

The Status of Green Synthesis of Silver Nanoparticles Using Plant Extracts during Last Fifteen Years

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Abstract: Nanoparticles (NPs) are tiny particles with their dimensions ranging between 1 and 100 nm. These are gaining cumulative attention owing to their vast use in different fields of applications. There are three main methods for synthesizing NPs; namely, physical, chemical and biological methods. Physical methods consume a lot of energy and time, require expensive vacuum systems and high temperatures and on top of all, they are not environmentally friendly. Chemical methods, in general, are expensive, increase the particle toxicity and perhaps harm human health and the environment. In addition, hazardous chemicals gather on the top of NPs and confine their applications. Therefore, green method is an alternative replacement to the traditional chemical and physical methods for synthesizing NPs. The existing phytochemicals, for instance in plant extracts, own a remarkably high ability for reducing metal ions within a short time comparing with other microorganisms, which require a longer incubation period. This study is concentrating on green synthesis of silver (Ag) NPs, owing to the significance of Ag NPs whose optical properties depend on their size and shape. In addition, Ag NPs possess numerous applications, especially in solar cells, water treatment and medicine. This review aims to highlight the remarkable growth of green synthesis of Ag NPs, in terms of publications, citations, active and productive researchers, targeting journals and the eminent countries in this regard. This review, also, highlights the most utilized plants for producing Ag NPs in fourteen years; i.e., 2007-2021. This review, also, evaluating the most acceptable proposed mechanism for biosynthesizing Ag NPs using plant extracts. We believe that this review article will facilitate and brighten the road in front of researchers who want to initiate their study with the biosynthesis of Ag NPs from plant extracts.

Keywords: Silver nanoparticles, Green synthesis, Plant extracts, Stabilizing agents, Reducing agents.

1. Introduction

Nanotechnology is a rapidly expanding subject that has likely been utilized in a wide range of commercial products. Through generating nanoparticles (NPs) and nanoproducts, new and size-dependent physical and chemical characteristics that differ considerably from bulk materials can be produced [1]. In recent years, the scientific community has made a significant progress in the field of nanoscience and nanotechnology [2]. Nanoparticles have improved properties due to certain features, such as high surface area per unit volume and quantum confinement. Quantum confinement causes a relatively larger value of energy band gap which can offer improved optoelectronic devices, thermal applications, batteries and sensors as a semiconductor material. Nanomaterials have been utilized in countless applications owing to their exclusive features. Innovative, effective requests of nanomaterials and nanostructures can be perceived in drug delivery [3, 4], nano-medicine [4, 5], food packing [5, 6], disinfected processes [7], correlative microscopy [8], imaging [9, 10], optics [11], micro-electronics [12], three-dimensional (3D) lithography [13, 14], renewable energy [15, 16], wastewater treatment [17] and catalysis [18, 19].

NPs can be categorized into two wide-ranging groups; *i.e.*, organic and inorganic NPs. Inorganic NPs are semiconductor NPs (ZnO, ZnS, CdS), metallic NPs (Au, Ag, Cu, Al) and magnetic NPs (Co, Fe, Ni) [20]. Organic NPs are carbon-based NPs for instance quantum dots, fullerenes and carbon nanotubes. The demands for gold (Au) and silver (Ag) NPs are increasing speedily owing to their greater features and flexible characteristics [21]. Metallic NPs, generally, have numerous compensations [22]. Firstly, their optical characteristics can be controlled effortlessly; in other words, they are outstanding optical absorbers [23]. Secondly, they can be employed in numerous requests to achieve some precise resolutions; for example, speedy thermal reaction [24], erosion resistance [25], recyclability [26] and many others.

In this review, the authors are focusing on Ag NPs owing to their sole and progressive applications in different fields, comprising medical, food, health-care, customer and industrialized resolves, owing to their exclusive physical and chemical characteristics. These,

also, comprise optical, electrical, thermal and biological features. In addition, the superiority of Ag NPs is as a result of their nature, dimension, crystallinity, configuration and construction compared to the bulk analogues [27, 28]. These innovations have been employed in a large scope of possible applications; for example, biomedical tools, medicine, renewable energies, makeups, ecological remediation, food, user and industrialized resolves [29].

Ag NPs synthesis, and in general that of other NPs, can be conducted through two main methods; *i.e.*, top-down and bottom-up methods [30]. In the top-down method, the NPs are created from the bulk material. In the bottom-up method, the NPs can be produced through the nucleation and growth processes of the atoms. The first method, also known as a physical method, consists of a set of separate techniques; ball or mechanical milling [31, 32], laser ablation [33-35], evaporation condensation [36], electromagnetic levitation gas condensation (ELGC) [37], ultra-sonication [38-40], lithography [41, 42], spray pyrolysis [43-45], radiolysis [46], arc discharge [47-49] and photo-irradiation [50] which are among the examples of the physical methods. These methods can be used for extensive construction, but they are expensive, not safe and time-consuming methods [51]. In the bottom-up, or chemical, methods, the chemical substances can be utilized to reduce metallic cations to procedure zero-charged metallic atoms, then these metallic atoms undergo nucleation and the growth state to form metallic NPs [52]. The chemical methods are mostly accompanied by the addition of stabilizers to deliver stability, avoid aggregation, control morphology and provide compatible properties [53]. Sol-gel method [54-56], traditional chemical reduction [57-59], inverse micelle [60, 61], co-precipitation [62], chemical vapor deposition [63], solvo-thermal [64, 65] and electrochemical reduction [66, 67] are the most utilized chemical methods for producing metallic NPs, such as Ag NPs [68]. The chemical methods provide a harmful impact on the manufacturers and operators due to employing hazardous chemical materials as reducing, capping and stabilizing agents. Consequently, the chemical methods cause numerous troubles for the human and the environment simultaneously. Hence, currently, investigators started focusing on the green

method for synthesizing NPs [69]. This interest sees its impact significantly in the number of

publications, especially in recent years (Fig. 1).

