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Green Synthesis of Metal nanoparticles: a Review

Shabir Ahmad Wani[*1], Bibi Ahmadi Khatoon[1], Farhath Khanum[2, 1]

[1] Department of Chemistry,Yuvaraja's College, University of Mysore, India
[2] Department of Nutrition, Biochemistry and Toxicology, Defence Food Research Laboratory Mysore, India

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*Corresponding Author:

Shabir Ahmad Wani
chemwanishabir@gmail.com

ABSTRACT

In this review paper we have collected data regarding the green synthesis of metal nanoparticles i.e silver, copper, zinc and their applicability in various fields. The various parameters which affect the formation of metal nanoparticles are the concentration of metal salts, the temperature of reaction and the duration of completion of the reaction. In this method the phytochemicals present in plant parts (leaf, fruit, stem, and flower) are responsible for the reduction of metal ions. Not only this, these plant extracts act as capping agents and stabilizing agents as well. The green method is cost-effective, simple and eco-friendly compared to other methods such as physical methods, chemical methods and biological methods which are very productive in terms of yield and less time-consuming. But their ultimate drawback is their waste material which is non-biodegradable and dangerous pollutants. Besides the waste material, the material and instruments used are of expensive nature.

Keywords: Metal nanoparticles, Phytochemicals, Hypogonadism

Introduction

Currently, tons of metallic nanoparticles (MNPs) are being produced and utilized in nano-enabled devises, personal care, medicinal, food and agricultural products. It is generally accepted that the reaction compounds and the techniques used in industrial production of MNPs are not environmental friendly. Nanoparticles (NPs) synthesized by green method are preferred over nanomaterials produced from physico–chemical methods [1]. NPs are generally synthesized following the physico–chemical methods [2, 4]. However, these methods are capital intensive and have many problems including use of toxic solvents, generation of hazardous byproducts and the imperfection of the surface structure. Chemical methods of synthesis of metal nanoparticles involve more than one chemical components or molecules that could increase the particle reactivity and toxicity and might harm human health and the environment due to the composition ambiguity and lack of predictability [5]. Copper nanoparticles have been shown to cause dose –dependent toxicity in drosophila via inducing reactive oxygen species [6] and in kidney cells [7]. The particles produced by green synthesis differ from those using physico–chemical approaches as green synthesis is a bottom up approach, similar to chemical reduction where an expensive chemical reducing agent is replaced by extract of a natural product such as leaves of trees/crops or fruits for the synthesis of metal or metal oxide NPs. This type of biogenic reduction of metal precursors to corresponding NPs is eco-friendly sustainable, free of chemical contamination [8, 9], less expensive [10] and can be employed for mass production [11]. One more advantage of biological synthesis of (NPs) is the recycling ofexpensive metal salts like gold and silver contained in waste streams. The biological molecules, mostly proteins, enzymes, sugars and even whole cells that stabilize NPs allow NPs to interact with other biomolecules and thus increase the antimicrobial activity by improving the interactions with microorganisms [12]. The metal nanoparticles synthesized using biological methods can be easily separated from the reaction media and also can beupconcentrated by centrifugation [13]. Biogenic silver NPs when compared to chemically produced NPs showed 20 times higher antimicrobial activity [14]. The choice of plant extracts to produce NPs is based on the added value of the biological material itself, for example algal cells of spirulinaplatensis have been chosen because, in addition to working as reducing agent it also exhibits pharmaceutical and nutraceutical properties [15]. Unicellular bacteria and extracts of multi-cellular eukaryotes in the reaction processes reduce metal precursors into NPs of desire shapes and sizes [16]. Apart from this, biological entities work as capping and stabilizing agents required as growth terminator and for inhibiting aggregation/agglomeration of nanoparticles. Moreover, Size and shape of NPs strongly depend on nature of biological entities, their concentrations, and growth medium conditions such as pH, temperature, salt concentration and exposure time [17, 18]. Enzymes, proteins, sugars, and phytochemicals such as flavonoids, phenolics, terpenoids, cofactors etc., mainly act as reducing and stabilizing agents [19]. The in-vivo productions of NPs have been reported using bacteria, yeast, fungi, algae and plants [20, 23]. Biological extracts are used mostly for in vitro synthesis, which involves extraction of bio-reducing agents and mixing them into an aqueous solution of the relevant metal precursor in a controlled manner. The reactions need heating and stirring [24]. However, sometimes reactionsmay occur spontaneously [25] as well. Among the biological agents mentioned above, plants or their extracts seem to be the best agents because they are easily available, suitable for mass production of NPs and their waste products are eco-friendly [26], unlike some microbial extracts. This review summarizes green synthesis of three metal nanoparticles; copper, silver, and zinc.

