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Short Review Article

Plant Extract Assisted Eco-benevolent Synthesis of Selenium Nanoparticles-A Review on Plant Parts Involved, Characterization and Their Recent Applications

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Abstract:
Selenium nanoparticles (SeNPs) have attracted a great deal of attention in distinctive fields such as anticancer, antioxidant, catalysis, photocopiers, rectifiers, solar cells, and xerography. This has ameliorated an immense development of different synthetic pathways for SeNPs production. Preparation of SeNPs depends largely on the known chemical and physical methods that involved noxious chemicals and harsh reaction conditions which have been identified as a major disadvantage and potential threats to environment, health and its usage. Alternatively, biogenic synthesis has gained popularity as it is eco-benign, cheap, clean, and safe, generating minimal waste. In this review, we summarized recent literature on green synthesis of the SeNPs using various plants and plant parts which have revolutionized technique of fabrication for their applications in various fields. Due to the biocompatibility of the SeNPs, it has found its stupendous applications in biomedical field. The protocol, characterization techniques and biosynthesis of SeNPs along with various recent applications were also discussed.

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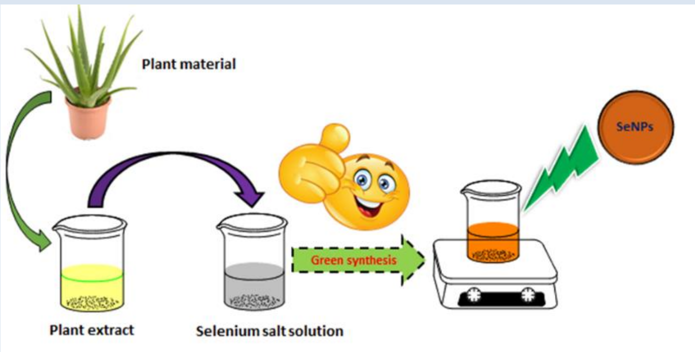
Keywords: Green synthesis; Plant extracts; Nanotechnology; SeNPs; Applications

Graphical Abstract:



Biography:

Prashant Korde obtained his M. Sc. degree from H.P.T. Arts and R.Y.K. Science College, Nashik, Savitribai Phule Pune University, Maharashtra in Organic Chemistry. At present he is pursuing his Ph.D. degree from Yashwantrao Chavan Maharashtra Open University, Nashik Under the guidance of Prof. Dhananjay Mane. His area of research interest is synthesis of nanomaterial and their applications.

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Dhananjay Mane presently working as Regional Director in Yashwantrao Chavan Maharashtra Open University, Nashik (India) and Professor of Chemistry in Shri Chhatrapati Shivaji College, Omerga (India). His area of research interest is synthesis of heterocyclic compounds and their biological applications.

1. Introduction

Nowadays, nanotechnology is an immensely ameliorating multidisciplinary field due to its wide range of applications in different domains of science and technology. Due to implicitly new or proliferated features/properties of NPs, their eclectic applications are growing swiftly on several fronts including, biomedical, transportations, biosensors, pharmaceuticals, automobiles, catalysis, drug delivery, food technology health care, agriculture, antimicrobial, and water purification [1-24]. Among the all noble metal NPs, SeNPs has attracted numerous research interests due to its nutritional supplementation value and low toxicity. However, selenium exists in various oxidation states like 0, +2, +4, +6 and -2. Therewithal, selenium can be present in Nature showing various polymorphic structures, either amorphous or crystalline. The most important non-crystalline forms of selenium are the black amorphous, red amorphous and vitreous selenium [25]. The crystalline forms include three allotropes of monoclinic selenium containing rings of Se8 with different packing to give red monoclinic forms (α, β and γ). Black trigonal crystalline form of selenium is the most stable at room temperature [26]. Hence, SeNPs finds immense applications (Figure 1) in areas such as biosensor [27], photocatalyst [28], solar cell [29], semiconductor [30], electronics, catalysis and sensing [31], water treatment [32], rectifier, photocopier and xerography [33]. In addition, SeNPs have anticancer [34], antioxidant [35], antibacterial [36], antibiofilm and antileishmanial [37], antifungal [38], wound healing, antiviral [39], antiproliferative [40] antihepatocarcinoma [41], antitumor [42], anti-inflammatory [43] and antidiabetic [44] due to their superior biomedical and therapeutic applications [45].