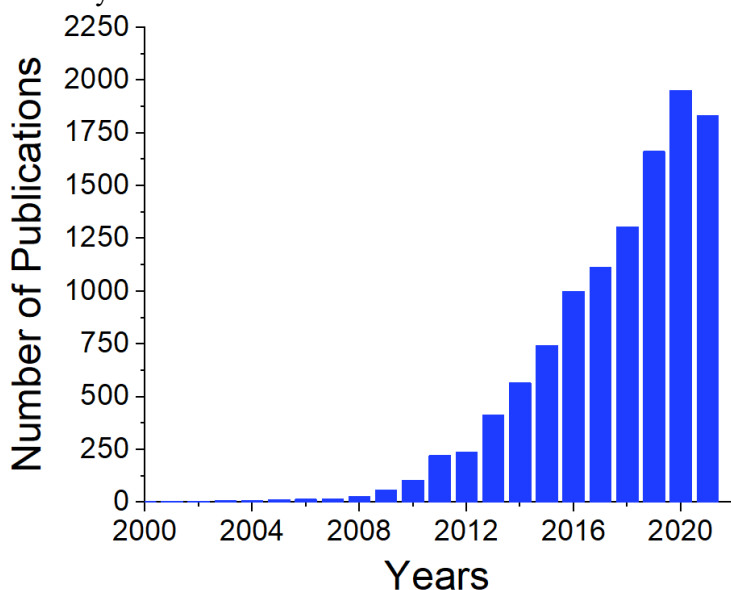


FIG. 1, Number of publications of green synthesis of NPs (using web of science).

In addition, the fabrication of nanomaterials using biological method is gaining more attention in many countries due to its ease, eco-friendliness, low cost and avoiding toxic chemicals (Fig. 2). Green synthesis of NPs includes using natural materials, such as plants

and microorganisms, such as bacteria, fungi, algae and yeasts [70]. Nevertheless, compared to bacteria, fungi, algae and yeasts, the available phytochemicals in plant extracts own an extremely higher aptitude for reducing metal ions in a short period of time [71, 72].

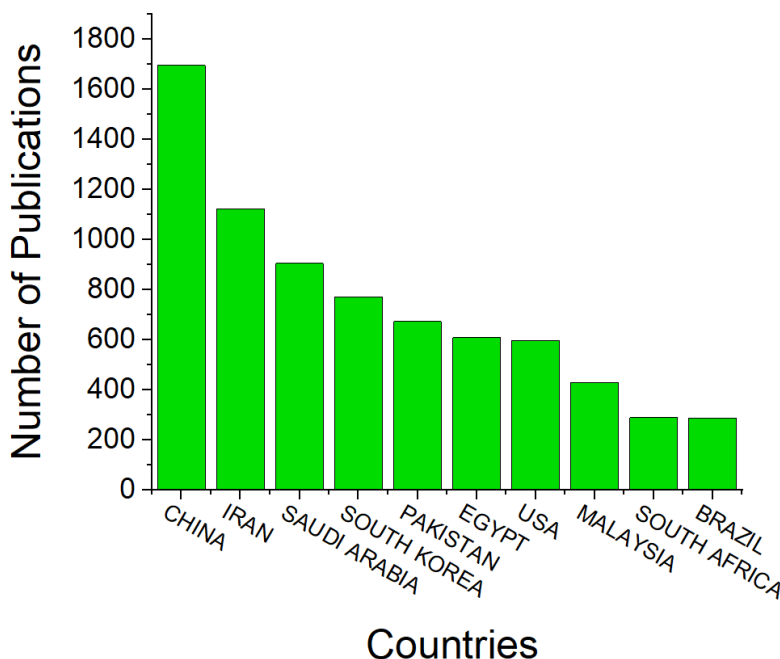


FIG. 2. Top-ten countries using green-synthesis methods for NPs preparation (web of science).

Thus, plant extracts are observed as an outstanding source for synthesizing metallic NPs. Besides, plant-based synthesis process, for synthesizing NPs, is a foremost procedure over the microorganism procedure owing to its straightforwardness, quickness and avoiding of

culture maintenance [73]. Likewise, plant supplies, such as flowers, leaves, seeds, stems, fruits and peels, have been utilized as reducing and capping agents in NPs fabrication procedure [74].

This review article is a continuation of our recent works [20, 75-85] regarding green synthesis of nanomaterials. This review is highlighting green synthesis of Ag NPs using plant extracts. The novelty of this review is that the relevant readers can get necessary information regarding green synthesis of Ag NPs in terms of publications, citations, productive researchers, targeting journals and countries in this respect. This review, similarly, highlights the most employed plant extracts for fabricating Ag NPs from 2007 to 2021. The most acceptable proposed mechanism for biosynthesizing Ag NPs using plant extracts is also presented in this investigation. According to our best knowledge, this review article will simplify and brighten the road for the relevant researchers who need to start their journey with the biosynthesis of Ag NPs from plant extracts.