1. Copper nanoparticles

Copper is one of the valuable elements belonging to the transition metals of the periodic table. The element has been used to make the utensils, wires and ornaments but with the advancement in science and technology its applicability has been increased to a great extent. Copper shows variable oxidation states due to which it form a large number of chemical compounds which are very essential for the survival. It is one of the metal ions present in animals, plants and humans to carry out many functions. Copper is present in all human tissues and is required for cellular respiration, peptide amidation, neurotransmitter biosynthesis, pigment formation, and connective tissue strength. Copper is a cofactor for numerous enzymes and plays an important role in the development of central nervous system, low concentrations of copper may result in incomplete development, whereas excess copper maybe harmful. Copper may be involved in free radical production, via the Haber-Weiss reaction, that results in mitochondrial damage, DNA breakage and neuronal injury. Evidence of abnormal copper transport and aberrant copper-protein interactions in numerous human neurological disorders supports the critical importance of this trace metal for proper development of nervous system and neurological function [27]. Copper nanoparticles (CuNps) have been used widely in various fields, including agricultural, industrial engineering and technological fields. Effective antibacterial activities exhibited by CuNps in agricultural research have increased development in the field of nanotechnology, leading to the establishment of intensively clean, cost-effective and efficient biosynthesis techniques of CuNps [28].

CuNP synthesis has attracted particular interest, compared to other NPs, as their useful properties are achievable at costs lower than silver and gold. Research in CuNPs has made significant progress in the areas of nanomedicine within the last decade due to their excellent catalytic, optical, electrical and antifungal/antibacterial applications [29, 30]. CuNPs have been prepared using thermal reduction and a polyol method [31]. In recent years, plant-mediated biological synthesis of nanoparticles has gained interest due to its simplicity and eco-friendly properties.

Copper plays an important role in metabolism in the humans, mainly because it allows many critical enzymes to function properly. Copper is essential for maintaining the strength of the skin, bloodvessels, epithelial and connective tissue throughout the body. Cuplays a role in the production of hemoglobin, myelin, melanin and it also keeps thyroid gland functioning normally [32]. Copper can act as both an anti-oxidant and a pro-oxidant. Free radicals occur naturally in the body and can damage cell walls, interact with genetic material, and contribute to the development of a number of health problems and diseases. As an anti-oxidant cu scavenges or neutralizes free radicals and may reduce or help prevent some of the damage they cause [33, 35]. When copper acts as a pro-oxidant at times, it promotes free radical damage and may contribute to the development of Alzheimer's disease [36, 37]. Maintaining the proper dietary balance of Cu, along with other minerals such as zinc and manganese, is important [38]. Although copper is an important mineral in the normal functioning of the body, there are many diseases related to impairment of metabolism [39]. Some of the disorders related to impaired copper metabolism are Wilson's disease leading to liver failure and neurological impairments. Liver cancer is caused due to excess copper accumulation in liver. High level of copper are also associated with hypogonadism (low testosterone level). Copper is closely related to thyroid function. Copper deficiency is associated with neurological defects and development of anaemia.

A number of plants such as Euphorbia esula.L, Magnolia kobus, Nerium oleander have been used for the biosynthesis of copper nanoparticles. The bioactivities of Eclipta prostrata, which is a widely used in traditional medicine and functional food, have been extensively explored. Previous Phytochemical analysis of *E.prostrata* revealed the presence of thiophene-derivatives, steroids, triterpenes [40] flavonoids, polyacetylenes, polypeptides [41] and used various for the treatment of diverse symptoms, including hyperlipidemia, atherosclerosis and skin diseases.

