Review Article
Trends in Sustainable Green Synthesis of Silver Nanoparticles Using Agri-Food Waste Extracts and Their Applications in Health

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Currently, silver nanoparticles have boomed in food and medicine due to their potential applications, such as antibacterial and anticancer activity. These nanoparticles have been synthesized by several techniques; however, green synthesis has taken on greater importance due to the non-generation of toxic residues. Green synthesis has been constructed from plant parts; however, the new trend comprises the use of agri-food waste extracts, known as sustainable green synthesis. The use of agri-food waste reduces environmental pollution and confers its added value. The main waste generated is found in agricultural crops and industry from fruits and vegetables, cereal, bagasse from the food industry, and alcoholic beverages, oil cake of the oil industry, among others. The main biomolecules in agri-food waste extracts include phenolic compounds, alkaloids, terpenes, cellulose, hemicellulose, lignin, and proteins, whose function is to reduce the agents of the silver ion. Therefore, the objective of this review was to promote the use of agri-food waste for the sustainable green synthesis of silver nanoparticles and its application as antibacterial and anticancer agents.

1. Introduction

Nanotechnology is considered a multidisciplinary science that aids in solving current problems, and where its function is to manufacture nanoscale materials [1, 2]. The main applications of nanotechnology lie in the areas of food, medicine, water treatment, solar energy conversion, and catalysis [2–4]. Specifically, nanoparticles exhibit completely new or improved properties based on characteristics such as size, distribution, and morphology [5]. These can be obtained from raw materials of natural origin (proteins and polysaccharides) [6, 7] or from inorganic precursors (metals, salts) [8]. Metallic nanoparticles have various applications, such as antibacterial [9–12], antiviral [13–15], and anticancer [16–18]. Also, different investigations focus on the synthesis of metallic nanoparticles by various means, including physical, chemical, and biological methods [19]. However, chemical methods employ chemical agents such as metal reducers.
that can be toxic and that limit their biomedical applications [20]. Therefore, methods more friendly to health and the environment have been implemented.

Silver nanoparticles have been synthesized from simple, biocompatible, non-toxic, and eco-friendly protocols [21]. This technique is known as green synthesis and can use microorganisms, enzymes, and plants or plant extracts, which have been suggested as possible eco-friendly alternatives [22]. The advantages of green synthesis over chemical and physical methods include respect for the environment, their profitability, and their easy scalability for the large-scale synthesis of nanoparticles; in addition, it is not necessary to use high temperatures, pressures, energy, and toxic chemicals [23]. Green synthesis from plant materials (including leaf, bark, fruit, peel, seed, and root extracts) [24–28] works under mild experimental conditions and replaces hazardous chemicals with polyphenols, flavonoids, proteins, saponins, or sugar as reducing agents as well as capping agents [29]. An alternative to the use of plant extracts for the synthesis of silver nanoparticles is agri-food waste, known as the new era of the green synthesis of metallic nanoparticles.

The use of agri-food waste for the synthesis of silver nanoparticles is based on the justification that food production is one of the most important human industries, which can be responsible for a majority of environmental impacts in developed countries [30]. Also, agricultural and food industry wastes possess a plethora of phytochemicals, proteins, and polysaccharides of commercial interest that can be recovered to decrease the generation of waste [31–33]. The main agri-food wastes are generated from the production of fruits [34], vegetables [35], cereals [36], and oilseeds [37]. Fruit and vegetable industries generate large amounts of waste biomass during processing, mainly in selecting, sorting, and peeling, producing different types of solid residues such as peel/skin, seeds, leaves, stems, and bark [38]. The use of agri-food waste extracts as reducing agents renders the synthesis of silver nanoparticles a sustainable system because, in one step, a green synthesis method is employed and agri-food waste is given added value. Therefore, the synthesis of silver nanoparticles from agri-food waste denominated sustainable green synthesis.

Food industries generate a large amount of agri-food waste at the level of agricultural crops, as well as during processing, with around 1.6 billion tons of primary product equivalents, and the total food wastage for the edible part of this amounts to 1.3 billion tons [39]. In the wine industry, wastes consist mainly in solid by-products, including marcs or pomace and stems and may account on average for nearly 30% (w/w) of the grapes used for wine production, and polyphenols have been identified as major compounds [40]. Other agricultural wastes are straw, stover, peelings, cobs, stalks, bagasse, and other lignocellulosic residues. The annual lignocellulosic biomass generated by the primary agricultural sector has been evaluated at approximately 200 billion tons worldwide [41]. Wine and lignocellulosic waste are examples of agri-food waste that can be utilized to obtain extracts with molecules that act as reducing agents for the synthesis of silver nanoparticles and capping agents.

The mechanism of green synthesis of silver nanoparticles from agri-food waste extracts is similar to synthesis from plant extracts, which is a bottom-up method [42]. The bottom-up method consists of the reduction of the silver atom, followed by nucleation and, finally, growth [43]. In addition, the importance of new methods of synthesis of silver nanoparticles is its powerful application as broad-spectrum antibacterial agents, mainly in Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Micrococcus flavus, Pseudomonas aeruginosa, Klebsiella pneumoniae, and Bacillus pumilus, among others [44]; and as an agent against cancerous human cells such as MCF7 breast, A549 lung cancer [45], PC-3 prostate cancer [46], A431 skin cancer [47], and HeLa of cervical cancer [48], among others.

Therefore, the use of agri-food waste extracts is an alternative for the sustainable green synthesis of silver nanoparticles, which broadens the panorama in terms of new precursor agents for the synthesis of nanoparticles, and also aids in reducing agri-food waste. The objective of this review was to promote the use of agri-food waste for the sustainable green synthesis of silver nanoparticles and promote its application as an antibacterial and anticancer agent.

2. Conventional Green Synthesis of Silver Nanoparticles: Plant Extracts

Current researchers have been intensely interested in silver nanoparticles, owing to their large surface-to-volume ratio, morphology, and small size, resulting in variations in their physical and chemical characteristics [49]. The advantages of green synthesis of silver nanoparticles include being an economical, eco-friendly, under mild experimental condition, and a simple method for preparing silver nanoparticles [49]. Currently, plants extract has been used for the synthesis of silver nanoparticles and have many advantages over chemical, physical, and microbial syntheses [50]. A great variety of plant extracts have been successfully utilized for synthesizing silver metal (Ag0) nanoparticles from silver ions (Ag+) [51]. In addition, for the green synthesis of silver nanoparticles, different concentrations and amounts of plant extract as reducing agents have been evaluated, as well as different concentrations of silver nitrate (AgNO3) as precursor of the synthesis [52, 53].

2.1. Extracts from Different Parts of the Plant. Aqueous extracts have been obtained from different parts of plants that contain phytochemicals and other biopolymers that act as reducing agents of silver metal [54] (Figure 1). Some recent parts of plant extracts reported include the following: leaf extracts of Croton sparsiflorus morong [55], Psidium guajava [56], Datura stramonium [57], Passiflora edulis f. [58], and Amnona reticate [59]; from the stem extracts of Saccharum officinarum [60], Diospyros montana [61], Vigna unguiculata [62], and Jasminum auriculatum [63], from the root extracts of Lithospermum officinale [64], Berberis vulgaris [65], Nepeta leucophylla [66], Bergenia ciliata, Bergenia stracheyi, Rumex dantatus, and Rumex hastatus [67]; from the fruit extracts of Cleome viscosa L. [16], Chaenomeles sinensis [68], Terminalia belarica [69], Cornelian cherry
spherical in shape and <100 nm in size. These authors concluded that, from the extract from *Cassia toral* L. root, a rapid synthesis of silver nanoparticles with an eco-friendly and convenient method was obtained.

Soshnikova et al. [94] synthesized silver nanoparticles from three distinct Cardamom fruits (5-year-old *Annonum villosum*, fresh *A. villosum*, and fresh *Elletaria cardamomum*). First, to obtain the fruit extract, 10 g of each fruit was ground thoroughly and autoclaved for 1 h at 100°C in 100 mL of sterile water and filtered with Whatman filter papers. For the synthesis, 1 mM of AgNO3 solution was added to the diluted extracts at room temperature. A color change in the reaction mixtures indicated the formation of nanoparticles. Nanoparticles were collected by centrifugation at 16,000 rpm for 10 min, washed thoroughly with sterile water, and finally washed with 80% MeOH. The best extract evaluated by UV-vis was 5-year-old *A. villosum*, and FE-TEM revealed a size between 5 and 15 nm and a spherical shape. Elemental analysis by EDX demonstrated the presence of silver nanoparticles. These authors concluded that silver nanoparticles had been conveniently synthesized by a rapid and green method utilizing the aqueous extract of *Fructus anomyi*. The methodology of green synthesis was innocuous, ecologically benign, and inexpensive.