2. Materials and Methods

The data of this investigation was collected *via* an online database. "Web of Science" version 5.35 as a data source was used. Since it contains a large number of authoritative data and is often used as a scientific, academic and fact-finding resource for scholarly publications, the Web of Science has been used to cover and access data. The current study, based mainly on the Web of Science, selected all the data related to the synthesis of green Ag NPs from 2007 until December 2021 and the research necessitated the

exact selection of titles, keywords and abstracts extensively.

3. Results and Discussion

Ag, possessing the atomic number 47, is a lustrous, ductile and malleable metal that is slightly harder than gold. It is one of the most fundamental components of our planet. It can be found in nature as a natural component, in amalgamation with other metals; for instance, gold, as well as raw materials; namely, chlorargyrite and argentite. Chemically, silver holds four dissimilar oxidation states; *i.e.*, Ag^0 , Ag^{1+} , Ag^{2+} and Ag^{3+} [86]. Nevertheless, it is a chemically inactive component; however, it can respond to nitric acid or hot intense sulfuric acid, making solvable silver salts. Even though it has outstanding heat and electrical conductivities, its uses in the electrical sector have been severely constrained owing to its higher cost [87]. The metallic form of silver is water-insoluble; nevertheless, its metallic salts; for instance silver nitrate (AgNO_3) and silver chloride (AgCl), are dissolving in water easily. This study is focusing on the green synthesis of Ag NPs using plant extracts, during 14 years, from 2007 to 2021. According to the Web of Science, there are 292 published articles, some of which are very essential and suitable, especially for new researchers in green synthesis of Ag NPs. It can be seen, in Fig. 3, that the pace of publishing increases exponentially over time. This trend is, perhaps, due to the importance of this topic.

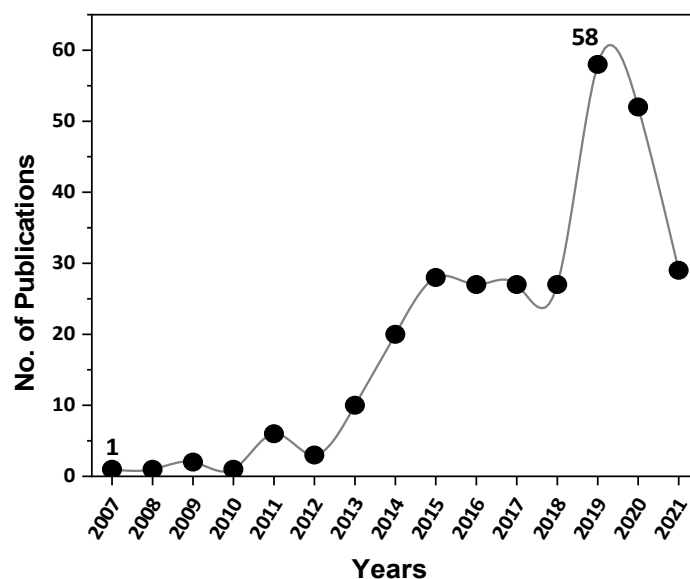


FIG. 3. Development of published articles regarding Ag NPs from 2007 to 2021.

It can be noticed from Fig. 3 that in 2007, there was only one published article about Ag NPs. After that, the number of scientific articles in this field increased dramatically. Consequently, one can predict that the applications of Ag NPs have increased intensely in several fields. These applications cover medical, food, sensors, solar cells, health-care, consumer and many industrial purposes. This is not astonishing, since Ag NPs possess unique physical and chemical properties when it goes to the nanoscale. Also, optical, electrical and thermal properties of Ag NPs improve compared

with the silver bulk analogues. In the last three years, one can observe that the number of publications is increasing noticeably. With all of the challenges that faced the world in 2020 owing to COVID-19 and social distancing, the greatest rate of publishing was in 2019 and the number of publications started to decrease in 2020. Although the number of published articles in 2020 has decreased slightly compared to 2019, the highest number of citations has been made for the articles that have been published in that year (Fig. 4).