Table 1: List some plants used for the biosynthesis of copper nanoparticles

Type of Cu used	Plant material used	Reaction conditions i.e. temperature and time duration	Applications	chemical composition of plant extract	References
$CuSo_4.5H_2o$ 0.001M	Magnolia kobus (Leaf extract)	25˚c -95˚c 24 hours	Anti-bacterial activity	Flavonoids, phenols, citric acid, ascorbic acid, polyphenolic, terpenes, alkaloids andreduct ase	[42]
(CH_3cooCu) 0.001M	Ecliptaprostrata (Leaf extract)	25˚c 24 hours	Anti-bacterial,anti-oxidant activity & cytotoxic activity	Coumestans, alkaloids, flavonoids, glycosides, polyacetylenes, triterpenoids. The leaves contain stigmasterol, a-terthienylmethanol, wedelolactone, demethylwedelolactone and demethylwedelolactone-7-glucoside	[43]

$CuSo_4$ 0.001M	Nerium oleander (Leaf extract)	25˚c 28 hours	Anti-bacterial	glycosides gentiobiosyloleandrin, gentiobiosyl-nerigoside and gentiobiosyl-beaumontoside	[44]
$CuSo_4$ 0.001M	Euphorbia esula L. (Leaf extract)	25˚c 24 hours	Catalytic activity	kaempferol, scopoletin, kaempferol 3-O-glucopyranoside, quercetin, vanillic acid, E-p-hydroxycinnamic acid, protocatechuic acid, 6, 7-dihydroxycoumarin, beta-sitosterol, and daucosterol	[45]
$CuSo_4$ 0.001M	Ficusreligiosa (Leaf extract)	25˚c 24 hours	Anti-cancer activity	Beta-sitosteryl, n-octacosanol, methyl oleanolate, lanosterol, sigmasterol, lupeol.	[46]
$CuCl_2$ 0.1M	Pomegranatum(Seed extract)	25˚c 4-6 hours	Photocatalytic activity	delphinidin-3-glucoside, cyanidin-3-glucoside, delphinidin-3,5-diglucoside, cyanidin-3,5-diglucoside, pelargonidin-3,5-diglucoside, and pelargonidin-3-glucoside with delphinidin-3,5-diglucoside	[47]
$CuCl_2$ 0.2M	Rumexcrispus(seed extract)	60˚c 20 minutes	Catalytical activity	quinines, anthraquinones, naphthalene, flavonoids, chromones, steroids, terpenoids	[48]
2.32g $Cu(No_3)_2$	GlorissaSuperbaL.(LEAF Extract)	400 ˚c 3-4 minutes	Anti-bacterial activity	alkaloid, flavonoids, glycosides, phenols, saponins, steroids, tannin and terpenoids.	[49]
$CuSo_4$.01M	Conocarpus erectus &Neriumindicum (leaf extract)	25˚c 15 minutes		flavonoids, tannins and saponins.	[50]
$CuSo_4$.01M	Henna leaves	25˚c 24 hours	Conductive nano bio composites	1,4-naphthoquinone, tannins, gallic acid, flavonoids, lipids, sugars, tri-acontyl tri-decanoate, mannitol, xanthones, coumarins, resins, tannic ingredients and lawsone.	[51]
$CuCl_2$ 0.001M	Gum karaya	75˚c 1 hour	Catalytic ,optical, electrical and anti-bacterial activity	8% acetyl groups and about 37% uronic acid residues. (+)–galactose, (–)–rhamnose, (+)–galacturonic acid and a trisaccharide acidic substance.1, 4-linked α–(+)–galacturonic acid along with 1, 2-linked (–)–rhamnopyranose units with a short (+)–glucopyranosyluronic acid.	[52]
$Cu(N0_3)_2$ 0.1M	*Pterospermumacerifolium* (leaf extract)	400 ˚c 5 minutes		methylprotocatechuate, vanillic acid and Protocatechuic acid (1, 3, 4). In addition to β-sitosterol-3-O-β–D-glucoside (2)	[53]