Heretofore, several physical and chemical techniques have been applied for the synthesis of SeNPs. Table 1 summarizes these synthetic routes of SeNPs. Nevertheless, some of them involve complicated, expensive, tedious and non-sustainable, time-consuming protocols. To overcome on these drawbacks, “*green nanotechnology*” plays an overriding role in the synthesis of SeNPs. However, SeNPs fabrication through “green approach” is a safe and non-noxious procedure that different natural sources such as enzymes, bacteria, fungi and plants can be utilized. Therewithal, the use of plant parts extracts reduces the expensive cost of microorganism’s isolation. Therefore, plant extract mediated NPs syntheses have become predominant due to the cheap, simplicity, swift synthesis, high yield and free of from perilous chemicals [3-4]. Moreover, plant extract mediated NPs generates a better methodology for SeNPs synthesis as they provide herbal capping and reducing/stabilizing agents. Furthermore, bioactive constituents present in plant extracts such as flavonoids, alkaloids, phenols, saponins, carbohydrates, proteins, quinine, glycosides, tannins and steroids can facilitate the procurable biosynthesis of SeNPs in a single-step process [5-6].

The main goal of the present review was to focus on the current knowledge concerning the capability of plant materials for biogenic synthesis of SeNPs and presents a database that future researchers may be based on the eco-benign synthesis of SeNPs using plants material sources.

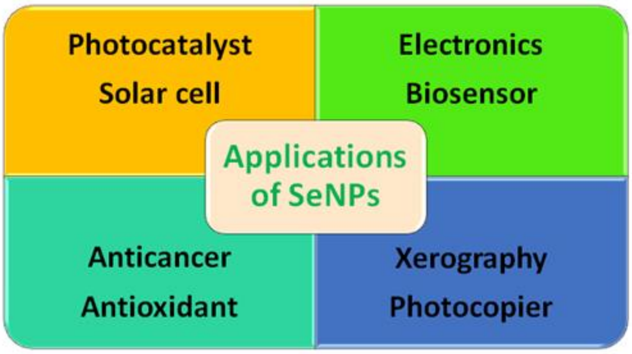

Figure 1. Various applications of SeNPs.

Table 1. Various methods for synthesis of SeNPs.

Entry	Name of the Synthetic Process	Reference
1	Pulsed laser ablation	[46]
2	Ionic liquid induced	[47]
3	Sol gel	[48]
4	Microwave	[49]
5	Hydrothermal	[50]
6	Solvothermal	[51]
7	Sonochemical	[52]
8	Vapor phase deposition	[53]
9	Solution phase approach	[54]
10	Electro kinetic technique	[55]
11	Radiolysis reduction	[56]

2. Eco-benign Synthesis of SeNPs

Day by day, green synthesis of noble metal NPs has been an imperative research area in the branch of green nanotechnology. The effective outcome of the green synthesis (Figure 2) over known chemical and physical methods is: cheap, sustainable, eco-benevolent, procurable, one pot and clean synthesis, moreover there is no need to use high amount of temperature, cost, energy, space and hazard associated with mephitic chemicals [1, 4-5].

Figure 2. Importance of green synthesis of metal oxide nanoparticles.

Using plant material for bio-fabrication of SeNPs has received an apt deal of attention due to its environmentally safe, cheap, swift, non-noxious, and procurable methodology which provides a concerted and single step technique for biogenic synthesis of SeNPs [3-4]. The green synthesis approach via plant extract involves many secondary metabolites such as flavonoids, alkaloids, phenols, saponins, carbohydrates, proteins, quinine, glycosides, tannins and steroids as natural reducers and/or stabilizers [5-6]. Some plants are already reported to facilitate SeNPs (Table 2). Several parts of plant such as buds, leaves, nuts, peel, fruit, seed and pulp can be used for synthesis of SeNPs with different morphologies and sizes by biological approaches. The aqua soluble chemical components are mainly responsible for creation and stabilization of SeNPs. Thereafter, the fabricated SeNPs need to be characterized using numerous known techniques.

Table 2. Green synthesis of SeNPs using different plant source with morphology and size.