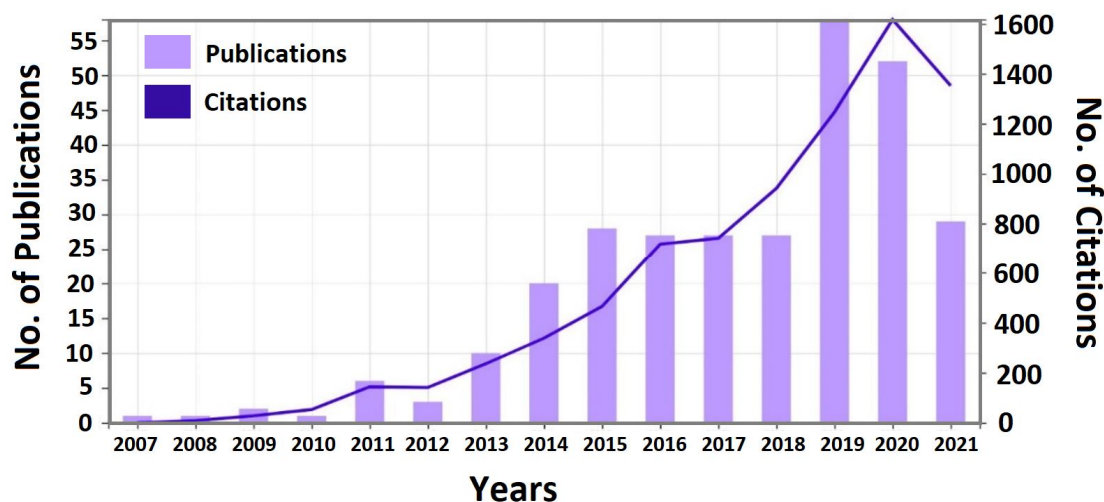


FIG. 4. Number of citations and publications per year.

3.1 Studying the Top Ten Journals

There are many scientific journals in which it is possible to publish extensive scientific studies in various fields of science. However, choosing the most appropriate and best one is an important matter that requires great knowledge and effort. In this part of our study, we highlighted the top ten journals in terms of the quantity of publications in the green synthesis of Ag NPs using plant extracts. It can be seen, from Table 1, that ten reputable journals have been selected according to their relatively high impact factors. It can be stated that during this selected time; *i.e.*, from 2007-2021, 62 publications, regarding green synthesis of Ag NPs using different plant extracts, were published in these journals. About 24% of these articles were published in “RSC advances” Journal, about 14% of these articles were published in the international journal of biological macromolecules, while the other remaining journals took about 8% each of the publications, respectively. In terms of the impact

factors of these selected journals, one can notice, from Table 1, that the highest impact factor goes to carbohydrate polymers journal, which published only 4 articles, while the lowest impact factor goes to materials research express journal, which published 5 articles during this period of time. In addition, in terms of the country of origin for these selected journals, each of the United Kingdom and Netherlands took 30% of these journals, while the United States took 20% and each of Germany and New Zealand took only 10% of these journals. Moreover, more than 38% of these articles were published in the United Kingdom, more than 30% in Netherlands and more than 16% in the United States. The remaining 16% went to Germany and New Zealand. Table 1 also shows that the highest accepting rate among these selected journals goes to the RSC advances, while the lowest accepting rate goes to both of carbohydrate polymers and international journal of nanomedicine, respectively.

TABLE 1. The top ten journals regarding green synthesis of Ag NPs during 2007-2021.

No.	Journal name	Number of publications	Country	Impact factor (2020)
1	RSC advances	15	United Kingdom	3.361
2	International journal of biological macromolecules	9	Netherlands	6.953
3	Materials science & engineering c-materials for biological applications	5	Netherlands	7.328
4	Applied surface science	5	Netherlands	6.707
5	Journal of applied polymer science	5	United States	3.125
6	Journal of cluster science	5	United States	3.061
7	Green processing and synthesis	5	Germany	2.83
8	Materials research express	5	United Kingdom	1.62
9	Carbohydrate polymers	4	United Kingdom	9.381
10	International journal of nanomedicine	4	New Zealand	6.4

3.2 The Countries/ Regions

The researchers in this review believe that investigating interest in the synthesis of green Ag NPs from plant extracts at the country level is important to researchers, but explaining the reason for this interest is even more important.

Accordingly, another attempt of this investigation was highlighting the top ten countries that have an active role in this field. Table 2 shows the most productive countries, in terms of number of publications, in the field of green synthesis of Ag NPs.

TABLE 2. Top ten countries for Ag NPs research during the study period.

No.	Country	Region	Number of publications
1	India	South Asia	118
2	China	East Asia	46
3	South Korea		33
4	United States		North America
5	Saudi Arabia	Middle East Asia	18
6	Iran	Central Asia	16
7	Turkey	Europe	10
8	Malaysia	Southeast Asia	9
	South Africa	South Africa	9
9	Brazil	South America	8
10	Egypt	Northeast Africa	7
	Taiwan	East Asia	7

It can be seen, from Table 2, that India is at the forefront in this group. Within this period of time, between 2007 and 2021, 118 reliable articles have been published in India regarding the green synthesis of Ag NPs using plant extracts between 2007 and 2021. The second country is China which published 46 articles in this area. Nanotechnology is a rapidly expanding field of science and it brings benefits to many areas of science and industry. East Asia region, including (China, Taiwan, South Korea, India and Iran), published (80.19%) of the publications in the top ten countries in fourteen years. It was followed by America (11.36%), Africa (5.19%)

and Europe (3.25%) regions, as shown in Fig. 5. The authors believe that the secret of this great interest is in the abundance of plants and the vast green space in these countries [88, 89]. These consequences show that Ag NPs represent one of the most popular types of NPs, owing to their application in many fields [90]. As stated before, there are many different ways to obtain Ag NPs; however, green-synthesis method using plant extracts is undoubtedly a leading method [91]. This is attributed to the many benefits associated with this method [92].