$CuCl_2$0.02M	CalotropisProcera extract	25˚c 24 hours	Anti-bacterial activity &photocatalytic activity	cardenolides, steroids, tannins, glycosides, phenols, terpenoids, sugars, flavonoids, alkaloids and saponins	[54]
$CuSo_4$ 0.01M	Cassia auriculata(leaf extract)	80˚c 1 hour	rheumatoid arthritis activity	3-O-Methyl-d-glucose (48.50%), α- Tocopherol-β-D-mannoside (14.22%), Resorcinol (11.80%), n-Hexadecanoic acid (3.21%) and 13-Octadecenal,(Z)-(2.18%).	[55]
$CuSo_4$ 0.01M	Desmodiumgangeti cum(root extract)	80˚c 1 hour	Biological activity	cis-Vaccenic acid (16.47%),γ sitosterol (13.73%) and stigmasterol (6.24%).18 ,9,12 Octadecadienoic acid (41.71%), nHexadecanoic acid (9.43%) and Octadecanoic acid (5.9%).	[56]
$CuCl_2$ 0.005M	Plantagoasiatica (Leaf extract)	80˚c 5 minutes	Cyanation of aldehydes	e phytol 13.22%, benzofuranone 10.48%, penthynediol 10.26% and benzene propanoic acid 10.18%; methanol extract were group of diglycerol 30.31% and glycol 18.91%; ethyl acetate extract were glycerine 30.70%, benzene 21.81% and dibuthyl phthalate 16.22%; n-butanol were phtalic acid 24.62%, benzene propanoic acid 16.83% and group of phenol 10.20%; and aqueous extract were phenol 27.47%, diathiapentene14.53%, napthalenone 14.13% and glycerine 12.02%.	[57]
$CuSo_4$ 0.001M	Ocimum sanctum (Leaf extract)	25˚c 24 hours		Eugenol (21.96%), β-caryophyllene (20.79%) and Bicyclogermacrene (20.38%).	[58]
$CuSo_4$ .01M	Aloe vera	80˚c 3 hour		cinnamic acids and other derivatives (e.g., caffeic and chlorogenic acids), chromones (e.g., aloesin and isoaloeresin D), anthracene compounds and derivatives (e.g., aloin A/B and emodin), and several C-flavonoids (e.g., orientin and isovitexin)	[59]
$CuSo_4$ 0.1M	Syzygium cumin (Leaf extract)	25˚c 24 hours	Anti-microbial activity	malieicacid, oxalic acid, gallic acid, tannins, cynidin glycoside, oleanolic acid, flavonoids, essential oils, betulinic acid, friedelin	[60]
CH_3COOCu 1%	Vitisvinifera (Leaf extract)	25˚c 12 hours	Anti-microbial activity	(3-hydroxybenzoic acid, caffeic acid, gallic acid, vanillin acid), flavonoids ((+)-catechin, (-)-	[61]

				epicatechin, apigenin, myricetin, quercetin, quercetin-4'-glucoside, rutin), and stilbenes	
$CuSo_4$ 0.001M	Cassia auriculata (Leaf extract)	750 wats 5minutes	Anti-microbial activity		**[62]**

2. Silver nanoparticles

Silver is one of most important element present in the earth's crust. The metallic nature and excellent physico-chemical properties of silver make it applicable in different field's i.e. in solar panels, water filtration, jewelry, ornaments, high-value tableware and utensils (hence the term silverware), in electrical contacts and conductors, in specialized mirrors, window coatings, in catalysis of chemical reactions, as a colorant in stained glass and in specialized confectionery. Its compounds are used in photographic and X-ray film. Dilute solutions of silver nitrate and other silver compounds are used as disinfectants and microbicides (oligodynamic effect), added to bandages and wound-dressings, catheters, and other medical instruments.

Although silver in its bulk form shows excellent applications yet the development of nanotechnology has revolutionized it in the form of silver nanoparticles. Silver nanoparticles show unusual properties when compared to their bulk properties. Agnps have been prepared by various physical, chemical, biological and green methods (using plant extracts). Most important physical methods used to synthesize silver nanoparticles are evaporation-condensation [63, 65]; chemical method used is chemical reduction [66, 68]. Green method is preferred over these methods wherein plants parts are used to synthesize nanoparticles [69, 71]. Green method is most important among all because it is eco-friendly, minimum chemical usage and the waste obtained is biodegradable.