Entry	Name of Plants	Part	Shape	Size (nm)	References
1	*Allium Sativum*	-	Spherical	40-110	[57]
2	*Allium Sativum*	Buds	-	7-45	[58]
3	*Allium Sativum*	-	Spherical	24.57	[59]
4	*Allium Sativum*	Buds	Spherical	8-52	[60]
5	*Alov vera*	Leaves	Spherical	9-58	[61]
6	*Alov vera*	Leaves	Spherical	50	[62]
7	*Asteriscus graveolens*	Leave	Spherical	20	[63]
8	*Broccoli*	-	-	50-150	[64]
9	*Catharanthus roseus*	Flowers	Spherical	32.02	[65]
10	*Peltophorum pterocarpum*	Flowers	Spherical	40.2	[65]
11	*Citrus recticulata*	Peel	Spherical	70	[66]
12	*Clausena dentate*	Leaves	Spherical	46.32	[67]
13	*Diospyros Montana*	Leaves	Spherical	4- 16	[68]
14	*Embilica officinalis*	Fruits	Spherical	15-40	[69]
15	*Fenugreek*	Seeds	Oval	50 -150	[70]
16	*Ficus benghalensis*	Leaves	Spherical	20-140	[71]
17	*Garlic*	Pulp	Spherical	48-87	[72]
18	*Hawthorn*	Fruits	Spherical	113	[73]
19	*Leucas lavandulifolia*	Leaves	Spherical	56-75	[74]
20	*Moringa oleifera*	Leaves	Spherical	18.85	[75]
21	*Orthosiphon stamineus*	Leaves	Ball	88-141	[76]
22	*Pelargonium zonale*	Leaves	Spherical	40-60	[77]
23	*Petroselinum crispum*	Leaves	Spherical	50-100	[78]
24	*Psidium guajava*	Leaves	Spherical	8-20	[79]
25	*Spermacoce hispida*	Leaves	Spherical	46.8	[80]
26	*Spermacoce hispida*	Leaves	Rod	120±15	[81]
27	*Tea extract*	Leaves	Spherical	83-160	[82]
28	*Theobroma cacao*	Seeds	Spherical	1-3	[83]
29	*Vitis vinifera*	Fruits	Spherical	3-18	[84]
30	*Withania somnifera*	Leaves	Spherical	40-90	[85]
31	*Prunus amygdalus*	Nuts	Irregular	150-330	[86]
32	*Azadirechta indica*	Leaves	Spherical	153-278	[87]
33	*Zingiber officinale*	Fruits	Spherical	100-150	[88]
34	*Lemon*	Fruits	Rod	90-100	[89]
35	*Oscimum tenuiflorum*	Leaf	Spherical	15-20	[90]

3. Protocol for Green Synthesis of SeNPs

In plant extract mediated method of SeNPs production using different plant parts such as leafs, buds, nuts, flowers, fruits and seeds are washed with distilled water, chopped into small pieces and boiled in distilled water to obtained aqueous extract. The aqueous plant extract can further be purified by various methods such as centrifugation and filtration. Different ratio of the selenium salts, selenium oxides, selenium acids, amorphous selenium and plant extract at different temperature and pH can be used for synthesis of SeNPs. The plant extract is simply mixed with the different concentrations of selenium acids/oxides/salts solution at room temperature and their conversion into SeNPs take place within minutes in one pot, single step and eco-friendly method. There is no need to add external perilous stabilizing/capping agents, because phytochemicals itself acts as herbal reducing and/or stabilizing agents. The reaction mixture is further incubated to reduce the metal salt and visually monitored by color change. The detailed protocol of green synthesis of SeNPs by *Ficus benghalensis* leaves extract is described by authors reported in [71]. Finally, the NPs can be separated by centrifuging at high speed, wash thoroughly in solvent/water and collected for further use.

4. Characterization Techniques for SeNPs

Several well-known characterization techniques can be applied to SeNPs to elucidate their elemental composition, exact morphology, and other physicochemical properties. While a detailed discussion of such characterization techniques is beyond the scope of this review, a brief overview covering the most important and widely used well-known techniques is warranted.