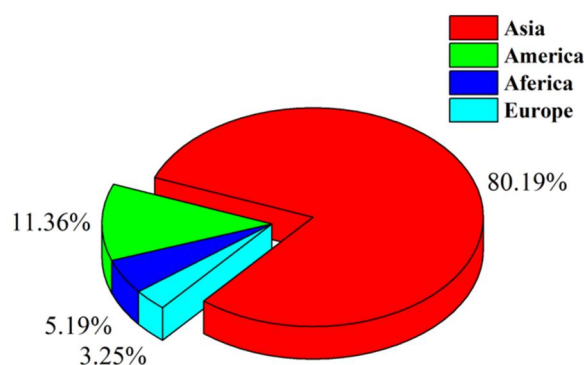


FIG. 5. Effective continental participation for the green synthesis of Ag NPs.

3.3 Covering Ten Most Cited Researches

A large number of published research indicates that the synthesis of NPs through biosynthesis methods is environmentally friendly and inexpensive [93]. Although the number of citations does not reflect the degree of importance of the published work, it indicates the interest of the scientific community in this work [94]. Table 3 lists the top ten most cited works in the field of green synthesis of Ag NPs. It can be noticed, from Table 3, that there are 2256 citations in all of the published research regarding green synthesis of Ag NPs. Kumar *et al.* conducted a research entitled; “Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil” in 2008, which possesses the highest citations (732). This work has been published in “Nature Materials” journal [95]. This study is about the addition of Ag NPs to paint that shows excellent antimicrobial properties through killing both Gram-positive human pathogens (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*). The process developed here is quite general and can be applied in the synthesis of a variety of metal NPs in oil medium. This approach is an eco-friendly method to synthesize metal NPs for embedded paint, in a single step, that can be utilized from household paint [95].

The second most cited publication belongs to Tolaymat *et al.* with 518 citations, entitled “An evidence-based environmental perspective of manufactured silver nanoparticles in syntheses and applications: A systematic review and critical appraisal of peer-reviewed scientific papers”. This study was published in the journal of “Science of the Total Environment” [96]. The third article is cited only 321 times and was published by Shao *et al.* in 2015 under the title of “Preparation, Characterization and Antibacterial Activity of Silver Nanoparticle-decorated Graphene Oxide Nanocomposite” [97]. The fourth investigation under the title “An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin core”, published in the journal “Nature Nanotechnology” in 2015 by Richter *et al.*, possesses 290 citations [98]. The fifth article was “Humic Acid-induced Silver Nanoparticle Formation under Environmentally Relevant Conditions” with 222 citations and was published in 2011 in the journal “Environmental Science & Technology” [99]. These articles are five out of the ten most cited research articles, helping related readers and researchers understand and summarize the status of the green synthesis of Ag NPs.

TABLE 3. Top ten cited studies regarding Ag NPs during the study time.

No.	Articles	Authors	Publishing journals	Year of publication	Citations
1	Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil	-Kumar, A -Vemula, PK -Ajayan, PM -John, G1	Nature Materials	2008	732
2	An evidence-based environmental perspective of manufactured silver nanoparticles in syntheses and applications: A systematic review and critical appraisal of peer-reviewed scientific papers	-Tolaymat, TM -El Badawy, M -Genaidy, A -Scheckel, KG -Luxton, TP -Suidan, M	Science of the Total Environment	2010	518

No.	Articles	Authors	Publishing journals	Year of publication	Citations
3	Preparation, Characterization and Antibacterial Activity of Silver Nanoparticle-decorated Graphene Oxide Nanocomposite	-Shao, W -Liu, XF -Min, HH -Dong, GH -Feng, QY -Zuo, SL	Acs Applied Materials & Interfaces	2015	321
4	An environmentally benign antimicrobial nanoparticle based on a silver-infused lignin core	-Richter, AP -Brown, JS -Bharti, B -Wang, A -Gangwal, S -Houck, K -Hubal, EAC -Paunov, VN -Stoyanov, SD -Velev, OD	Nature Nanotechnology	2015	290
5	Humic Acid-induced Silver Nanoparticle Formation under Environmentally Relevant Conditions	-Akaighe, N -MacCuspie, RI -Navarro, DA -Aga, DS -Banerjee, S -Sohn, M -Sharma, VK	Environmental Science & Technology	2011	222
6	Green synthesis of silver nanoparticles: Biomolecule-nanoparticle organizations targeting antimicrobial activity	-Roy, A -Bulut, O -Some, S -Mandal, AK -Yilmaz, MD	Rsc Advances	2019	206
7	Green synthesis of biopolymer-silver nanoparticle nanocomposite: An optical sensor for ammonia detection	-Pandey, S -Goswami, GK -Nanda, KK	International Journal of Biological Macromolecules	2012	186
8	Phytosynthesis of Silver Nanoparticles Using <i>Gliricidia sepium</i> (Jacq.)	-Rajesh, R -Jaya, L -Niranjan, K -Vijay, M -Sahebrao, K	Current Nanoscience	2009	178
9	Physicochemical properties of gelatin/silver nanoparticle antimicrobial composite films	-Kanmani, P -Rhim, JW	Food Chemistry	2014	174
10	Graphene oxide and shape-controlled silver nanoparticle hybrids for ultrasensitive single-particle surface-enhanced Raman scattering (SERS) sensing	-Fan, W -Lee, YH -Pedireddy, S -Zhang, Q -Liu, TX -Ling, XY	Nanoscale	2014	161

It can be seen, from Table 3, that the citation number is decreasing dramatically from article 5 to 10. According to the best of our knowledge, analyzing the top 10 articles in terms of the number of citations as well as the target journal helps related researchers reach the corrected journal easily, in addition to showing the importance of the selected articles in terms of science, application and presentation.

