a reducing agent to prepare silver nanoparticles (Ahmad et al., 2012). Thus resulting nanoparticles were spherical, which absorbed at UV-Vis wavelength of 427 nm and possessed FCC crystal structure with 5–10 nm average particle size. In the other study performed by Shanmugavadivu et al. (Shanmugavadivu et al., 2014), the prepared silver nanoparticles were in the range of 5–50 nm and showed absorption at 371 nm. The prepared particles showed great antibacterial activity against *Staphylococcus aureus*. In this study, primary and secondary amines groups were proposed as major functional groups, and other aromatic groups as implementers of silver nanoparticles synthesis.

In a similar study, a group of researchers have demonstrated the synthesis of silver nanoparticles using *Punica granatum* peel extract. The presence of silver nanoparticles was confirmed by the brownish yellow solution along with the presence surface plasmon peak at 432 nm. The particle size was observed as 30 nm with distorted spherical shape (Edison & Sethuraman, 2013). The prepared silver nanoparticles were successfully utilized in catalytic reduction of 4-nitophenol.

Synthesis of silver nanoparticles has also been performed using oak fruit hull extract under optimized reaction conditions ($AgNO_3$ concentration = 40 g/L; pH = 9; and temperature 45 °C) (Heydari & Rashidipour, 2015). The characterization results showed that the prepared silver nanoparticles were spherical and of 40 nm particle size. The cytotoxic activity of the particles was checked against human breast cancer cell. Another study demonstrated the use of defatted cashew nut shell starch to produce silver nanoparticles. The prepared silver nanoparticles (particle size 10–50 nm) were found structurally identical with the commercial silver nanoparticles (Velmurugan et al., 2015b).

The synthesis of silver nanoparticles was also reported using coconut shell extract as raw material. UV-visible spectroscopy (absorption peak at 432 nm) and TEM (particle size approximately 10–25 nm) techniques were used to confirm the production of silver nanoparticles. The prepared particles were found efficient toward antibacterial activity against human pathogens *Staphylococcus aureus*, *Listeria monocytogenes*, *E. coli*, and *Salmonella typhimurium* (Sinsinwar et al., 2018).

In a similar study, bilberry waste and spend coffee grounds were chosen as raw materials for the synthesis of silver nanoparticles. The phenolic extract of bilberry waste and spend coffee grounds was prepared using ethanol solvent and mixed with $AgNO_3$ solution at 25 °C. The size and shape (10–20 nm and spherical) of silver nanoparticles were observed via XRD, SEM, and DLS techniques (Chianese et al., 2016).

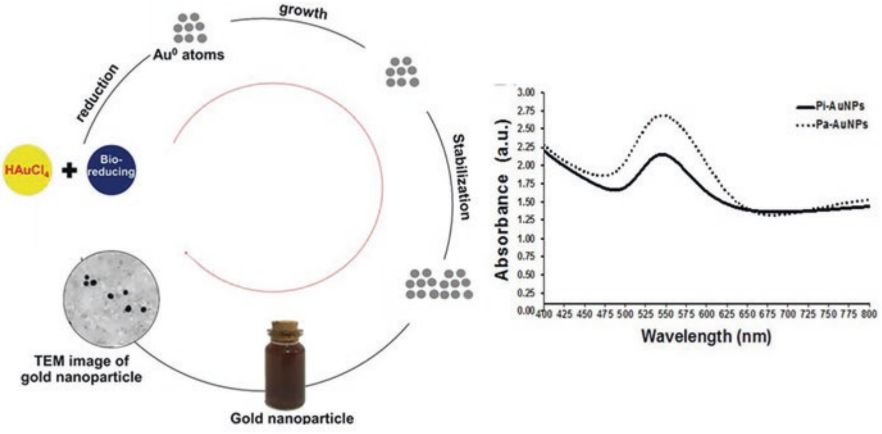
3.2 Synthesis of Gold Nanoparticles

Gold nanoparticles have potential applications in biomedical fields due to their great biocompatibility and nontoxic nature. Also gold nanoparticles are widely utilized in several applications such as catalytic reactions, antioxidant and antimicrobial activities, and in bio-sensing and bio-imaging purposes (Oladipo et al., 2017). In the previous studies, gold nanoparticles have been synthesized via various conventional physical and chemical methods, but these methods are costly and produce hazardous by-products. Thus, in the recent studies, the synthesis of gold nanoparticles via green methods using plant extracts and agricultural wastes such as banana peels and custard apple peels are being explored. The presence of phenolic compounds in these agricultural wastes is responsible for the production of nanoparticles (Mojumdar & Deka, 2019; Patra & Baek, 2015).