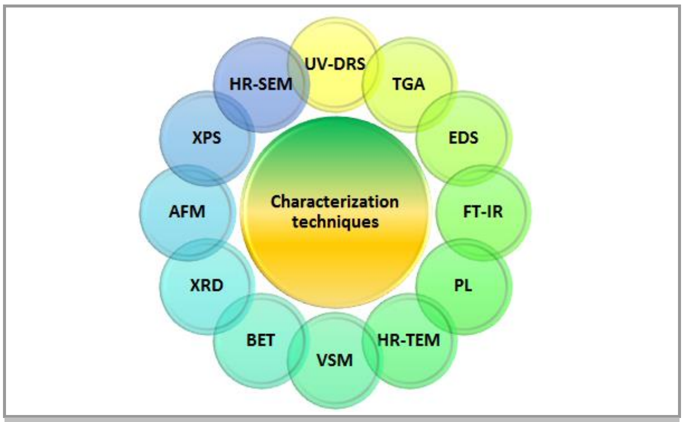

Figure 3. Characterization techniques for NPs.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are two major methods that can be used to determine the exact morphology and detailed structures of SeNPs. Swift progress in electron microscopy has resulted in the development of ancillary techniques such as high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDS), elemental mapping, and scanning tunneling microscopy (STM). These methods have been routinely applied to characterize SeNPs not only in terms of their texture but also with respect to their elemental composition, their attachment to support the materials. X-ray diffraction (XRD) is another invaluable technique that enables elucidation of the size, crystallinity and structure of a SeNPs. This method has been used extensively to determine lattice parameters for SeNPs. Although, XPS (X-ray photoelectron spectroscopy) technique has also been used to determine the oxidation states and elemental composition of surfaces of SeNPs. In addition to the aforementioned characterization techniques, gas adsorption/desorption technique are often used to collect information about the specific surface areas of SeNPs and to determine their pore sizes and volumes. Such information is particularly useful for characterizing porous SeNPs, and for correlating their structure with their aspect of catalytic activity.

5. Various Applications of Biogenically Synthesized Se NPs

SeNPs have lots of stupendous applications in several fields of biomedical and therapeutic. However, the anticancer, photocatalytic, antioxidant and antimicrobial activities of the biogenically synthesized SeNPs are very prominent nowadays. Accordingly, we have described in detail their curative and eclectic applications as guidance to new researchers for future prospects (Table 3).

Benelli *et al*. [57] stated that the SeNPs synthesized via green method using *Allium sativum* extract in aqueous medium exhibited appreciable cytotoxicity against vero cell line. Vyas *et al*. [58] reported the biosynthesis of SeNPs using the buds extract of *Allium sativum* and showed their pronounced antioxidant activity using DPPH, ABTS and FRAP assay. Thirunavukkarasu *et al*. [59] revealed the effective DNA targeted chemotherapy of green approach mediated SeNPs *Allium sativum* extract. Moreover, same author reported green synthesis of SeNPs using fenugreek seed extract and examine their cytotoxicity study against human breast cancer cell lines (MCF-7) [70]. Vyas *et al*. [60] reported the biogenic synthesis of SeNPs using *Allium sativum* buds extract and evaluate their antimicrobial activity against *Staphylococcus aureus* and *Bacillus subtilis* by using well diffusion method. Malmiri et al. reported the biosynthesis of SeNPs using *Aloe vera* leaf extract and also studied their antibacterial and antifungal activity. They showed that, SeNPs possess significant antibacterial activity against the gram positive and gram negative bacteria such as *Staphylococcus aureus*, *Escherchia coli* and antifungal activity against *Colletotrichum coccodes*, *Penicillium digitatum* [62]. Zebaree et al. synthesized SeNPs using *Asteriscus graveolens* leaves extract and investigate cytotoxicity against HepG2 cells at IC_{50} 3.8 µg/mL [63]. Balakrishnaraja *et al*. [66] described peel extract of citrus reticulata mediated biosynthesis of SeNPs using effect of pH and temperature. They showed SeNPs could be possessing anti-algal activity. Shivakumar et al. reported biosynthesis of SeNPs using leaves extract of *Clausena dentate* and examined the larvicidal activity of the prepared NPs. These SeNPs exhibited high mortality with very low concentration (LC_{50}) were 240.714 mg/L; 104.13 mg/L, and 99.602 mg/L for *Anopheles stephensi*, *Aedes aegypti*, and *Culex quinquefasciatus*, respectively [67]. Sujatha et al. described biosynthesis of SeNPs using leaves extract of *Diospyros Montana* and they also examined the antioxidant, antimicrobial and anticancer activity of as-prepared NPs. These biosynthesized SeNPs showed potential antioxidant property using DPPH assay and exhibited significant antimicrobial activity against *Staphylococcus aureus*, *Escherchia coli* and *Aspergillus niger*. In addition, the synthesized SeNPs were able to inhibit the cell growth of human breast cancer cell lines (MCF-7) in a dose-dependent manner [68]. Dass et al. reported the biogenic synthesis of SeNPs using fruit extract of *Embilica officinalis* and evaluate their antioxidant performance using DPPH, ABTS assay and antimicrobial activity against foodborne pathogens including *Escherichia coli*, *Listeria monocytogenes*, *Staphylococcus aureus*, *Enterococcus faecalis*, *Aspergillus brasiliensis*, *A. flavus*, *A. oryzae*, *A. ochraceus*, *Fusarium anthophilum* and *Rhizopus stolonifer* [69]. Mittal *et al*. synthesized SeNPs using *Ficus benghalensis* leaves extract and reported for the photocatalytic activity. They demonstrated that, the photocatalytic degradation of methylene blue up to 57.63 % in 40 min by using SeNPs as a photocatalyst [71]. Li *et al*. [73] prepared the SeNPs using Hawthorn fruit extract as the stabilizer/reductant and reported their antitumor activity against HepG2 cells. Kirupagaran *et al*. [74] stated that the SeNPs synthesized via green approach using *Leucas lavandulifolia* leaves extract exhibited appreciable antibacterial activity against *Streptococcus aureus*, *Staphylococcus epidremidies*, *Escherchia coli* and *Salmonella typhi*. Hassanien *et al*. reported a green approach for SeNPs biosynthesis using *Moringa Oleifera* leaves extract without using any noxious substances and investigated their photocatalytic and anticancer activity. They showed that the photodegradation of sunset yellow using solar radiation was slightly higher than UV irradiation with 83.8 and 76.6%, respectively in presence of SeNPs as a catalyst. In addition, the synthesized SeNPs showed potent anticancer activities against Caco-2 cells, HepG2 cells, and MCF-7 cells [75].