3.4 Authors' Profiling

There are several international standards that highlight the reputation of researchers and highlight the reliability of their research. Among these standards are the number of publications, H-index, total citations and field of the research, which measure the academic output of a researcher [100]. Table 4 highlights the top ten most productive researchers in the field of green

synthesis of Ag NPs, as measured by the number of publications, H-index, total citation and citation per study. Vijay Kumar acknowledged 5 papers in the topic of green synthesis of Ag NPs, with a total of 118 citations. Each of Sneha Mohan Bhagyaraj, Baskaralingam Vaseeharan, Sekar Vijayakumar and Shishir V. Kumar has published four articles in the field of green synthesis of Ag NPs. Individually, Sangiliyandi

Gurunathan, Chen, Xi, Resat Apak, Ravi Kumar Gundampati and Hasan, Syed Hadi has published three articles in the field of green synthesis of Ag NPs. On the other hand, Resat Apak comes on the top researchers in the list through having 435 articles and 16414 citations. Sangiliyandi Gurunathan, in turn, has the highest H-index: 61, followed by Resat Apak who has H-index: 58.

TABLE 4. Top ten authors in the field of Ag NPs along the study period.

No.	Authors	Publication in the field of study	All publications	H-index	Total citations	Citations in this field
1	Vijay Kumar	5	57	12	453	118
2	Sneha Mohan Bhagyaraj	4	35	11	478	85
3	Baskaralingam Vaseeharan	4	236	44	7047	81
4	Sekar Vijayakumar	4	66	23	1796	81
5	Shishir V Kumar	4	11	7	215	50
6	Sangiliyandi Gurunathan	3	192	61	15350	186
7	Chen, Xi	3	6	6	155	131
8	Resat Apak	3	435	58	16414	114
9	Ravi Kumar Gundampati	3	62	14	680	113
10	Hasan, Syed Hadi	3	92	34	3349	113

3.5 Mechanism of the Biosynthesis of Ag NPs from Plant Extracts

Biosynthesis, photosynthesis or green synthesis of NPs has the advantages of reducing energy consumption [101]. This synthesizing method is far away from using hazardous/toxic chemical elements, sophisticated and costly laboratories for NPs preparation [102]. In plant extracts-mediated green synthesis of Ag NPs (Fig. 6), it is possible to produce NPs through the reaction of the secondary metabolites present in the plant extracts, such as flavonoids, terpenes, alkaloids, phenols, saccharides and many others [103]. The available phytochemicals in the plant extracts are acting as reducing, capping and stabilizing agents [104]. These hydroxyl groups are able to reduce Ag^+ ions into metallic zerovalent Ag^0 [105]. After the reduction process, the zerovalent metal will go to the nucleation stage (Fig. 6) within a short burst. After that, the capping process will initiate around the surface of the Ag NPs. These capping agents work as stabilizers or binding molecules that stop over agglomeration and stabilize the interaction of NPs within the surrounding medium [106]. The race among capping and growth rate regulates the size of the NPs [107]. The key function of a capping agent throughout the synthesizing of the NPs is to control the nucleation procedure and agglomeration when

the essential amount is utilized to successfully stabilize the NPs. The outcomes of the UV-Vis spectroscopy analysis indicated that all the synthesized Ag NPs possess blue-shifted absorption spectrum, while the surface Plasmon resonance of the bulk Ag is around 1000 nm [108]. Incalculable chemical capping agents are employed to control the synthesis of NPs. Nevertheless, in the green synthesis method using plant extracts, for instance, the plant extract can provide the capping agents and there is no need to add external capping agents [109]. Normally, the flavonoids initiate the capping on the NPs, while phenolic combinations make multi-chelating bonds and stabilize the NPs after nucleation, resulting in the formation of different-sized NPs [110]. Additionally, proteins are an outstanding basis of characteristic functional groups that can be employed in moderating the surface of the NPs; *i.e.*, as a capping agent [111]. In the absence of the capping agent, metal, after reduction, will agglomerate and precipitate out. Both reducing and stabilizing agents play important roles in controlling the particle sizes, shapes, monodispersity and polydispersity phases. In general, the available phytochemical in the plant extract plays a very important role in the synthesizing process, especially in protecting the process from unexpected agglomeration and controlling the size and shape of the NPs [112].

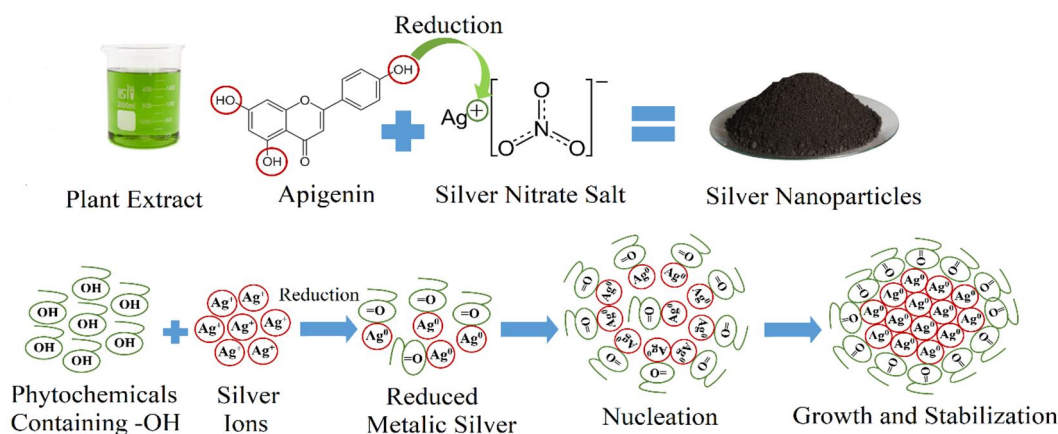


FIG. 6. The biosynthesis of Ag NPs from plant extracts has been proposed as a process.