A recent study provides the green synthesis of biocompatible gold nanoparticles using waste fruit peel extracts of *Ananas comosus* (pineapple) and *Passiflora edulis* (passion fruit) for reduction of gold (III) chloride trihydrate ($HAuCl_4$) (Fig. 4a). The chemicals present in the fruit extracts, including proteins, minerals, lipids, vitamin, phenolic compounds, flavonoids, and carotenoid, act as reductants and nanoparticle stabilizers. The prepared gold nanoparticles exhibit a characteristic red coloration and UV-visible spectral absorption maximum around 545.5 nm and 545 nm using pineapple and passion fruit extracts, respectively (Fig. 4b). The resulting gold nanoparticles showed non-cytotoxic effects toward normal and cancer cells, which indicate their biocompatibility and thus their wide applications in medical field (Chiravoot et al., 2021).

Some researchers have synthesized gold nanoparticles using watermelon rind extract and evaluated their antibacterial activity against foodborne pathogens. The results indicated that the prepared gold nanoparticles possessed high antioxidant and anti-proteasome inhibitory potential, showing potential as an anticancer agent. The particles were spherical with 20–140 nm size and showed absorption maxima at 560 nm (Patra & Baek, 2015).

Another agricultural waste reported in the literature for the production of gold nanoparticles is mango peel extract. The particles were obtained with approximately



(a) (b)

Fig. 4 (**a**) Synthesis mechanism of gold nanoparticles using fruit peel extract. (**b**) UV-Vis absorption spectra of gold nanoparticles using pineapple and passion fruit extracts, respectively

20 nm size and were found biocompatible with African green monkey kidney normal cells (CV-1) and normal human fetal lung fibroblast cells (wI-38) at a high concentration of 160 μg/mL (Yang et al., 2014).

In a similar study, grape waste was utilized to produce gold nanoparticles with the particle size in the range of 18–25 nm. The particles showed maximum absorbance at 537 nm in UV-visible spectrophotometer. The researchers proposed that the gold nanoparticles were formed due to the presence of some phenolic compounds in the grape waste (Krishnaswamy et al., 2014).

Malhotra et al. have reported the synthesis of gold nanoparticles using rice bran extract. The characterization results revealed that the ferulic acid present in the extract is responsible for the reduction of Au^{+3} to Au^0 (Malhotra et al., 2014).

Furthermore, some researchers have utilized aqueous extract of de-oiled *Jatropha* waste to produce gold nanoparticles under optimized reaction conditions. The produced nanoparticles were of different shapes (triangle, hexagonal, and spherical) with the particle size in the range of 10–15 nm. The surface plasmon resonance peak was obtained at 520 nm, which confirms its high compatibility in several biomedical applications such as tissue imaging, drug delivery, and photothermal therapy (Kanchi et al., 2018).

In a similar study, seed shells and detoxified-defatted seed meal aqueous extracts of *Jatropha curcas* were utilized to produce gold nanoparticles with the particle size in the range of 5–20 nm under optimized reaction conditions (temperature = 60 °C and seed meal/shell:$HAuCl_4$ = 1:1). The characterization results showed that on increasing concentration of reducing agent, time, and temperature, the shape of the particles also changes. Thus, produced gold nanoparticles were found biocompatible with brain cancer glioma GI-1 and neuronal HCN-1A cell lines. Along with this, the prepared particles possessed significant bio-imaging and photoluminescent properties (Sheikh Mohamed et al., 2013).

Moringa oleifera flower extract is also reported to produce gold nanoparticles. The presence of proteins, carotenoids, phenolics, flavonoids, and alkaloids were responsible for the conversion of Au^{+3} to Au^0. The prepared particles showed absorption maxima at 540 nm in UV-visible spectroscopy. The particles were of different shapes and sizes (triangular, hexagonal, and spherical and approximately 5 nm) showing efficient catalytic activity toward reduction of 4-nitrophenol and 4-nitroaniline (Anand et al., 2015).