Moreover, Sivakumar *et al*. [76] demonstrated the *Orthosiphon stamineus* leaves extract mediated SeNPs and were tested for cytotoxic effect against L6 rat skeletal muscle cell lines. Malmiri et al. reported biosynthesis of SeNPs using leaf extract *Pelargonium zonale* and analyzed the antibacterial and antifungal activity of the as-prepared nanoparticles. These SeNPs exhibited good antibacterial activity against pathogenic bacteria such as *Escherichia coli*, *Staphylococcus aureus* and antifungal activities against *Colletotrichum coccodes* and *Penicillium digitatum* [77]. Sardar *et al*. [79] described the *Psidium guajava* leaf extract mediated SeNPs and reported their antibacterial and cytotoxicity study. They showed good antibacterial activity against *Escherichia coli*, *Staphylococcus aureus* and significant cytotoxic activity against HepG2 and CHO cell lines. Thayumanavan et al. reported a green approach for SeNPs biosynthesis using *Spermacoce hispada* leaf extract without using any noxious substances and evaluated against acetaminophen induced liver and kidney injury in rat [80]. Vennila et al. described biosynthesis of SeNPs using leaves extract of *Spermacoce hispada* and they also examined the antioxidant, antibacterial, anti-inflammatory and anticancer activity of as-prepared NPs. These biosynthesized SeNPs showed potential antioxidant property using DPPH, ABTS, FRAP assay and exhibited significant antibacterial activity against *Staphylococcus aureus* and *Escherchia coli*. In addition, the synthesized SeNPs were able to inhibit the cell growth of HeLa cancer cell lines and examine anti-inflammatory activity using protein denaturation inhibition protocol [81]. Zhang *et al*. reported the biosynthesis of SeNPs using *tea* extract and examined antioxidant activity of SeNPs. These SeNPs exhibited better antioxidant activity using DPPH and ABTS free radical scavenging assay [82]. Moreover, Garrigós *et al.* described bio-fabrication of SeNPs using *Theobroma cacao* seed extract and investigated their excellent antioxidant properties using ABTS and FRAP methods [83]. Venugopal *et al*. described green synthesis of SeNPs using leaves extract of *Withania somnifera* and they also examined the antioxidant, antibacterial, anti-proliferative and photocatalytic activity of as-prepared NPs. These synthesized SeNPs possessed significant antioxidant property using DPPH radical scavenging assay and showed considerable antibacterial activity against *Bacillus subtilis*, *Klebsiella pneumoniea* and *Staphylococcus aureus*. In addition, the synthesized SeNPs showed great growth control against A549 cells. Furthermore, SeNPs efficiently degraded methylene blue dye in the presence of sunlight [85].