2.2. Biomolecules as Reducing Agents. The reduction of the silver ion (Ag+) of silver nitrate (AgNO3) to the silver atom (Ag0) is due to the biomolecules found in plant extracts as reducing agents. Sathishkumar et al. [95] reported this effect of silver ion reduction by terpenoids (cinnamaldehyde, ethyl cinnamates, and β-caryophyllene) of the *Cinnamom zeylanicum*—bark extract. The identification of color change is a primary tool that confirms the ability of compounds of plant
Figure 2: Continued.
extracts in nanoparticle synthesis [96]. This color change is due to the excitation of surface plasmon resonance (SPR) in the nanoparticles [97, 98]. Figure 2 presents how the biomolecules reduce the silver ion to the silver atom for the synthesis of silver nanoparticles.

Vidhu et al. [99] mention that several factors exert an influence on the formation of silver nanoparticles, such as the plant source and the organic compound in plant extract. For example, phytochemical analysis of the Macrotyloma uniflorum extract has indicated the presence of phenolic acids such as caffeic acid and p-coumaric acid. These biomolecules possess hydroxyl and carbonyl groups, which are able to bind to metals and which may inactivate ions by chelating. This chelating ability of phenolic compounds is probably related to the high nucleophilic character of the aromatic rings rather than to specify chelating groups within the molecule. In caffeic acid, active hydrogen may be responsible for the reduction of silver ions leading to the formation of silver nanoparticles, as depicted in Figure 2(a). Edison and Sethuraman [100] report that the major biomolecules present in the Terminalia chebula fruit are hydrolyzable tannins, polyphenols, gallic acid, and chebulagic acid. The possible mechanism for the reduction of Ag+ can form intermediate complexes with the phenolic groups (–OH) present in hydrolysable tannins, which subsequently undergo oxidation to quinone forms, with a consequent reduction of silver ion (Ag+) to silver metal (Ag0) (Figure 2(b)). Ahmad et al. [101] report that luteolin is a common flavone found in the aerial parts of the basil plant. Formation of the enol form of the luteolin freely releases reactive hydrogen, which is responsible for the conversion of Ag+ into Ag0 and the subsequent formation of nanoparticles, as shown in Figure 2(c).

Then, the biomolecules reduce the silver ion into metallic silver as a first phase, and two additional phenomena are observed for the synthesis of silver nanoparticles, known as nucleation and growth (Figure 3). The nucleation phase occurs when particles of the metal plates tend to migrate toward other metal particles, forming agglomerates called clusters [2]. These clusters then tend to form small silver nanoparticles. Then, the growth phase occurs where the adjacent small nanoparticles spontaneously begin to coalesce to form larger particles. This spontaneous process, controlled...
thermodynamically, is due to that the larger particles are energetically favored with respect to the smaller particles, this is known as Ostwald ripening [104].

The growth part concludes with the end size of silver nanoparticles and with different shapes is obtained. The shape will be conferred by the conditions of synthesis such as temperature and pH, as well as rate and time of synthesis. In different investigations, spherical, irregular, hexagonal, and triangular shapes have been obtained and are shown in Figure 4. Ravichandran et al. [105] reported silver nanoparticles of a spherical shape (Figure 4(a)). To obtain this shape, the nanoparticles were reduced to AgNO3 by adding 1.5 mL of *Atrocarpus altillis*-leaf extracts to 1 mL of the 0.01 M AgNO3 solution, and the volume was raised 10 mL with deionized water in a 25-mL volumetric flask at 25 \( \pm 0.5 \) °C for 24 h. Singh et al. [106] reported silver nanoparticles with an irregular shape (Figure 4(b)). First, *Symphytum officinale* aqueous extract was diluted in water at a ratio of 1:5 (v/v). To this solution, the final concentration of 1 mM filter-sterilized solution of AgNO3 was added and the reaction mixture was maintained at 65 °C. On the other hand, Wang et al. [107] reported silver nanoparticles with two shapes: hexagonal and triangular (Figures 4(c) and 4(d)). For biosynthesis with these shapes, 5 mL of *Dendropanax moribifera*-leaf extract was mixed with 45 mL of deionized water, and AgNO3 solution was added at a final concentration of 1 mM to the reaction mixture, which was then incubated at 80°C for 1 h.

2.3. Biomolecules as Capping Agents. During the synthesis process, biomolecules of the extract, in addition to acting as a reducing agent for silver ion, function as capping agents [108]. The capping process refers to the incorporation of biomolecules on the surface of silver nanoparticles. This incorporation aids in stabilizing silver nanoparticles, avoiding agglomeration [109, 110]. Ajitha et al. [102] note that the biomolecules of *Latana camara*-leaf extracts comprise lipids, proteins, and carbohydrates, also common secondary
metabolites (phenolics, flavonoids, terpenoids, and alkaloids, and trace amounts of phytosterols, saponins, tannins, and phycobatannin). Biomolecules carry out the capping process and, specifically, the carbonyls groups of the amino acids present in proteins and peptides possess a strong ability to bind metal ions. This nanoencapsulation surrounding the nanoparticles forms a protective coat-like membrane in order to avoid agglomeration (Figure 2(d)). Edison et al. [103] reported that the biomolecules of *Terminalia cuneata*-bark extract are of the polyphenol-, tannin-, and gallic-acid type and contain a high density of hydroxyl groups. They mention that the phenolic compounds present in the extract subsequently undergo oxidation and are converted into their quinone form. Thus, the electrochemical potential difference between Ag+ and phytocatalysts drives the reaction. The silver nanoparticles formed were stabilized through the lone pair of electrons and the pi electrons of the quinone structures (Figure 2(e)).

3. Sustainable Green Synthesis of Silver Nanoparticles: Agri-Food Waste Extracts

The XXI century has been viewed as a turning point in the history of humankind with regard to the awareness of the environmental problem [111]. In this context, agricultural and food wastes (agri-food waste) should be thought of as sources of plentiful value-added products, and this should be the path taken to achieve a zero-waste economy [112, 113]. These wastes are high in volume, with low-value materials, and are rather inexpensive [111, 112]. Around 89 million tons of food are wasted annually in the European Union [114]. Therefore, agri-food waste can be used for the green synthesis of silver nanoparticles. This new era of the green synthesis of silver nanoparticles from agri-food waste extract as reducing agents is known as sustainable green synthesis. However, the valorization of waste biomass for the synthesis of silver nanoparticles should include processes that generate far less, or even zero, further waste; otherwise, a concept of “sustainable” could not be substantiated [115]. Therefore, the synthesis of silver nanoparticles from agri-food waste is considered a sustainable green synthesis because of the following five points:

1. It does not generate toxic waste for the environment and health. Thus, it is considered an eco-friendly system
2. Easy to obtain and economically viable
3. Extracts are obtained from agri-food waste, conferring added value
4. Use of agri-food waste promotes the reduction of pollution
5. The system of synthesis does not generate new waste

In this regard, different agri-food wastes are generated each year that can be used for the sustainable green synthesis of silver nanoparticles, as depicted in Figure 5, as follows: (1) from fruits and vegetables, we find those that are cut, torn, or bruised and that are not suitable for industrial processing, and also residues of pulp or peel/skin generated from the agri-food industry; (2) from cereal crops, there are crops with low-quality food and that are of a low quality for export, straw generated after the grain harvest, and by-products generated during grain processing, such as DDGS and GM; (3) bagasse from different lignocellulosic sources; (4) oil cake from the oil industry, and (5) individual biomolecules from agri-food waste. These agri-food wastes for the sustainable green synthesis of silver nanoparticles are discussed in the following sections. Table 1 presents the agri-food waste extracts employed for the sustainable green synthesis of silver nanoparticles and particle size obtained.

3.1. Fruit- and Vegetable-Waste Extracts. Fresh fruits and vegetables comprise the largest subgroup of retail food waste [168]. These can range from pomace (leftovers after pressing) to cabbage cut-offs [169]. The total value of fruit and vegetable losses at the retail and consumer levels in the United States was $42.8 billion in 2008, or roughly $141 per person [170]. These can be generated in different steps of the food supply chain, from farm to fork, thus including both pre- and post-consumer stages, such as the processes of harvesting, transportation, storage, marketing, and processing [114, 171]. Fruits and vegetables comprise an abundant source of polyphenols, dietary fibers, enzymes, and proteins [170] that can function as reducing agents for the sustainable green synthesis of silver nanoparticles. Examples of such fruit waste include the citrus, banana, apple, and pear waste remaining after industrial processing. Also, citrus, which includes oranges, grapefruits, lemons, limes, and mandarins, is the most abundant crop in the world [172]. Wine industry wastes, which consist mainly of solid by-products, include marc or pomace, and stems, and may account on average for nearly 30% (w/w) of the grapes used for wine production [40].

Mythili et al. [116] reported the use of vegetable waste obtained from a market in India for the sustainable green synthesis of silver nanoparticles. The vegetable-waste extract was used in the reduction of AgNO3 into AgNP, and bioreduction was visually confirmed by the color change in the reaction mixture, ranging from colorless to brown. The crystalline nature of the synthesized AgNP was confirmed using XRD analysis. TEM results showed that the AgNPs were dispersed uniformly and were spherical in shape, with a size range of 10-90 nm.