In a separate study, palm oil mill waste was utilized to produce spherical gold nanoparticles with average particle size of 18.75–5.95 nm (Gan et al., 2012). In addition, banana peel has been utilized to produce gold nanoparticles. The extracted banana peels were first crushed, boiled and precipitated using acetone, and mixed with $HAuCl_4$ and stirred under optimized reaction conditions (Bankar et al., 2010). Thus, produced nanoparticles were characterized using UV-visible spectroscopy, X-ray diffraction pattern, SEM, and FTIR analysis. The particles showed significant antimicrobial activities.

3.3 Synthesis of Silica Nanoparticles

Silica nanoparticles are gaining incredible attention of researchers due to their potential applications in different industries and medical fields (Briceño-Ahumada et al., 2021; Gu et al., 2013). Conventional synthesis of silica nanoparticles uses toxic and costly precursors. Therefore, green alternatives of these precursors such as agricultural wastes (rice husk, wheat husk, rice straw, corncob, sugarcane bagasse, and bamboo leaves) (Shim et al., 2015; Velmurugan et al., 2015a) are widely utilized in the recent scenario. Synthesis of silica nanoparticles using agricultural wastes makes the process green and environmentally friendly.

The use of rice husk for the synthesis of silica nanoparticles is well documented in the literature. A group of researchers have reported the use of different acids for extraction of silica nanoparticles from rice husk. Among all acids, HCl was found efficient to produce silica nanoparticles with the highest surface area (Liou & Yang, 2011). Similarly, alkali fusion and acid precipitation method are also reported to extract silica nanoparticles from rice husk. The produced silica nanoparticles were in the range of 20–25 nm and 274 m^2/g surface area (Yuvakkumar et al., 2014a). Furthermore, a separate study shows the extraction of silica nanoparticles from rice husk via pyrolysis method. The process involves the mixing of H_3PO_4 with sodium silicate solution (between pH 3 and 6) and further addition of PEG (polyethylene glycol), which helps to generate porosity on the silica surface. Thus produced silica nanoparticles possessed high surface area with 2.30 nm diameter (Li et al., 2011). Similar investigation was done at different temperatures ranging from 500 to 650 °C. Maximum yield of silica nanoparticles were obtained in temperature from 500 to 610 °C, which decreased on further increasing temperature (Ghaferi et al., 2021). Rice husk–derived silica nanocomposites with good tensile strength and uniform distribution are also well documented in the literature (Ban & Saddam, 2017).

Chen et al. have demonstrated the synthesis of highly porous silica nanoparticles from rice husk via extraction with ionic liquids. For this purpose, firstly rice husk was dissolved in ionic liquids and filtered (Fig. 5). The obtained rice husk residue

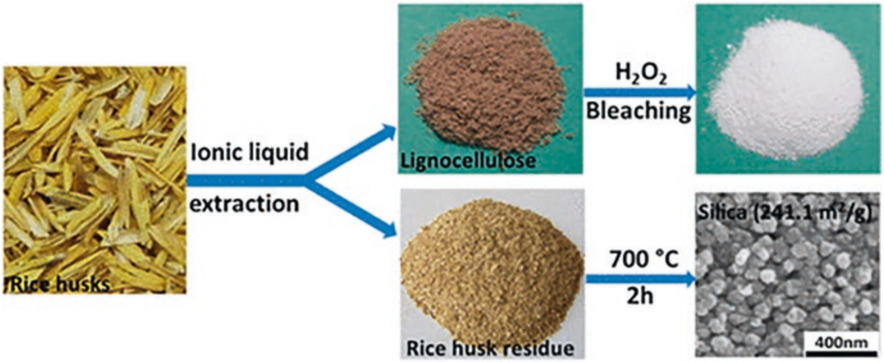


Fig. 5 Conversion of rice husk into nanosilica

(contains high silica content) was then thermally activated to get highly pure and amorphous nanosilica (Chen et al., 2013).