Thereafter, Pawar *et al*. [86] reported the biosynthesis of SeNPs using *Prunus amygdalus* nuts extract and evaluate their antimicrobial activity against *Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli*, *Proteus vulgaris* and *Bacillus subtilis* by using well diffusion and Kirby-Bauer disc methods. Pawar *et al*. described *Azadirechta indica* leaves extract mediated SeNPs and reported their antibacterial and cytotoxicity study. They showed promising antibacterial activity against *Proteus vulgaris, Pseudomonas aeruginosa, Staphylococcus aureus, Bacillus cereus* and moderate cytotoxic activity against L929 cell lines by MTT assay [87]. Shanmugan *et al*. reported the biogenic synthesis of SeNPs using fruit extract of *Zingiber officinale* and checked their antioxidant performance using DPPH assay and antimicrobial activity against selected pathogens including *Escherichia coli, Klebsiella sp., Pseudomonas sp., Staphylococcus aureus and Proteus* sp. The antibacterial efficacy of SeNPs was found to be significantly effective against *Proteus* sp. [88]. Sawant *et al*. [89] synthesized rod shaped SeNPs using *Lemon* fruit extract and reported for the development of H_2O_2 sensor through naked eye cost effective spectrometric sensing method.

Table 3. Various applications of SeNPs synthesized using different plant extracts.

Entry	Name of Plants	Applications	References
1	*Allium Sativum*	Cytotoxicity study	[57]
2	*Allium Sativum*	Antioxidant activity	[58]
3	*Allium Sativum*	DNA targeted chemotherapy	[59]
4	*Allium Sativum*	Antimicrobial activity	[60]
5	*Alov vera*	Antibacterial and antifungal activity	[62]
6	*Asteriscus graveolens*	Cytotoxicity study	[63]
7	*Citrus recticulata*	Anti-algal activity	[66]
8	*Clausena dentate*	Larvicidal activity	[67]
9	*Diospyros Montana*	Antioxidant, antimicrobial and anticancer activity	[68]
10	*Embilica officinalis*	Antioxidant and antimicrobial activity	[69]
11	*Fenugreek*	Cytotoxicity study	[70]
12	*Ficus benghalensis*	Photocatalytic activity	[71]
13	*Hawthorn*	Antitumor activity	[73]
14	*Leucas lavandulifolia*	Antibacterial activity	[74]
15	*Moringa oleifera*	Photocatalytic and anticancer activity	[75]
16	*Orthosiphon stamineus*	Cytotoxicity study	[76]
17	*Pelargonium zonale*	Antibacterial and antifungal activity	[77]
18	*Psidium guajava*	Antibacterial and cytotoxicity study	[79]
19	*Spermacoce hispida*	Cytotoxicity study	[80]
20	*Spermacoce hispida*	Antioxidant, antibacterial, anti-inflammatory and anticancer activity	[81]
21	*Tea extract*	Antioxidant activity	[82]
22	*Theobroma cacao*	Antioxidant activity	[83]
23	*Withania somnifera*	antioxidant, antibacterial, anti-proliferative and photocatalytic activity	[85]
24	*Prunus amygdalus*	Antibacterial activity	[86]
25	*Azadirechta indica*	Antibacterial and cytotoxicity study	[87]
26	*Zingiber officinale*	Antimicrobial and antioxidant activity	[88]
27	*Lemon*	H_2O_2 sensing	[89]

4. Conclusion

This review offered an overview of multifarious plant and plant parts used in the procurable synthesis of SeNPs for various stupendous applications such as anticancer, antioxidant, antibacterial, solar cell and photodegradation of dyes. The biogenic fabrication of SeNPs using plant extract is a swift, clean, cheap, eco-benign, non-noxious, sustainable, and safe route that can be used for a variety of applications for the wellbeing of human beings. Role of solvents may also affect the efficiency in the extraction of phytochemical constituents and eventually affecting the final product of NPs. However, it can be concluded that, there is no universal extraction routes that is ideal and each extraction procedures is unique to the parts of plants. This review also discussed the future prospect of the biogenic synthesis of SeNPs and the various possible applications of the SeNPs.

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Disclosure statement

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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