3.2. Fruit- and Vegetable-Peel Waste Extracts. Peels are the major waste obtained during the processing of various fruits and vegetables, and these were shown to be a good source of various bioactive compounds. Significant quantities of fruit peels (20-30% for banana and 30-50% for mango) are discarded as waste by the processing industries, giving rise to real environmental problems [173]; these peels can be used for the sustainable green synthesis of silver nanoparticles. Another peel waste generated includes those of apples, white and red grapes, and red beets [174]. Examples of fruit and vegetable peels are shown in Figure 6. On the other hand, 115 million tons of citrus fruits are produced annually, and about 30 million tons are processed industrially for juice...
After industrial processing, citrus-peel waste accounts for nearly 50% of the wet-fruit mass [172]. Orange is the most important citrus fruit, with 50 million tons, with its peel representing 44% as waste [175]. Some studies of fruit- and vegetable-waste extracts have been reported. Ibrahim [117] reported the use of banana-peel extracts for the sustainable green synthesis of silver nanoparticles. Bananas are consumed all over the world. After consumption of the pulp, banana peels are generally discarded. Banana peels are rich in biomolecules such as lignin, cellulose, hemicellulose, and pectins. Results showed that, at 1.75 mM of salt and 3.0 mL of extract, highest intensity peaks were observed by UV-vis. The TEM image showed monodispersed silver nanoparticles with a spherical shape, and the average particle size by DLS was 23.7 nm. Ibrahim concludes that banana peels as agricultural waste material were successfully utilized for the consistent and quick synthesis of silver nanoparticles. Sharma et al. [118] reported the sustainable green synthesis of silver nanoparticles from different vegetable-peel extracts, including the vegetable-peel waste of Lagenaria siceraria, Luffa cylindrica, Solanum lycopersicum, Solanum melongena, and Cannabis sativus was collected from kitchen waste. The result demonstrated maximal absorbance at 430 nm, which confirmed the synthesis of AgNP UV-vis. Also, spherically shaped AgNP had sizes up to 20 nm as revealed by TEM analysis. These authors concluded with the use of vegetable waste in the synthesis of silver nanoparticles, depicting an eco-friendly method. Joshi et al. [119] reported the sustainable green synthesis of silver nanoparticles from pomegranate-peel extract as a reducing agent. Sixty percent of the weight of pomegranate fruit comprises peel waste. The biomolecules present in pomegranate-peel extract include vitamins, phenolics, flavonoids, and antioxidants. The results suggest that AgNPs are crystalline in nature. Particle size ranged from 57.7 to 142.4 nm and exhibited a spherical shape by SEM. The authors conclude that silver nanoparticles could be synthesized rapidly and successfully, within 5 min using pomegranate-peel extract environmental conditions. Soto et al. [120] reported the sustainable green synthesis of silver nanoparticles utilizing different fruit-peel (grape and orange) waste extracts. The results demonstrated that shape was nearly spherical by SEM and TEM. Diameters ranging from 3 to 14 nm and from 5 to 50 nm for silver nanoparticles were obtained from the grape and orange extract, respectively. The authors concluded that aqueous extracts from orange peel and grape pomace were used to synthesize AgNP through the reduction of Ag+ ions and the stabilization of silver nanoparticles by their secondary metabolites.

3.3. Cereal Waste Extracts. Cereal wastes are generated during the harvesting of the grain, as well as during the processing of same. The main waste generated during harvest comprises straw, stover, peelings, cobs, stalks, bagasse, and other lignocellulosic residues. The annual lignocellulosic biomass generated by the primary agricultural sector has been evaluated at approximately 200 billion tons worldwide [41]. In addition, during the processing of grain, by-products such as Gluten Meal (GM) and Dried Distillers’ Grains and Solubles (DDGS) are generated. The U.S. generated around 44 million tons of DDGS in 2018, being the main generator of these [176]. Also, over 840,000 tons of corn GM are produced in China every year, mainly being used as feedstuff or discarded [177]. Therefore, due to their high production, the waste from cereals obtained added value as reducing agents for the synthesis of silver nanoparticles. Figure 7 illustrates agri-food waste from wheat, corn, and rice cereals for the potential obtaining of extracts as reducing agents. Straw and husk waste are composed of

Figure 5: Agri-food waste as potential reducing agents for the sustainable green synthesis of silver nanoparticles.
Table 1: Agri-food waste extracts used for the sustainable green synthesis of silver nanoparticles.

| Resource           | Agri-food waste                       | Size (nm) | Shape                       | Reference |
|--------------------|---------------------------------------|-----------|-----------------------------|-----------|
| Vegetable          | Fresh skins and fresh/damaged leaves  | 10–90     | Spherical                   | [116]     |
| Banana             | Peel                                  | 23.7      | Spherical                   | [117]     |
| Vegetable          | Peel                                  | Up to 20  | Spherical                   | [118]     |
| Pomegranate        | Peel                                  | 60-150    | Spherical and agglomeration  | [119]     |
| Grape              | Peel                                  | 3-14      | Spherical                   |           |
| Orange             | Peel                                  | 5–50      | Nearly spherical            | [120]     |
| Wheat              | Bran xylan                            | 20-45     | Spherical                   | [121]     |
| Corn               | Straw                                 | ≈20       | Spherical                   | [122]     |
| Rice               | Straw                                 | 30        | Mainly spherical            | [123]     |
| Rice               | Husk                                  | <20       | NS                          | [124]     |
| Wheat              | Straw                                 | ≈20       | Spherical                   | [125]     |
| Sugarcane          | Bagasse                               | ≈22       | Spherical                   | [126]     |
| Sugarcane          | Bagasse                               | 8-30      | Semi-spherical              | [127]     |
| Coconut            | Oil cake                              | 10–70     | Spherical                   | [128]     |
| Cottonseed         | Oil cake                              | 10-90     | Spherical                   | [129]     |
| Sesame             | Oil cake                              | 6.6-14.80 | Spherical                   | [130]     |
| Annona squamosa    | Peel                                  | 20-60     | Irregular, spherical        | [131]     |
| Mandarin           | Peel                                  | 5-20      | Spherical                   | [132]     |
| Cocoa              | Pod husk                              | 4-32      | Spherical                   | [133]     |
| Neem               | Cake                                  | 30-50     | Spherical                   | [134]     |
| Vigna mungo        | Seed hull                             | 28.21-91.28 | Agglomeration          | [135]     |
| Rambutan           | Peel                                  | 100-200   | Triangle and hexagonal      | [136]     |
| Lansium fruit      | Peel                                  | NS        | NS                          | [137]     |
| Cavendish banana   | Peel                                  | 23–30     | Spherical                   | [138]     |
| Orange             | Peel                                  | 10-135    | Nanowires, irregular, spherical, and aggregates | [139]     |
| Carica hypogaea    | Peel                                  | 20-50     | Spherical                   | [140]     |
| Pomegranate        | Peel                                  | 5-45      | Irregular and spherical     | [141]     |
| Dragon fruit       | Peel                                  | 25.3-26.2 | Spherical                   | [142]     |
| Carica papaya      | Peel                                  | 10–35     | Spherical                   | [143]     |
| Banana             | Peel                                  | ≈10       | Spherical                   | [144]     |
| Kimnow mandarian   | Peel                                  | NS        | NS                          | [145]     |
| Carica papaya      | Peel                                  | 15-20     | Spherical and a few agglomerated | [146]     |
| Punica granatum    | Peel                                  | 20-40     | Spherical                   | [147]     |
| Citrus limon       |                                        |           |                             |           |
| Citrus sinensis    | Peel                                  | 9–46      | Spherical                   | [148]     |
| Citrus limetta     |                                        |           |                             |           |
| Citrus × clementina| Peel                                  | 5-25      | Spherical and small agglomeration | [149]     |
| Pomegranate        | Peel                                  | 3–13      | Spherical                   | [150]     |
| Pomegranate        | Peel                                  | 89        | Different                   | [151]     |
| Citrus sinensis    | Peel                                  | 3–12      | Spherical                   | [152]     |
| Pomegranate        | Peel                                  | NS        | Spherical                   | [153]     |
| Parkia speciosa    | Hassk pods                            | 20–50     | Mainly spherical            | [154]     |
| Citrus sinensis    | Soda lignin bagasse                   | 19.1      | Spherical                   | [155]     |
| Wheat              | Straw                                 | 9-24      | Nearly spherical            | [156]     |
| Rice               | Straw                                 | NS        | NS                          | [157]     |
| Peach              | Kernel shell                          | <20       | Spherical                   | [158]     |
| Sal                | Deoiled seed cake                     | 35–70     | Polygonal and irregular     | [159]     |
| Tea                | stalks and dust                       | 45        | Torispherical               | [160]     |
| Grape              | Seed                                  | 25-35     | Spherical and polygonal     | [161]     |
Table 1: Continued.

| Resource | Agri-food waste                  | Size (nm) | Shape     | Reference |
|----------|----------------------------------|-----------|-----------|-----------|
| Grape    | Stalk                            | 9.55 ± 8  | Spherical | [162]     |
| Orange   | Hesperidin and nanocellulose peel| 25.4      | Spherical | [163]     |
| Sapota   | Pomace powder                    | 8-16      | Isotropic | [164]     |
| Coconut  | Shell                            | 14.20–22.96 | Spherical | [165]     |
| Pineapple| Peel                             | 11-26     | Spherical | [166]     |
| Banana   | Blossom peel                     | NS        | NS        | [167]     |

Figure 6: Examples of fruit- and vegetable-peel waste as potential reducing agents for the sustainable green synthesis of silver nanoparticles [117–120].