Apart from the use of rice husk, bamboo leaves, high silica–containing material have also been utilized for the production of silica nanoparticles. Wang et al. have demonstrated the use of bamboo leaves in the production of silica nanoparticles (5–8 nm size and 300 m^2/g surface area) via thermal decomposition and magnesiothermic reduction (Wang et al., 2015a). In a separate study, silica nanoparticles were produced from bamboo leaves via ultrasonic method. Thus, the produced nanoparticles were comparatively of smaller size (Dirna et al., 2020). Furthermore, bamboo leaves derived silica nanoparticles have been utilized in producing silica supported Fe_2O_3 photocatalyst with crystallite size 20–70 nm. The photocatalytic activity of the catalyst was checked in degradation of Rhodamine B dye (Fatimah et al., 2019a). Similarly, silica supported TiO_2 and silica supported ZnO photocatalysts have also been synthesized using bamboo leaves, and the photocatalytic activity was evaluated in degradation of methylene blue and Rhodamine B dye, respectively. The degradation study suggested that the efficiency of the catalyst increased with increase in TiO_2 content (Fatimah et al., 2019b, 2021).

The use of corncob for the synthesis of silica nanoparticles is also well documented in the previous studies. The high silica content in corncob makes it suitable for the production of silica nanoparticles (Duque-Acevedo et al., 2020; Okoronkwo et al., 2013; Velmurugan et al., 2015a). A study reports the synthesis of silica nanoparticles via sol-gel method followed by alkali treatment of corncob. The produced silica nanoparticles were found in the range of 50 nm particle size (Velmurugan, Shim et al., 2015; Duque-Acevedo et al., 2020) Corncob ash–derived silica nanoparticles were utilized to prepare faujasite nanosheets under optimized conditions (temperature 85 °C and 0.030 M TPOAC) (Salakhum et al., 2018). In a separate study, corncob was converted into carbon nanocomposite material. The prepared nanocomposite was found efficient for the removal of methylene blue dye and U(VI)/Cr(VI) ions from the aqueous solution.

Sugarcane bagasse, a by-product of ethanol industries, contains high amount of silica. A group of researchers have synthesized silica nanoparticles from sugar cane bagasse via alkali fusion followed by acid precipitation method (Falk et al., 2019; Vaibhav et al., 2015). Similarly, silica nanoparticles with high surface area and pore volume have been produced via acid treatment of sugarcane bagasse. A separate study demonstrated the use of sugar cane bagasse in the synthesis of silica supported TiO_2 photocatalyst with 5–20 nm particle size. The catalytic activity was tested on degradation of methyl orange dye. Falk et al. have synthesized high purity silica nanoparticles with 10 nm particle size via sol-gel method (Falk et al., 2019). Similarly, the synthesis of silica nanoparticles (80–100 nm particle size) via sol-gel method followed by freeze drying and heat drying was also investigated. The study revealed that the nanoparticles formed via freeze drying method were possessed high surface area and porosity as compared to the particles formed via heat drying method (Boonmee & Jarukumjorn, 2020). In a recent study, biogenic nanosilica has been synthesized using different agricultural wastes such as groundnut shell, banana peel, coconut husk, orange peel, and walnut shell via alkali treatment. The SEM and

TEM analysis of the obtained nanosilica confirmed the presence of agglomerated nanosized particles. The results indicated that nanosilica derived from groundnut shell possessed high surface area (0.829 μm) as compared to the nanosilica derived from other agricultural wastes. The particle size distribution for walnut shell–derived nanosilica was found 12.18 μm to 912 μm for nanosilica derived from banana peel (Peerzada & Chidambaram, 2021).

In a separate study, magnetic silica nanoparticles were synthesized using waste barley husk via a two-step green route (Fig. 6). Barley husk was treated with acid and then thermally activated to prepare silica nanoparticles, which then treated with Fe_3O_4 to synthesize magnetic silica nanoparticles. The characterization results of thus obtained silica nanoparticles confirmed the average diameter of 162 nm with a large surface area ~ 120 m^2/g. The prepared magnetic silica nanoparticles were found to be an efficient adsorbent for removing petrol contaminants (with removal efficiency of more than 80%) from waste (Akhayere et al., 2020).