3.6 Covering the Plant

The biosynthesis method using plant extracts provides a large-scale production of Ag NPs, which is a logical remedy for the increasing demand for Ag NPs. Plant extract, in general, possesses diverse active biomolecules, such as phenolic acids, sugars, terpenoids, alkaloids, polyphenol and proteins that play a vital role in this biological reduction and stabilization of silver ions [113]. The leaves of the plant are more preferential than the whole plant in the synthesizing process due to the availability of the important phytochemicals that participate in reducing, capping and stabilizing the NPs [114]. The structure of some active biomolecules is capable of reducing and stabilizing Ag ions. Structures of some secondary metabolites, such as *Rutin*, *Genistein*, *Quercetin*, *Gallic acid*, *Daldzein* and *Papaverine*, are important for reducing and stabilizing stages in synthesizing Ag NPs. The size and shape of Ag NPs depend on the following parameters: concentration of the utilized plant extract, concentration of the Ag salts, reaction temperature, reaction time and reaction pH value [115]. Kumar *et al.* [116] studied the use of marine seaweed, *Gracilaria corticata*, in an attempt to produce Ag NPs. The extract was gradually heated to 60 °C for 20 min in a heating mantle for the reduction of metal ions to occur. The study revealed that the Ag NPs possess a spherical shape and the NPs sizes were in the range 18–46nm. The synthesized Ag NPs were characterized by UV–Vis spectroscopy, FTIR spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS) measurements and zeta potential. The result showed that the biosynthesized Ag NPs from *Gracilaria corticata* have an effective antifungal activity

against *Candida albicans* and *C. glabrata* [116]. In another attempt by Prakash *et al.* [117], Ag NPs were synthesized using *Mimusops elengi*, L.leaf extract. The extract of *Mimusops elengi* L. was mixed with AgNO₃ solution. This reaction continued uninterrupted until the solution appeared to change its color from light green to dark brown. The synthesized Ag NPs were reported to exhibit a spherical shape and the range of the NPs size was between 55 and 83 nm. The biosynthesized Ag NPs were characterized using different characterization techniques. In addition, the green synthesized Ag NPs showed higher antimicrobial efficacy against multi-drug resistant clinical isolates [117]. Muniyappan *et al.* [118] synthesized Ag NPs using *Dalbergia spinosa* leaves extract. The results showed that the reducing sugars and flavonoids were primarily responsible for the bio-reduction process of Ag ions. TEM analysis showed that the Ag NPs were nearly spherical in shape with an average size of 18 ± 4 nm. Ag NPs were characterized by UV-Vis spectroscopy, TEM and FTIR analysis [118]. In another attempt, Singh *et al.* [119] biosynthesized Ag NPs using *Anabaena doliolum* and their antimicrobial and antitumor activities have been investigated. Singh *et al.* results indicated that the original color of the mixture was changed from reddish blue to dark brown after the addition of silver nitrate solution within one hour, suggesting the formation of Ag NPs. The formation of the Ag NPs was also monitored by the UV-Vis spectroscopy analysis when the SPR peak was recorded at 420 nm. TEM images revealed well-dispersed, spherical Ag NPs with particle sizes ranging from 10 to 50 nm. The X-ray diffraction analysis suggested a highly crystalline nature of the Ag NPs. FTIR analysis indicated that the hydroxyl (-OH) group is

available around the biosynthesized Ag NPs due to the sincerity of these NPs for moisture [120]. On the other hand, *Enteromorpha flexuosa* was utilized by Yousefzadi *et al.* [121] as a reducing and stabilizing agent for synthesizing Ag NPs. They stated that the colorless reaction mixture was turned into a dark brown color solution after 60 minutes, indicating the biotransformation of ionic Ag to reduced Ag atoms, as a result of the surface Plasmon resonance phenomenon. The color change was occurring because the active molecules present in the extract reduce the Ag metal ions into Ag NPs. The intensity of the color change was increased in direct proportion

to the incubation period of nanoparticle synthesis. The formation of Ag NPs was monitored by UV-Vis absorption spectra at 200 to 600 nm, where an intense band was clearly detected at 430 nm, confirming the formation of Ag NPs [121]. Salari *et al.* [122] biosynthesized Ag NPs using *Spirogyra varians* extract. The average crystalline size was estimated to be around 17.6 nm and the SEM analysis confirmed the formation of relatively uniform NPs. These NPs showed an absorption peak at 430 nm in the UV-Vis spectrum [122]. Table 5 summarizes utilizing 27 different types of plants used for synthesizing Ag NPs.

TABLE 5. The utilized plant extracts for synthesizing Ag NPs.