Figure 7: Cereal waste: straw, GM, and DDGS as potential reducing agents for the sustainable green synthesis of silver nanoparticles.
cellulose, hemicellulose, and lignin [178, 179], and GM and DDGS are composed mainly of protein [180, 181]. Some studies have reported the use of straw, husk, and bran extracts as reducing agents.

Harish et al. [121] reported the use of wheat-bran xylan extracts as a reducing agent for the sustainable green synthesis of silver nanoparticles. Wheat bran obtained through food processing is considered a waste biomass. Xylan is a heteropoly saccharide composed of β(1–4) and/or β(1–3) xylene residues and may contain substitutions such as galactopyranosyl, glucuronosyl, arabinosyl, and acetyl residues. The presence of the reducing sugar xylose and free hydroxyl groups renders it a promising biopolymer for use in the synthesis of silver nanoparticles. The silver nanoparticles obtained by means of wheat-bran xylan were spherical in shape with size ranging from 20 to 45 nm. In conclusion, the authors reported a simple, safe, cost-effective, and eco-friendly method for the preparation of silver nanoparticles using xylan and more economical on a large industrial scale.

Chen et al. [122] reported the sustainable green synthesis of silver nanoparticles from corn straw extract. Corn straw is the waste from corn after the corn cob is removed. The main biomolecules in corn straw are alcohols, phenols, and aromatic compounds. These components are all reducible for the synthesis of silver nanoparticles. Results showed silver nanoparticles with an almost spherical shape and size was around 20 nm. They conclude that corn straw is a good reducing agent for the synthesis of silver nanoparticles. Chen et al. [123] reported the sustainable green synthesis of silver nanoparticles using rice-straw extract as reducing agent. Rice straw is one of the most abundant agricultural wastes in China, with an average annual production of $1.8 \times 10^8$ tons. Synthesis was carried out and the silver nanoparticles were mainly spherical in shape with average diameter of 30 nm. In conclusion, the synthesis of silver nanoparticles using rice-straw extract as a reducing agent was obtained.

Lieu et al. [124] reported the use of rice-husk extracts as a reducing agent for the sustainable green synthesis of silver nanoparticles. Phenolic acids are the major biomolecules in rice husk, and include gallic acid, protocatechuic acid, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, vanillic acid, caffeic acid, syringic acid, p-coumaric acid, and ferulic acid. The phenolic acids of rich rice-husk extract might be used as safe reducing agents for the synthesis of silver nanoparticles. Size according to the XRD of the silver nanoparticles synthesized was less than 20 nm. Also, these silver nanoparticles can be inferred as being surrounded by phenolic acids, which that formed negatively charged layers and presented a space hindrance to prevent the aggregation of silver nanoparticles by electrostatic repulsion. In conclusion, the abundant phenolic acids in rice extract were considered reducing agents and protective agents that enabled the stable dispersion of the sustainable green synthesis of silver nanoparticles.

Saratale et al. [125] reported the sustainable green synthesis of silver nanoparticles from wheat straw-extracted lignin. Lignin is the most renewable, non-toxic, highly branched natural aromatic biopolymer. Lignin is a valuable by-product of the pulp and paper industries and is produced at a rate of nearly 50-70 million tons per annum. Results showed that lignin acts as a reducing agent of silver ion. Also, pH 8.0, 50 °C, and 1 mM of AgNO3 are the optimal conditions for maximal silver-nanoparticle production. HR-TEM revealed uniformly monodispersed silver nanoparticles and that are spherical in shape with a size around 20 nm. These authors concluded that the wheat straw-extracted, lignin-mediated, one-step process of silver nanoparticles was developed and is simple, eco-friendly, and follows the principles of green chemistry.

3.4. Bagasse-Waste Extracts. Other agri-food waste extracts are those obtained from bagasse generated by the food industry and can be used in nanotechnology for the production of metal nanoparticles. Worldwide, the main bagasses generated include sugarcane bagasse and sweet sorghum bagasse [182–184]. Global sugarcane production is around 1.9 billion tons annually; however, this is around 570 million tons of wet bagasse, or one-half of this amount if dried [185]. Sugarcane bagasse contains cellulose (40–50%), hemicelluloses (25–35%, predominantly xylans), and lignin (20–30%) [185]. Also, in Mexico, the main bagasses generated derive from the alcohol industries of tequila, bacanora, mescal, and tequilana. In 2017, 956,000 tons of Agave tequilana were consumed in terms of tequila production and around 40% of these are discarded as bagasse [187]. The agaves are also a source of lignocellulosic material [188]. Therefore, these examples of bagasse, among others generated in the food industry, comprise the source of biomolecules as reducing agents for the sustainable green synthesis of silver nanoparticles.

Shen et al. [126] reported the sustainable green synthesis of silver nanoparticles from sugarcane bagasse. Bagasse is a polymer complex mainly containing cellulose, hemicellulose, and lignin, is abundant in nature, and has gradually been attracting the interest of scientists due to its low value. Mainly hemicelluloses and lignin of bagasse can be used as green reducing and stabilizing agents to prepare silver nanoparticles. Results have demonstrated that the optimal condition for this experiment was the ratio of 20 mL bagasse extract, 0.1 g AgNO3, a temperature of 90 °C, and a time of 40 min. Also by TEM images, it was observed that the particles were nearly spherical in shape and their size was about 22 nm.

Aguilar et al. [127] reported the use of sugarcane-waste extracts as a reducing agent for the sustainable green synthesis of silver nanoparticles. In Mexico, the sugarcane industry produces more than 49 million tons per year. Around 30% of the processed cane is transformed into bagasse. The latter is composed of lignin (20%) found in sugarcane support tissue, hemicellulose (25%), and cellulose (45%). Results showed that a silver plasmon band was observed for pH 7 and 12. The size of silver nanoparticles synthesized at pH 7 ranged from 8 to 30 nm with semi-spherical shape. The authors concluded that a green, rapid, inexpensive, and reliable additive-free method was developed for the synthesis of silver nanoparticles using sugarcane bagasse as a reducing and capping reagent in a Soxhlet system.
3.5. Oil-Cake Waste Extracts. The extraction of edible oil from oilseeds is one of the main food industries worldwide. However, this importance is reflected in the large production of waste generated. The most important waste generated from the oil extraction of the seed is oil cake [189]. Of the total oil-cake production increase of 23 million tons, 17 million tons derives from developing countries including India, Brazil, and Argentina [189]. The main sources of oil plants from this oil cake that is obtained are sunflower [190], safflower [191], canola [192], and sesame [193, 194] among others. The oil cake consists of highly lignified husk lignocellulosic fibers (40%), protein (35%), and phenolic compounds (5.7%) [195, 196]. These biomolecules present in oil cake possess the ability to reduce the silver ion.

Govarthanan et al. [128] reported the sustainable green synthesis of silver nanoparticles from the coconut-oil cake extract. The authors mention that in India, various types of oil cakes are produced on a large scale, as a by-product of the oil manufacturing industry. A by-product obtained after oil extraction from dried copra is coconut-oil cake. It contains starch, soluble sugars, proteins, lipids, and a trace amount of nitrogen. In this work, coconut-oil cake was evaluated for the synthesis of silver nanoparticles. Results demonstrated that the intensity of the color increased after 12 h of incubation, indicating the reduction of Ag ions. Also, the EDS quantitative analysis revealed the presence of silver. Silver nanoparticles were spherical in shape and mostly present in aggregates. The size of the particles ranged from 10 to 70 nm. In conclusion, this study reported this simple and cost-effective method for the synthesis of silver nanoparticles.

Govarthanan et al. [129] reported the use of cottonseed-oil cake extract as a reducing agent for the sustainable green synthesis of silver nanoparticles. Cotton is an economical plant from which cottonseed oil is a cooking oil extracted from the seeds of the cotton plant. Cottonseed-oil cake is generated as a by-product of the cottonseed-oil manufacturing industry. Its by-product is rich in protein, which was used to reduce silver ion. Results showed that a clear dark brown color formed within 4 h when the cottonseed-oil cake extract was added to the 1 mM AgNO₃. This color change was attributed to excitation of Surface Plasmon vibrations within the synthesized silver nanoparticles. SEM-EDS exhibited the presence of silver atoms in nanoparticles. TEM images revealed that the particles were spherical in shape with an average size of 10 to 90 nm. This study reported the simple, cost-effective, and eco-friendly agroindustrial waste-mediated synthesis of silver nanoparticles using cottonseed-oil cake extract.