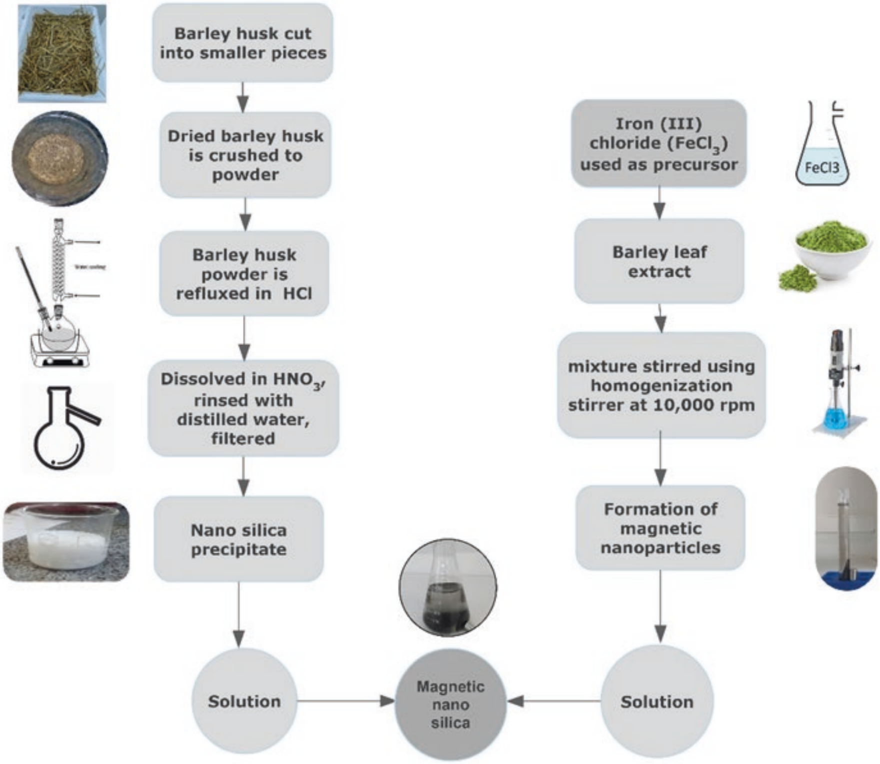


Fig. 6 Synthesis method for production of magnetic silica nanoparticles from waste barley husk. (Adapted, in part, with permission from Akhayere et al., 2020)

3.4 Synthesis of Other Metal/Metal Oxide Nanoparticles

The synthesis process of metal and metal oxide nanoparticles from different waste materials is less expensive and environmental friendly. Papaya leaves have been utilized to prepare iron oxide nanocomposites via thermal decomposition method (Ahmed & Ahmaruzzaman, 2015). These agricultural wastes well preserve several minerals and food reserves and also contain some organic compounds such as phenols, alkaloids, flavonoids, terpenoids, proteins, enzymes, and carbohydrates. These organic compounds act as reducing or stabilizing agents to produce nanoparticles (Bachheti et al., 2020). A study revealed the synthesis of Mn_3O_4 nanoparticles from banana peel extract, which reduce $KMnO_4$ to Mn_3O_4 (Yan et al., 2014). Another study demonstrated the use of tea wastes in producing hydrated aluminum nanoparticles via co-precipitation method. In this process, $Al_2(SO_4)_3$ and NaOH were mixed with tea waste and polyacrylamide, and the obtained precipitate of porous aluminum was washed and dried (Cai et al., 2015).

Another study reports the synthesis of biogenic ZnO nanoparticles from rambutan peels. The process includes the mixing of zinc nitrate hexahydrate with rambutan peel extract at 80 °C for 2 h. The obtained zincellagate complex was dried at 40 °C and further calcined at 450 °C. The resulting ZnO nanoparticles fabricated on cotton were found efficient antibacterial agent toward *E. coli* and *S. aureus* bacteria (Yuvakkumar et al., 2014b). A similar study has been demonstrated by Yuvakkumar et al., showing the synthesis of NiO nanocrystals from rambutan peels (Yuvakkumar et al., 2014c). The presence of polyphenols in the extract was responsible for the reduction of $Ni(NO_3)_2$ to NiO nanocrystals. The obtained NiO crystals fabricated on cotton were shown antibacterial properties against *E. coli* and *S. aureus*, respectively.