No.	Name of plant	Size and morphology	UV-Vis SPR peak	Date of publication	Reference
1	<i>Gracilaria corticata</i>	18-46nm; Spherical	420nm	25-Jul-2012	[116]
2	<i>Mimusope elengi</i>	55-83nm; Spherical	434nm	18-Mar-2013	[117]
3	<i>Piper nigrum</i>	4-50nm; hexagonal and Spherical	460nm	15-Jan-2014	[123]
4	<i>Aloe vera</i>	70nm; Spherical	400nm	20-Nov-2014	[124]
5	<i>Dalbergia spinosa</i>	18nm; spherical	439nm	8-Mar-2014	[118]
6	<i>Anabaena dolioluma</i>	10-50nm; Spherical		30-Jun-2014	[120]
7	<i>Enteromorpha flexuosa</i>	2-32nm; Spherical	430nm	20-Aug-2014	[121]
8	<i>Spirogyra varians</i>	17.6nm; quasi-spheres	430nm	12-Oct-2014	[122]
9	<i>Pedaliium murex</i>	10-150nm; Spherical	424-430nm	16-May- 2015	[125]
10	<i>Calliandra haematocephala</i>	70nm; Spherical	414nm	16-Jun-2015	[126]
11	<i>Eucalyptus globulus</i>	1.9-4.3nm and 5-25nm, with and without microwave treatment; Spherical	428nm	1-Jul-2015	[127]
12	<i>Ocimum sanctum</i>	14.6nm; Spherical	429nm	30-Jul-2015	[128]
13	<i>Synechococcus sp.</i>	140nm; Spherical	420+3.2	17-Dec-2015	[129]
14	<i>Phlomis</i>	19-30nm; Spherical	440nm	16-Jan-2016	[130]
15	<i>Gracilaria birdiae</i>	20.2-94.9nm; Spherical	400-420nm	22-Apr-2016	[131]
16	<i>Saccharina japonica</i>	14.77nm; Spherical	432nm	21-Sep-2016	[132]
17	<i>Convolvulus arvensis</i>	28nm; Spherical	430nm	19-Dec-2016	[133]
18	<i>Elephantopus scaber</i>	37nm; Spherical	420nm	6- Jul-2017	[134]
19	<i>Enteromorpha compressa</i>	4-24nm; Spherical	421nm	14-Mar-2017	[135]
20	<i>Erythrina suberosa</i>	15-34nm; Spherical	~428nm	17-Mar-2017	[136]
21	<i>Cichorium intybus</i>	Various sizes depending on [metal]-to-[extract] ratio; Spherical	~420	25-Mar-2017	[137]
22	<i>Caulerpa serrulata</i>	10nm; Spherical-ellipsoidal	412nm	23-Jun-2017	[138]
23	<i>Salvia leriifolia</i>	27nm; Spherical	460nm	23-jul-2017	[139]
24	<i>Caulerpa racemose</i>	10nm; Spherical	413nm	13-Aug-2017	[140]
25	<i>Alpinia katsumadai</i>	12.6nm; quasi-spherical	416-420nm	15-Aug-2017	[141]
26	<i>Phyllanthus amarus</i>	30-42nm; flower-like	421nm	17-Oct-2017	[142]
27	<i>Nelumbo nucifera</i>	12.9nm; quasi-spherical	415nm	18-Jan-2018	[143]

It can be stated that Table 5 is extremely important, since it shows the suitable plant extracts for producing the desirable size, morphology and shape of Ag NPs.

4. Conclusion

Recently, Ag NPs have received massive consideration by researchers owing to their potential applications in many fields of science. The traditional methods for synthesizing Ag NPs have an operative harvest; however, they are accompanied by restrictions, like utilizing toxic materials and high operating cost and energy requests. The use of plant extracts to synthesize Ag NPs is the subject of this review, since this method is the most widely used, sustainable, inexpensive and easy one of all methods being used. This method attracted the consideration of researchers owing to the fact that plant extracts are safe to use and a source of numerous phytochemicals. The available phytochemicals inside plant extracts have been utilized as potential reducing, capping and stabilizing agents for synthesizing Ag NPs. There are sufficient published articles regarding green synthesis of Ag NPs; however, the current review, unlike previous reviews, summarizes the green synthesis method of Ag NPs in terms

of the top ten journals, top ten countries, ten most cited researches and top ten authors in this field. The most suitable mechanism of the biosynthesis of Ag NPs from plant extracts is discussed extensively. The utilized plant extracts for synthesizing Ag NPs from the top articles analyzed alongside with the impact of numerous parameters on the size, shape, morphology of Ag NPs have been studied comprehensively.

This study precisely focused on the status of green synthesis of Ag NPs using plant extracts in the last 15 years, starting from 2007 to 2021. This extensive review helps in understanding and identifying new developments regarding the green synthesis of Ag NPs, as well as directing researchers, especially new ones, to the most important findings of the case studies and studying the gaps in order to find opportunities for conducting relevant research. Moreover, this study covers a large number of the most significant plants that were used to prepare Ag NPs with different sizes and shapes, which will help researchers in determining the best plant type and working on it. This study showed that the number of publications is increasing dramatically. The trend is continued, with the exception of a modest dip in 2020, owing to the COVID-19 pandemic and global social isolation.

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