Alfuraydi et al. [130] reported the sustainable green synthesis of silver nanoparticles from sesame-oil cake extract. Sesame (Sesamum indicum L.) is one of the most important crops throughout the world. Sesame oil contains nutritive constituents such as polyunsaturated fatty acids, proteins, carbohydrates, sesamin, sesamolin tocopherol, phytosterols, vitamins, and minerals. Results showed that the process of the synthesis of silver nanoparticles from AgNO₃ was traced after incubating with the extract of sesame-oil cake. The colorless solution change to dark brown in color is due to surface plasmon resonance (SPR) at room temperature. The TEM study revealed that the synthesized silver nanoparticles were spherical in shape with a particle size ranging from 6.6 nm to 14.80 nm. The authors concluded that the oil cake was final product of oil process, which contains more nutritional values with low fat. Silver nanoparticles were successfully synthesized utilizing the sesame-oil cake.

Figure 8 demonstrates other agri-food wastes that have been employed to obtain extracts as reducing agents, including peel, bagasse, oil cake, and husk. Also, it shows the morphology and size of silver nanoparticles by TEM and SEM equipment, depending on the investigation being conducted.

3.6. Recovery of Individual Biomolecules from Agri-Food Waste. In addition to sustainable green synthesis from agri-food waste extracts containing multiple biomolecules as reducing agents, individual biomolecules can be recovered. These individual biomolecules can be obtained from agri-food waste extracts and function as reducing agents. Banerjee et al. [197] reported that biomolecules are essentially primary and secondary metabolites of agri-food waste. Phenolics, alkaloids, glycosides, volatile oils, mucilage, gums, and oleoresins are some of the examples of secondary...
metabolites. Also, fruit-peel waste, straw, and bagasse comprise an important source for the recovery of cellulose, hemicellulose, and lignin [198–200]. Fruit and vegetable waste contains vitamins A, C, and E, minerals, glucosinolates, isothiocyanates, polyphenols, and pigments such as carotenoids, among others, which can be recovered [201].

Figure 9 presents some agri-food waste for the possible recovery of individual biomolecules. Also, different studies have recovered individual biomolecules from agri-food waste. de Andrade Lima [202] recovered carotenoids from vegetable waste. Angelov et al. [203] recovered trans-resveratrol from grapevine stems. Munde et al. [204] recovered quercetin from onion solid waste. Choi et al. [206] recovered quercetin from onion-skin waste. Muhia et al. [207] recovered kafirin from DDGS. Gupta et al. [208] recovered zein from DDGS. Santana et al. [209] recovered starch from turmeric wastes. All of the individual biomolecules recovered in the investigations described previously, among others, are potential reducing agents for the sustainable green synthesis of silver nanoparticles.

4. Mechanistic Aspects of Green Synthesis of Nanoparticles

Currently, the mechanistic aspect by which the green synthesis of silver nanoparticles is carried out is still unknown; however, several investigations already mention the potential elucidation of certain compounds of plant extracts and currently of extracts from agri-food waste, mainly of those that contain phenolic compounds (phenolic acids and flavonoids), terpenoids, organic acids, proteins, and polysaccharides and in general of lignocellulosic materials. Some mechanistic aspects as solvent medium, environment, and stability material among others are reported below.

4.1. Phenolic Compounds. Phenolic compounds are secondary metabolites more abundant in nature (more than 8000
Silver ion 
Proteins/polysaccharides/phenolic compounds 
safflower waste

Reduction 
Metallic silver 
Nucleation 
AgNO₃ + H₂O 
Growth 
Capping and stabilization

Ag Np

(a)

Safflower waste extract
AgNO₃
Ag nanoparticles-extract

Wavenumber (cm⁻¹)
Transmittance (%)

(b1) (b2) (b3) (b4)

(b)

(c)

Figure 10: Continued.
known structures) and formed in the pentose phosphate, shikimate, and phenylpropanoid pathways in plants, and further play major roles in plant growth and reproduction; also, they provide protection against pathogens and predators [210, 211]. Phenolic compounds are further divided into two groups, phenolic acids and flavonoids. Phenolic acids are aromatic carboxylic acids, which can be further distinguished into two sub-classes based on their C1−C6 and C3−C6 backbones: (1) hydroxybenzoic acids as vanillic, gallic, ellagic acid; and (2) hydroxycinnamic acids as p-coumaric, ferulic, caffeic, chlorogenic acids [212]. Flavonoids have a similar structure as they consist of two aromatic rings which include A and B attached to 3C atoms to give an oxygenated heterocycle such as ring C, and are divided into 6 sub-classes according to the type of heterocycle involved: flavanones, anthocyanidins, flavonols, flavones, flavanons, and isoflavones [211].

The mechanistic aspects by which phenolic compounds reduce the silver ion to zero silver and its subsequent growth, stabilization, and capping have recently been elucidated. This is given by the chemical structure of each compound; however, they can be generalized for phenolic acids and flavonoids.

Flavonoids. This group of molecules can reduce the silver ion to zero silver and its subsequent growth, stabilization, and capping have recently been elucidated. This is given by the chemical structure of each compound; however, they can be generalized for phenolic acids and flavonoids.

Figure 10: Formation of silver nanoparticles from flavonoids and other compounds present in the safflower waste extract: (a) Mechanism of formation, (b) (b1−b4) silver nanoparticles shape, (c) (c1−c2) corroboration of nanoparticle synthesis by FT-IR, and (d) flavonoid structures present in extracts. Adapted from Del-Toro-Sánchez et al. [214] and Rodríguez-Félix et al. [215].
single-electron transfer—proton transfer (SET-PT), and (3) sequential-proton-loss-electron-transfer (SPLLET). Enthalpy of O-H bond dissociation decreases with the increase in the number of introduced methoxy groups and corresponds to the experimental increase in antioxidant properties [218]. Therefore, it can be concluded that a similar process occurs during the bioreduction process for the highest efficiency of metal nanoparticle formation, depending on the type of phenolic acid present in the extract. Omran [219] reported the green synthesis of silver nanoparticles using mandarin peel extract, which contains phenolic acids among other compounds that reduce the silver ion for the formation of silver nanoparticles. They observed the preliminary indication for the formation of AgNPs was the change in coloration from yellow to dark brown and report that the color change is due to excitation of AgNPs’ free electrons, which in turn results in phase fluctuation and refers to surface plasmon resonance (SPR). El-Desouky et al. [220] reported the use of coffee waste extract for the green synthesis of silver nanoparticles. Firstly, in this study, the presence of phenolic acids such as caffeic and chlorogenic acid was demonstrated from the phytochemical analysis by HPLC. The synthesis of silver nanoparticles was carried out and corroborated by UV-vis, attributed to the accumulated oscillations of free electrons located at the surface of metallic nanoparticulate validated the development of AgNPs, see Figure 11.

Therefore, in flavonoids and phenolic acid present in agri-food waste extracts, the presence of strongest constituents has antioxidant activity and is able to reduce Ag⁺ to Ag⁰ and these contents perform capping and stabilizing agent as well owing to the reduction affinity accompanied with the electron-donating capability of such as phenol hydroxyl. Primarily responsible for preserving and reducing ability are the structure of phenolic hydroxyl groups and the position and chemical number [221].

4.2. Terpenoids. Terpenoids, also known as polyisoprenes, are of major class of natural compounds, with several thousand known compounds (more than 50 000 structures), with diverse molecular architectures and biological functions [222, 223]. According to the number of isoprene units, terpenoids can be classified as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes, and carotenoids [223, 224]. Terpenoids, being a very wide
classification of molecules, the mechanism by which the green synthesis can occur, is very varied and unknown to many of them; however, it can be generalized for the main groups and present in agri-food waste and plants, such as carotenoids (α-carotene, β-carotene, lycopene, lutein, zeaxanthin, and among others) [225]. C10-skeletal monoterpenes are grouped in acyclic (p-menthane, pinane, bornane/camphane, thujane, and carane types) and the C15-skeletal sesquiterpenes are arranged as acyclic (cadinane, Caryophyllene, eudesmane, germacrane, aromadendrene, and bisabolane types) [226] and triterpenes (maslinic, oleanolic, and ursolic acids and erythrodial) [227].

Carotenoids. This group is an important phytoconstituent that is considered responsible for the protective effects of health by fruits and vegetables. There are different by-products for obtaining carotenoids, among which are the tomato (peel and pomace which is a mixture of skins, crushed seeds, and residual pulp), 5–15% of the fruit [227]. In this sense, the use of tomato skin for the synthesis of silver nanoparticles has been promising and some mechanisms of the carotenoids involved have been proposed. Carbone et al. [227] synthesized silver nanoparticles from tomato skin extract. The results obtained, mainly by FT-IR, predict that the compounds reduce silver ions through functional groups –CO, –OH, and –NH present in molecules constituting the waste and that played a crucial role in the nanoparticle formation and stabilization. Carbone et al. [228] synthesized nanoparticles from the extract of Mimusops coriacea, which was mainly attributed to the chlorophyll and carotenoids present in the extract. They predict that the formation of silver nanoparticles was carried out by a redox process, where the donor species of electrons is oxidized in the presence of the metallic salts in the solution. Also, the neutral atoms collide forming a stable nucleus, plus ions are reduced leading to particle growth, step that can be controlled by illumination, temperature, pH, and reagent concentration. The stabilization is due to depletion of the metal ions in the solution or by the coating of the particle by substances present in the extract.