In a recent study, crystalline platinum nanoparticles with 15–25 nm size have been synthesized using *Punica granatum* peel extract. The negative zeta potential shows the high stability of the prepared platinum nanoparticles. The study revealed that the presence of phenolic compounds in the peel extract was responsible for the capping and stabilization of prepared particles. The prepared platinum nanoparticles were found efficient toward the reduction of 3-nitrophenol (Dauthal & Mukhopadhyay, 2015).

From the above discussion, it is apparent that agricultural wastes have a wide scope for the synthesis of various metal and metal oxide nanoparticles due to the presence of various biomolecules, which can act as reducing or capping agents. The richness and easy availability of agricultural wastes can be successfully exploited on a large scale for the biogenic synthesis of nanoparticles. The system is cost-effective and can create wealth and useful products through nanotechnology.

A summary of nanoparticles synthesized from agricultural wastes is given in Table 1.

Table 1 Nanoparticles synthesized from various agricultural wastes

Agriculturalwastes	Name of nanoparticles	Synthesis method	Properties	References
Plant extract	Au, Ag, Cu, Pt, Pd, ZnO, TiO_2	Biosynthesis	Show potential applications in environmental and biomedical fields	Jadoun et al. (2021), Barnawi et al. (2022), and Chaudhary et al. (2023)
Fruit and vegetable peels	Ag and Au, TiO_2, ZnO	Green method using fruit and vegetable peel extracts	Silver and gold nanoparticles have average particle size range of 5–20 nm, exhibited potential antioxidant and antibacterial activity	Mojumdar and Deka (2019) and Oyekanmi et al. (2022)
Plant roots	Au	Green synthesis	Show antioxidant, antimicrobial, anti-inflammatory, anticancer activities, catalytic action	Varghese et al. (2021)
Safflower waste	Ag	Green synthesis using safflower waste aqueous extract	Show potential application as antibacterial agents in food and pharma industries	Rodríguez-Félix et al. (2021)
Bamboo leaves	Si and SiO_2	Magnesiothermal reduction, ultrasonic method	Less than 10 nm size and high lithium storage capacity	Wang et al. (2015b) and Dirna et al. (2020)
Wheat straw	Ag	Reduction of silver salt using straw extract	Antimicrobial and antioxidant silver nanoparticles showed FCC crystal structure with the average particle size of 15–20 nm	Saratale et al. (2019)
Watermelon rind extract	Au	Green synthesis using rind extract	Particles had spherical shape and have a size distribution of 20–140 nm, showed bio potential applications	Patra and Baek (2015)
Grape waste	Au	Green reduction using phenolic compounds present in grape fruit waste	Mean particle size range from 20 to 25 nm	Krishnaswamy et al. (2014)

(continued)

Table 1 (continued)

Agriculturalwastes	Name of nanoparticles	Synthesis method	Properties	References
Rice bran	Au	Bio mineralization of gold using ferulic acid present in rice bran extract	Spherical gold nanoparticles with average particle size of 50–100 nm	Malhotra et al. (2014)
Rice husk	SiO_2	Extraction using mineral acids, alkali fusion, pyrolysis, and acid precipitation method	Higher surface area with particle size range 20–25 nm, good tensile strength	Liou and Yang (2011) and Yuvakkumar et al. (2014b)
Seed shell	Au	Reduction method	5–10 nm sized gold nanoparticles were found biocompatible with brain cancer cells and possessed bio-imaging and photoluminescent properties	Sheikh Mohamed et al. (2012)