Sowani et al. [229] proposed a mechanism involved in the synthesis of silver nanoparticles by the carotenoids. Both, 1′-OH-4-keto-γ-carotene (Carotenoid K) and 1′-OH-γ-carotene (Carotenoid B) contain a tertiary hydroxyl group (red circles in the figure). Then, under alkaline conditions (prevailing during nanoparticle synthesis), these OH groups were eliminated and oxidized forms of the carotenoids (4-keto-γ-carotene and γ-carotene) were formed. They mentioned that carotenoids promoted the reduction of silver ions to their elemental form as nanostructures. Also, all nanoparticles were stable for six months at room temperature, indicating that the carotenoids were acting as reducing and stabilizing agents (Figure 12).

Terpenes. Monoterpenes consist of two linked isoprene units and are classified as acyclic (e.g., geraniol), monocyclic (e.g., thymol), and bicyclic (e.g., myrtenal and pinene) [230]. Synthesis of silver nanoparticles from monoterpenes molecules in food waste is mainly due to color change by the surface plasmon resonance (SPR) phenomenon of silver nanoparticles in the reaction mixture. Donga and Chanda [231] mention that seeds from fruits and vegetables are thrown away into the environment causing pollution; their disposal is also problematic. These seeds are rich in terpenes and other compounds, that can be used to reduce the silver ion to zero silver. Rasaei et al. [232] studied Satureja hortensis as a starting material for the formation of silver nanoparticles, from the aqueous extract that mainly contains compounds such as carvacrol, terpinene cymene, and Caryophyllene. Results showed that color change was indicative of the formation of silver nanoparticles, where color change was yellow to brownish-red after addition of AgNO3 and stirring at room temperature was due to excitation of the surface plasmon resonance.

4.3. Organic Acid. Organic acids are important targeted chemicals worldwide due to their variety of functionalities in various fields, as in the chemical, food, cosmetic, pharmaceutical, and beverage industries owing to their various functional properties and are also used for their nematicidal effect [232, 233]. Also, it can be produced through chemical processes of fossil raw materials as well as by the microbial fermentation of natural occurring biomass [233]. Carboxylic acids are the organic acids categorized by the existence of a carboxyl group in which a carbonyl group bonded to a hydroxyl group. Depending on the attached carboxyl group, they can be (1) monocarboxylic acid, with a single carboxyl group such as formic-, acetic-, propionic-, butyric-, benzoic-, and benzene acetic acid; (2) dicarboxylic acids, with two carboxyl groups as oxalic-, malonic-, succinic-, adipic-, itaconic acid; and (3) tricarboxylic acid, with three carboxyl groups such as citric acid [234].

Tricarboxylic acid. The residues that are frequently generated in industry and in homes and that are a source of a large amount of organic acids are the poop of citrus fruits such as lemon, tangerine, orange, and grapefruit, among others, and that can be used for the synthesis green of silver nanoparticles from the reduction of silver ions [235–237]. Dauthal and Mukhopadhyay [238] synthesize silver nanoparticles from Citrus aurantifolia peel extract. They report that green synthesis was mediated by compounds present in citrus peel such as citric acid and ascorbic acid along with different polyphenolic compounds (flavonoid and phenolic acid), with excellent reducing properties. The result of FT-IR showed that C. aurantifolia peel extract at around 3,411 cm–1 indicated the involvement of O-H functional group of phenols and carboxylic acids for the synthesis of NPs and the peak shift in 2,920 cm–1 stretching vibration was attributed to the possible involvement of C-H stretching vibration of aliphatic acids in NP synthesis. Also, -OH and C=O groups of these bioorganic compounds (mainly citric acid) showed strong ability to bind metal ions. This is related to its antioxidant potential, where these compounds have the ability to donate electron/hydrogen atom. This reactive hydrogen is responsible for bioreduction of metal ions to zero valent form and number of bioorganic compounds acts synergistically in bioreduction reaction and produces corresponding oxidized compounds.

4.4. Protein. The food industry generates a large amount of protein-rich waste that can be used as silver ion reducing...
agents. The main industries that generate this type of waste are the starch, oil, and ethanol industries, among others. The wastes from the industries are called cake and meal waste. Nayak et al. [239] Obtained silver nanoparticles using *Jatropha curcas* seed cake extract. The conditions were as follows: 2.5 mL of *Jatropha curcas* seed cake extract was added to 22.5 mL of 1 mM aqueous AgNO₃ prepared in deionized water and mixed thoroughly. Color change in the resulting solution was measured using UV-vis spectrophotometer at 360–700 nm range at regular intervals. The spectroscopic properties showed color change in the reaction mixture from light yellow to brown that indicated the synthesis of silver and FT-IR results confirmed the reduction in the intensity of the peak at 3338 cm⁻¹ in nanoparticles synthesized from *Jatropha curcas* seed cake extract, and the peak was present in the extract also, which confirms the fact that the primary amines are involved in reducing the metal salts to nanoparticles. C-N stretching vibrations of aliphatic and aromatic amines at 1318 cm⁻¹ and C-O stretching vibration and C-H stretching of methylene groups of proteins at 2924 cm⁻¹ were seen both on the surface of nanoparticles as well as in the extract which confirms the capping of plant phytochemicals on the surface of the nanoparticles thereby stabilizing them.

Al-Thabaiti et al. [240] propose a mechanism for the formation of nanoparticles from the amino acids present in proteins. The study was based on the reduction of silver ion from bovine serum albumin rich in the amino acid tryptophan. In this sense, it is known that tryptophan participates in the acid-base equilibria and cationic, zwitter ionic, and anionic species exist in an aqueous due to the presence of pH sensitive groups such as –COOH and NH₂. Firstly, the rate-determining step is a one-step, one electron oxidation-reduction (equation 6) and this reaction results in the formation of Ag⁰ and radical, then, the slow electron transfer step, radical reacts with Ag⁺ (equations 7 to 9) may follow and finally, the resulting Ag⁰ under goes fast complex formation and adsorption, which leads to the formation of the stable species of AgNP. Figure 13 shows the mechanism of formation and capping of silver nanoparticles from proteins and proposed by Al-Thabaiti.

### 4.5. Polysaccharides

Currently, 37 million tons of agricultural waste are generated worldwide, causing serious problems (economic and environmental). The main waste generated is skin and seed fruits. An alternative of this type of waste is the use for the extraction of macromolecules, mainly polysaccharides to be used as reducing agents of metallic nanoparticles. Also, polysaccharides from agro-food industry waste constitute one of the most important renewable resources [241]. Polysaccharides from waste are mainly lignin, cellulose, hemicelluloses, pectins, gums (galactomannan), stach, and other non-starch polysaccharides, such as inulin and oligosaccharides. Polysaccharides contain several important functional groups (hydroxyl and carboxyl groups), that can reduce the silver ion and the subsequent

![Figure 12: Synthesis mechanism of silver nanoparticles from carotenoids. Obtained of Sowani et al. [229].](image-url)
formation of nanoparticles. The synthesis mechanisms are based on the quantity and ability of these functional groups to donate the hydrogen atom and electrons.

Pectins. These polysaccharides are regarded as the fruit waste where the extraction is done from the citrus fruit peels (Figure 14). Pectin consists of α-1,4-D-galacturonic acid units linked by α-glycosidic bonds. Advantages of pectin are non-toxic and stability throughout the gastrointestinal tract and it is feasible as a carrier to contain drugs. Therefore, functions both as a capping agent and a stabilizing agent for silver nanoparticles [242]. The pectin schematic structure consists of a homogalacturonan (HG) backbone and xylogalacturonan (XGA), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II) regions (Figure 14(b)). The RG-I region (20–35% of pectin) is composed of arabinan and galactan side chains, which contain hydroxyl groups. Due to the shift of the tautomeric equilibrium (cyclo-oxo-tautomerism), the free hemiacetal hydroxyl groups may be converted to free aldehyde

\[
\begin{align*}
&\text{(cationic)} \quad -\text{NH}_2\text{CHCOOH} \rightleftharpoons -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \quad (\text{4}) \\
&\text{(zwitter ionic)} \quad -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \rightleftharpoons -\text{NH}_2\text{CHCOO}^+ \quad (\text{5}) \\
&\text{(anionic)} \quad -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \rightleftharpoons -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \quad (\text{6}) \\
&\text{(imine cation)} \quad -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \rightleftharpoons -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \quad (\text{7}) \\
&\text{(anionic)} \quad -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \rightleftharpoons -\text{NH}_2\text{CHCOO}^- + \text{H}^+ \quad (\text{8}) \\
2\text{Ag}^0 + 2\text{Ag}^+ &\text{Fast} \rightarrow \text{Ag}^{2+} \quad (\text{10})
\end{align*}
\]

Try of BSA

$\begin{align*}
\text{NH} + \text{Ag}_4^{2+} &\rightleftharpoons \text{NH}_2\text{CHCOO}^+ + \text{CH}_2\text{COO}^- \\
\text{NH} + \text{Ag}_4^{2+} &\rightleftharpoons \text{NH}_2\text{CHCOO}^+ + \text{CH}_2\text{COO}^- \\
\text{NH} + \text{Ag}_4^{2+} &\rightleftharpoons \text{NH}_2\text{CHCOO}^+ + \text{CH}_2\text{COO}^-
\end{align*}$

**Figure 13:** Development of silver nanoparticles from proteins. (a) Synthesis mechanism, (b) capping of nanoparticles, (c) verification of synthesis of silver nanoparticles by UV-vis, and (d) shape of nanoparticles. Adapted from Al-Thabaiti et al. [240].
Homogalacturonan (HG)  Xylogalacturonan (XGA)  Rhamnogalacturonan I (RG-I)  Rhamnogalacturonan II (RG-II)

Figure 14: Continued.
groups in an alkaline medium, which are responsible for the reducing property of pectin. RG-1 reduces metal salts to metal nanoparticles (Figure 14(c)) [243]. Another study of Wang et al. [244] synthesizes silver nanoparticles using pectin extracted from citrus peel. Silver nanoparticles capped by pectin macromolecules were fabricated by a “green” approach via chemical reduction of Ag⁺ cations under ultrasonic condition. Therefore, pectin acted as a reducing and stabilizing agent. Free hemiacetal hydroxy groups in pectin determine its reducing properties in an alkaline medium; also, the arabinans and galactans contain hydroxy groups capable of exhibiting the reducing properties.

Gums. There are different plants and their waste from which gum-type polysaccharides can be extracted. *Leucaena leucocephala* (Lam.) is a tropical tree that grows in Egypt (perennial thornless, with a height of around 8 m, and belongs to the subfamily Mimosoideae), with bulk volumes of solid wastes (leaves, ripened fruits, pods, and sedes). Galactomannan gum (structure of linear chains of β-(1-4)-d-mannose units substituted by single a-d-galactose units at O-6) is the predominant constituent in the seeds of *L. leucocephala* with insignificant levels of tannins, organic acids, oils, and the amino acid of mimosine [245]. Taher et al. [245] developed a well-stabilized AgNP solution and was prepared using the extracted polysaccharides from *L. leucocephala* seed wastes as reducing agents for silver ions to produce AgNPs. The confirmation of the synthesis was from the color change, which shows brownish color in an aqueous solution due to excitation of surface plasmon vibration of AgNPs. FT-IR analysis confirmed the synthesis and capping, where the presence of a peak at 3422 cm⁻¹ in AgNP is assigned for hydroxyl stretching, offering the capping efficacy of galactomannan gum.

5. Applications of Silver Nanoparticles

5.1. Antibacterial Activity. Silver nanoparticles, due to their antibacterial properties, have been used widely in the health industry, in food storage, textile coatings, and in a number of environmental applications [23, 246]. The antibacterial action of silver nanoparticles can be categorized into two types: (1) those with inhibitory action, and (2) those with bactericidal action. In the former strategy, bacterial cells are not killed, but their division is prevented, whereas in the latter, bacterial cells will die due to the action of silver nanoparticles [247]. Also, the antibacterial activity of silver nanoparticles exerted on Gram-negative and Gram-positive bacteria is not similar, but competes one against the other [247]. Silver nanoparticles inhibit Gram-positive growth such as *Bacillus subtilis*, *Bacillus cereus*, *Lactococcus lactis*, *Listeria monocytogenes*, *Streptococcus pyogenes*, and *Staphylococcus aureus* [248–251]. Also, silver inhibit nanoparticles Gram-negative growth such as *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, *Escherichia coli*, and [248, 250, 252]. Moodley et al. [253] used silver nanoparticles synthesized by *Moringa oleifera* leaf extract to inhibit the growth of bacteria such as *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Escherichia coli*, and *Enterococcus faecalis*. Results showed a Minimum Inhibitory Concentration (MIC) of 25 µg mL⁻¹ for *K. pneumoniae*, *P. aeruginosa*, and *S. aureus*, and an MIC of 12.5 µg mL⁻¹ for *E. coli* and *E. faecalis*. Also, the authors note that the effective inhibition of both Gram-negative and Gram-positive bacteria by silver nanoparticles derived from *M. oleifera* leaf extracts is of great significance, in that it demonstrates their broad-spectrum antibacterial activity. Perven et al. [254] reported the use of silver nanoparticles synthesized from lychee-peel extract to inhibit the growth of bacteria such as Gram-negative strains (*Alcaligenes faecalis* KJB33793 and *Klebsiella pneumoniae* KJB33791) and two Gram-positive strains (*Enterococcus faecium* ORGIF and *Microbacterium oxydans* KJ729148). Results for TEM showed silver nanoparticles with a spherical shape. Antibacterial activity revealed that Streptomycin-conjugated silver nanoparticles obtained a greater inhibition zone in Gram-positive strains, with 53.00 ± 1.41 mm for *Enterococcus faecium* and 53.50 ± 4.24 mm for *Microbacterium oxydans*. For Gram-negative strains, Amoxicillin- and Cefixim-conjugated silver nanoparticles exhibited a more effective inhibition zone, with 48.25 ± 5.65 mm and 91.50 ± 1.41 mm for *Alcaligenes faecalis*.
and 36.25 ± 1.414 and 55.25 ± 2.828 mm for *Klebsiella pneumoniae*. When the antibiotics conjugated with silver nanoparticles, then, along with the inhibition of cell-wall synthesis, they also caused the generation of Reactive Oxygen Species (ROS) as a result of damage to genetic material and the cell wall, followed by cell death.

On the other hand, different mechanisms have been proposed of how silver nanoparticles can cause cell damage and death in bacteria. Furthermore, smaller-sized silver nanoparticles that present a larger available surface area provide better contact with microorganisms. These particles are capable of penetrating the cell membrane or attaching to the bacterial surface based on their size [255–257]. The mechanisms proposed are presented below and in Figure 15 [23, 256, 258, 259].

(i) Cell-wall/membrane damage: cell-wall/membrane disruption and leakage of its cellular contents

(ii) Interaction with proteins: bonding to functional groups of enzymes causing protein denaturation and cell death

(iii) Interaction with enzymes: important enzymes of metabolism...
| Waste                                | Size (nm) and shape | Bacteria                                      | Concentration effect or inhibition halo | Antibacterial mechanism                                                                                                                                                                                                 | Reference |
|--------------------------------------|---------------------|-----------------------------------------------|------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Leaf-stem waste of *Carthamus* 
tictorius                                    | 8.67 ±4.7, and spherical | *S. aureus, P. fluorescens*                   | 1.9 μg/mL *S. aureus* and 15.6 μg/mL *P. fluorescens* | Generation of ROS, such as radicals OH, hydrogen peroxide. Silver can interact with these components inside and outside the cell membrane, resulting in bacterial inactivation. Silver ion interacts with the phosphorus present in DNA and proteins, causing the inhibition of enzymatic activities. Oxidative stress in the bacteria and attack the lipids of the outer membrane, causing lipid oxidation, as well as damage to proteins, RNA, and DNA | [215]     |
| Non-edible part of fruit of *Cynara* 
scolymus L.                                    | Around 10.59, and spherical | *S. aureus, B. Subtilis, E. Coli, P. aeruginosa* | 0.12 and 0.25 μg/mL were effective on Gram-positive *S. aureus* and *B. subtilis*. 0.07 and 0.13 μg/mL were effective on *P. aeruginosa* and *E. coli* in Gram-negative | Silver ions interact with the negatively charged cell membranes of microorganisms cause an increase in reactive ROS and cell-wall structure is disrupted | [262]     |
| Onion peels                                      | Not shown            | *S. typhimurium, S. aureus*                   | Zone of inhibition of 8 mm and 9 mm respectively | Metal nanoparticles show good activity against both the strains studied Antimicrobial effect of phenolics products in Np can involve various modes of action such as enzyme inhibition by the oxidized products, maybe through reaction with sulfhydryl groups or through more nonspecific interactions with the proteins | [263]     |
| *Raphanus sativus* L. waste                  | 10-14, spherical and agglomeration | *E. coli, P. aeruginosa, S. typhimurium, S. aureus* | 65.67 ± 0.91 mm *P. aeruginosa* of inhibition halo | Strong bioactivity against both microorganisms. The highest zone of inhibition against *B. subtilis* (14.2 mm) and *E. coli* (9.3 mm) is found at concentrations of 4.0 ppm and 2.0 ppm, respectively | [264]     |
| Waste banana stem                           | <20 and spherical    | *B. subtilis* (Gram positive) and *E. coli* (Gram negative) | Strong bioactivity against both microorganisms. The highest zone of inhibition against *B. subtilis* (14.2 mm) and *E. coli* (9.3 mm) is found at concentrations of 4.0 ppm and 2.0 ppm, respectively | Not shown                                                                                                                                            | [265]     |
| Crushed, wasted, and spent *Humulus lupulus* | 92.42 ± 2.41 DLS and 17.40 ± 2.4 nm TEM, and spherical | Gram-positive *S. aureus* (ATCC 29213) and Gram-negative *E. coli* (ATCC 25922) | Inhibition zone of 12 ± 0.81 mm against *S. aureus* and 15.33 ± 0.94 mm for *E. coli* with 500 μg/mL AgNPs | Disruption of the cell membrane leading to cell lysis, interaction with the genetic materials leading to DNA damage, and formation of ROS causing cellular stress and, finally, death. AgNPs are also known to damage protein synthesis and interfere with the; synthesis of capsular polysaccharides, other cellular functions | [260]     |
5.2. Effect of Size and Shape. Table 2 shows the relationship of size and morphology of silver nanoparticles and their antibacterial activity mechanism synthesized from agri-food waste. The toxicity of silver nanoparticles toward bacterial cells is dependent on several parameters such as nanoparticle size, surface charge, nanoparticle composition, the chemical nature of nanoparticle surface, and agglomeration state. The hydrodynamic size of silver nanoparticles is quite smaller than that of the bacterial membrane pore. Thus, it can easily pass through the pores and can interact with the genomic material [260]. Previous studies mention that the antibacterial activity is influenced by the particle size, namely, particles smaller than 50 nm, specifically between 1 and 10 nm, exhibit better antioxidant activity than aggregates of silver nanoparticles larger than 50 nm. AgNPs found inside the cells have similar sizes (1 to 10 nm) to those NPs attached to the cell membrane, indicating that only the AgNPs bound to the membrane are able to get into the bacteria. The properties in this size range are highly reactive facets, electronic effects, and a larger surface to volume ratio, all of which make silver NPs with smaller size more efficient for direct interaction with bacterial, and finally causing the death of the cell [261].