4 General Applications

Metal and metal oxide nanoparticles produced from solid agricultural waste materials have wide applications in many fields such as catalysis, drug-delivery, industrial, environmental, and energy sectors (Fig. 7). Silver and gold nanoparticles show antimicrobial and antioxidant properties; thus, these can be utilized in drug-delivery and food industry applications (Rodríguez-Félix et al., 2021). Silver nanoparticles extracted from coconut shell waste have been used as an antibacterial agent against severe human pathogens such as *E.coli* and *S. typhimurium* (Sinsinwar et al., 2018). Platinum, iron, and palladium nanoparticles extracted from different fruit peel waste have been utilized as catalysts, while ZnO and NiO nanocrystals derived from plant waste have also shown antibacterial activities (Adelere & Lateef, 2016). Biosensing, bio-imaging, and bio-labeling are other applications of metal and metal oxide-based nanoparticles. Such nanoparticles are also used in degradation of dyes, additives in paints, and removal of anthropogenic pollutants. Magnetic iron oxide nanoparticles can be produced from fruit peel waste and can be used as catalysts in different organic and environmental reactions (Adelere & Lateef, 2016). Thermal insulation, semi conductivity, and energy storage are other applications where such nanoparticles can also be utilized. Silica nanoparticles have been also used in multifaceted applications such as catalysts in Suzuki coupling reactions, oxidation reactions, and multicomponent organic reactions (Malpani & Goyal, 2022). They are also used in adsorption of toxic contaminants such as nitrate ions, carcinogenic polycyclic aromatic hydrocarbons, and dyes such as methylene blue, Rhodamine B, and methyl orange. They also behaved as nanocarriers in various drug-delivery

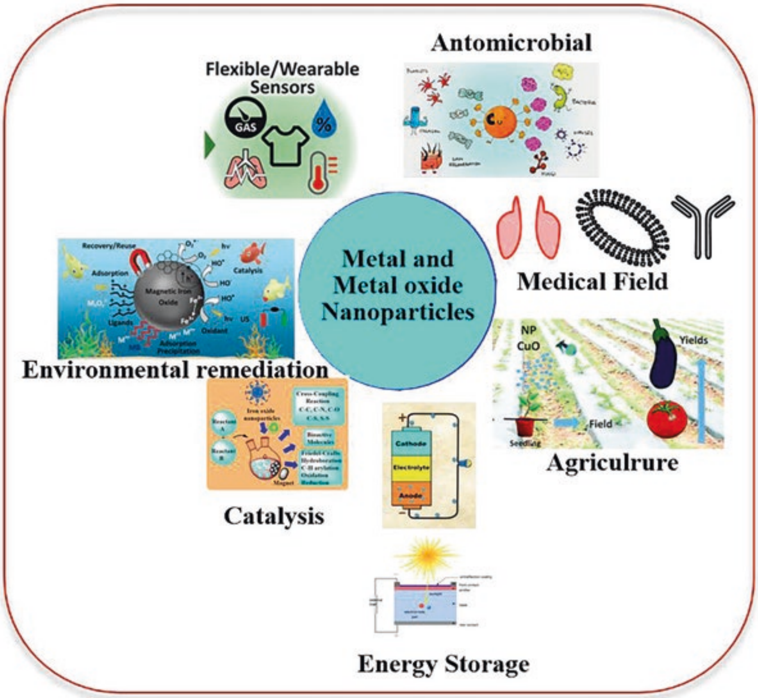


Fig. 7 Applications of metal and metal oxide nanoparticles

applications. They have been also utilized as anodes in Li-ion batteries, solar cells, and energy storage batteries.

5 Future Perspectives

Nanoparticles, particularly metal and metal oxide nanoparticles, have garnered substantial attention over the past few decades due to their unique physicochemical properties that differ significantly from bulk materials. The reduced size and high surface-to-volume ratio provide these nanoparticles with remarkable reactivity, strength, electrical conductivity, and optical properties. Some future perspectives of metal and metal oxide nanoparticles are summarized below:

1. *Medicine:*
    - *Targeted Drug Delivery:* Metal nanoparticles can be functionalized with specific ligands or antibodies to target specific cells or tissues, enabling localized treatment and minimizing side effects.

- *Thermal Ablation and Photothermal Therapy:* Gold nanoparticles, for instance, can absorb near-infrared light and convert it into heat, which can be used to destroy cancer cells.
- *Diagnostics:* Metal nanoparticles can be used as contrast agents in various imaging techniques, such as MRI and CT scans.