The shape is related to the high production of silver ions (Ag⁺). There are different shapes that have been studied such as spheres, cubes, rods, and platelets. Helmlinger et al. [267] synthesized and studied different morphologies for the synthesis of silver nanoparticles and mention that nanoparticles in the form of spheres have greater antimicrobial potential because they have a greater amount of silver ions that can cross the membrane or disrupt its permeability. Also, spherical shape contains higher concentration of particles than other shapes, e.g., spherical shape with $8.43 \times 10^{10} \text{ mL}^{-1}$ and platelet shape with $5.06 \times 10^{11} \text{ mL}^{-1}$. Another parameter is the surface area/volume per particle, where spherical shape has about $0.100 \text{ nm}^{-2}$ and platelets, cube, and road 0.234, 0.038, and 0.040 nm², respectively. An advantage of using agri-food waste is that most of the time during the synthesis the spherical shape and very small sizes predominate; therefore, a better antimicrobial activity is favored than by other chemical or physical methods where silver nanoparticles have multiple shapes.

5.3. Anticancer Activity. Currently, cancer is one of the most serious problems and health subjects worldwide. Based on their origin, a variety of cancers exist, such as thyroid, prostate, bladder, kidney, pancreatic, breast, melanoma, leukemias of all types, oral cancer, and colon-rectal combined cancer, among others [268]. Cancer is the most lethal disease at present; it involves the uncontrolled proliferation and growth of the cell and becomes more dangerous when found under a metastatic condition and is very difficult to control using conventional therapies [269]. One strategy to combat these types of cancer is the use of silver nanoparticles synthesized by sustainable green chemistry [270, 271]. Several investigations have focused on the evaluation of the anticancer activity of silver nanoparticles such as A549 lung cancer cells [272], MG-63 osteosarcoma cells [273], skin stromal cells and colon cancer cells [274], Hep-G2 liver cancer cells [275], and MCF-7 breast cancer cells [276] among others.

Majeed et al. [269] evaluated the anticancer activity of silver nanoparticles in the treatment of the MG-63 human osteoblastoma cell and the MCF-7 human breast cancer cell. The synthesis of silver nanoparticles was conducted by means of the Artocarpus integer-leaf extract. Results showed the change of color of the aqueous extract to brown upon the addition of silver nitrate, indicating the biosynthesis of silver nanoparticles. The silver nanoparticles ranged from 5.76 to 19 nm in size and were spherical in shape. The result of anticancer activity showed, for
MCF-7, an IC50 value of $90 \mu g \text{mL}^{-1}$ but for MG-63, an IC50 value of $70 \mu g \text{mL}^{-1}$ after 24 h of incubation. These silver nanoparticles produce the ROS that cause membrane blabbing and damage. They concluded that the silver nanoparticles exhibited good anticancer activity against MCF-7 and MG-63 cell lines. Saravanakumar et al. [277] reported the use of silver nanoparticles synthesized from bark derived from Toxicodendron vernicifluum as treatment in A549 human lung carcinoma cells. Results showed that silver nanoparticles were synthesized and confirmed by APR ranged from 400 to 450 nm by UV-vis spectrophotometry. The shapes of the nanoparticles were spherical and oval, and they ranged in size from 2 to 40 nm. Silver nanoparticles induced the death of human lung cancer cells in the A549 cell line in a concentration-dependent manner. The Annexin V FITC/P-based apoptosis assay also demonstrated about 95% cell death with treatment of silver nanoparticles at $320 \mu g \text{mL}^{-1}$. Also, AO/EB and DCFH-DA staining results revealed cell damage and ROS generation to exposure at $320 \mu g \text{mL}^{-1}$. The mechanism derives from increase of ROS-mediated apoptosis in human lung cancer cells, the induction of oxidative stress, and the reduction of the generation of ATP required for cellular energy.

On the other hand, for the majority of cells, the uptake of AgNP, mainly through endocytosis, depends on time, dose, and energy, and the major target organelles include endosomes and lysosomes. The silver nanoparticles can induce toxicity in cancer cells by means of several proposed mechanisms and are presented below and in Figure 16 [278–280]

(i) Induction of the production of ROS directly once they are exposed to the acidic environment of the lysosomes.
(ii) ROS are highly reactive, result in oxidative damage to proteins and DNA, and induce mitochondrial dysfunction

(iii) Silver nanoparticles and silver ions interact with the thiol nanoparticles of different molecules present in the cytoplasm, cell membrane, and inner membrane of mitochondria, which might release lipid peroxide and increase the permeability of the cell membrane and mitochondrial systems

(iv) Damage to the cell membrane results in leakage of cytoplasmic contents and eventual necrosis

(v) Rupture of lysosomal membranes activates lysosome-mediated apoptosis

(vi) Damage to mitochondria impairs electron transfer, thereby activating mitochondrion-dependent apoptosis

(vii) Silver nanoparticles could readily diffuse into, and translocate to, the nucleus through nuclear pore complexes, thereby leading to the formation of ROS, which directly trigger DNA damage and chromosomal abnormalities

(viii) DNA damage by silver ions

6. Conclusion and Future Perspectives

Currently, a great number of investigations have been published that demonstrate the green synthesis of silver nanoparticles from plant extracts. However, the new trend is obtaining silver nanoparticles from agri-food waste extracts. These wastes are abundant and generate environmental pollution. Therefore, by enhancing their use in the synthesis of silver nanoparticles, their impact decreases. Synthesis from agri-food waste is known as sustainable green synthesis. Waste that is generated, to the greatest extent, is from fruits and vegetables, includes the following: bruised fruits or parts of these and their peel; cereal waste such as straw, husk, GM, and DDGS; bagasse from the food industry and alcoholic beverages; and oil cake from the oil industry, among others. The main compounds of the extracts obtained from these residues comprise phenolic compounds, alkaloids, terpenes, cellulose, hemicellulose, lignin, and proteins, which function as reducing agents of the silver ion. Therefore, the silver nanoparticles synthesized from agri-food waste extracts are easy to manage, extremely low energy-based, eco-friendly, and sustainable, and it is an economic process with potential use in health with antimicrobial and anticancer activity.

The future perspectives on this topic are that more research is carried out in this line of knowledge generation, that is, in using more waste and by-products generated in the field during agriculture, in the industry during food processing and in homes (statistically it is the place where the largest amount of waste is generated) and to be able to minimize negative aspects such as pollution. The mechanisms by which the compounds present in agri-food waste (proteins, polysaccharides, organic acids, and phenolic compounds, terpenoid compounds, among others) promote the green synthesis of metallic nanoparticles and the engineering conditions to be able to synthesize them as a solvent must be thoroughly studied, also of pH of synthesis, silver nitrate and extract concentration. In addition, the toxicological effects of nanoparticles synthesized from waste should be studied, as well as their size and shape, and correlate it with their biological activity. There is a lack of economic studies on the cost-benefit of nanoparticles synthesized by different methods and even more so from agri-food waste, which, at a glance, shows that the cost decreases considerably with respect to other methods (physical and chemical). Therefore, it is an upcoming challenge that must be done to change the new way of making green synthesis and give added value to waste and make more friendly and less expensive methods for the reach of society.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors have declared no conflict of interest.

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