2. *Catalysis:*
    - Due to their high surface area and enhanced reactivity, metal and metal oxide nanoparticles serve as efficient catalysts for various chemical reactions, potentially reducing the energy input required and increasing yield.
3. *Energy:*
    - *Hydrogen Storage:* Some metal nanoparticles can absorb hydrogen and thus can be utilized in fuel cells.
    - *Solar Cells:* Metal nanoparticles can enhance light absorption, leading to increased efficiency in photovoltaic devices.
    - *Batteries:* Metal oxide nanoparticles can enhance the charge storage capacity and rate capabilities of batteries.
4. *Environmental Applications:*
    - *Water Treatment:* Metal oxide nanoparticles can degrade organic pollutants in water.
    - *Air Purification:* Metal/metal oxide nanoparticles can help remove harmful pollutants from air, especially when incorporated into filters or coatings.
5. *Electronics:*
    - Metal nanoparticles can be used in memory storage devices, sensors, and other electronic components due to their unique electrical properties.
6. *Agriculture*:
    - Metal nanoparticles can be used for the controlled release of pesticides or fertilizers, reducing the amount needed and minimizing environmental impact.
7. *Antimicrobial Applications:*
    - Silver nanoparticles, for instance, exhibit strong antibacterial properties and can be incorporated into textiles, coatings, and medical devices to prevent microbial growth.

6 Concerns

We have tried to point out the most familiar types of solid agricultural wastes, metal and metal oxide nanoparticles produced from these wastes, and a few common applications of such nanoparticles in this chapter. However, many possibilities exist which can be unveiled by exerting more serious attempts from researchers, environmentalists, industrialists and government officials. The conception of generating value-added materials from solid wastes is quite tempting and satisfies the notion of principles of green chemistry and circular economy. But this area is lacking from gaps in knowledge, information, and implementation. Many engineered nanoparticles developed in research labs fail to compete in the real world/market due to lack of sufficient technologies for their mass production, generation of by-products or secondary wastes, easy degradation, costlier handling, transportation, etc. Prior to transition from lab to practical world, life-cycle assessment, risk analysis, market research, cost-benefit analysis, management of toxic by-products should have been conducted thoroughly. Data available in this field is deprived of these factors. Thus, it has become a limiting factor and should be addressed primarily. Precautions should have been applied throughout all phases of the life cycle, that is, production, usage, and then final disposal of these waste-derived nanoparticles. Even though the green chemistry and sustainability principles have been completely followed during the development phase, it is not necessary that nanoparticles produced are safe to use and do not cause ill effects on human beings and ecological systems. For example, copper, nickel nanoparticles, carbon nanotubes, and nano fullerenes could be carcinogenic. Some of the major concerns associated with the use of metal/metal oxide nanoparticles in our day-to-day life are outlined as follows:

1. *Toxicity and Environmental Impact:* The potential toxicological effects of metal and metal oxide nanoparticles on human health and the environment are still not fully understood. More comprehensive studies are needed to ascertain their safety.
2. *Scalability:* While lab-scale synthesis of nanoparticles is well established, large-scale production maintaining the same quality, cost, and properties remains a challenge.
3. *Stability:* Some nanoparticles tend to agglomerate over time, losing their unique properties. Methods to ensure their stability and shelf life during storage and use are essential.
4. *Regulations:* As the use of nanoparticles becomes more widespread, appropriate regulatory frameworks will need to be developed to ensure their safe application.

Given the rapid advancements in nanotechnology, it is expected that new applications and improvements in existing technologies will continue to emerge. Collaborative efforts between scientists from various disciplines, industries, and policymakers will be crucial in harnessing the full potential of metal and metal oxide nanoparticles while ensuring their responsible and sustainable use.

7 Conclusion

In conclusion, this chapter summarizes the concept of solid agricultural wastes, their types with some contemporary examples, and how most popular metal and metal oxide nanoparticles can be produced from such wastes. Some researches related to how these nanoparticles are derived from solid agricultural wastes are also summarized with their characteristic results. It also outlines the common applications of these nanoparticles in the field of catalysis, environmental remediation, energy storage, drug delivery, and other biomedical sectors. This work also suggests that an overall target-oriented system should be designed of both government and private organizations, which can help in mass-scale production of metal and metal oxide–based nanoparticles from agri-wastes. The process parameters should be optimized to achieve these goals. Researchers and their labs should be equipped with sufficient data and market study to make these products industry fit. Future prospects of use of metal and metal oxide nanoparticles in various sectors are also discussed. This chapter also pointed out a few concerns correlated with extensive usage of these nanoparticles.

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