Table 2: List of some plants used in the preparation of silver nanoparticles

Type of Ag used	Plant material used	Reaction conditions i.e. temperature and time duration	Applications	Chemical composition of plant extracts	References
$AgNo_3$ 0.001M	Catharanthusroseuslinn.g.don (Leaf extract)	25˚c 6 hours	Antiplasmodial activity	ajmalcine, vinceine, resperine, vincristine, vinblastine and raubasin. Vincristine and vinblastine	[72]
$AgNo_3$ 0.001M	Beniumpersecium (Seed extract)	70˚c 1 hours	catalytic reduction of organic dyes**.**		[73]
$AgNo_3$ 0.001M	Tulsi (Leaf extract)	30˚c 1 hours	Catalytic activity	eugenol (61.76%), isopropyl palpitate (11.36 %), α-cubene (3.85%), 2, 3-dihydroxy propyl elaidate (5.10%), 1-methyl-3-(1-methyl) benzene (1.73 %), 2-methoxy-4-(1-propyl) phenol (2.65%), vanillin (1.27%), 1, 4-diethyl benzene (1.03%), hexadecanoic acid methyl ester (2.51%), [2-methyl-4-(1-propyl) phenoxy] silane (2.01%).	[74]
$AgNo_3$ 0.001M	Azadirachtaindica (Leaf extract)	25˚c 24 hours	Anti-bacterial activity	β-Elemene (33.39%), γ-Elemene (9.89%), Germacrene D (9.72%), Caryophyllene (6.8%),Bicyclogermacrene (5.23%),pentacosane (18.58%), tetracosane (10.65%), β-germacrene (9.73%), β-caryophyllene (5.84%),dodecene (4.54%)	[75]
$AgNo_3$ 0.001M	Allamandacathertica (Leaf extract)	25˚c 24 hours	Anti-microbial activity	Sitosterol, actinidiolide, tetramethylhexadecenol, campesterol,stigmasterol, α-Tocopherol, pyrrolidinebutanoic acid,Jasminol, lupeol, 19-octacosenoic pyrrolidine, methyl octadecadienoate, methyl isostearate, and octyltetrahydropyranone ,2,3-Bis-(1-methylallyl)-pyrrolidine, ethyl hexadecenoate, methyl linolenoate and stigmast-5-en-3-ol, oleate	[76]
$AgNo_3$ 0.001M	Ricinuscommunis (Castor oil)	25˚c 24 hours	Antibacterial activity	ricinoleic acid, 86.96% palmitic (0.56%), oleic (5.1%),Octanoic acid 0.29%,pentanoic acid 1.33%	[77]

$AgNo_3$ 0.003M	Berberis vulgaris (Leaf and Root extract)	25˚c 1 hours	Antibacterial activity	tetracosanoic acid, methyl ester (26.36%), followed by phthalic acid, diisooctyl ester (20.93%), 1,2-bis(trimethylsiloxy) ethane (10.26%), and 1,2-benzendicarboxylic acid, diisononyl ester (8.70%),N-methyl-4-(hydroxybenzyl)-1,2,3,4-tetrahydroisoquinoloine (28.82%), 9-α-hydroxy-17β-(trimethylsilyl-oxy)-4-anderostene-3-methyloxime (13.97%), ribitol, pentaacetate (9.76%), 1-methyl-4-[4,5-dihydroxyphenyl]-hexahydropyridine (6.83%), and 2-ethylacridine (4.77%).	**[78]**
$AgNo_3$ 0.01M	Menthapulegium (Leaf extract)	25˚c 1 hours	Antibacterial, antifungal and anticancer activity	pulegone (43.5 %), piperitone (12.2 %), p-menthane-1,2,3-triol (6.5 %), γ-elemenene (3.6 %), guaiene (cis-β) (3.0 %), carvacrol acetate (2.6 %) and phenyl ethyl alcohol (2.4 %)	**[79]**
$AgNo_3$ 0.001M	Piper nigrum Concoction (Fruit extract)	80˚c 10 minutes	Anticancer activity	palmitic,hexadecenoic, stearic, linoleic, oleic, higher saturated acids, arachidic, and behenic acids	**[80]**
$AgNo_3$ 0.001M	Cleome viscosa L. (Fruit extract)	25˚c 24 hours	Antibacterial and anticancer activity	palmitic acid (10.2–13.4%), stearic acid (7.2–10.2%), oleic acid (16.9–27.1%) and linoleic acid (47.0–61.1%), free gallic acid, gallotannins, iridoid, saponins and terpinoidpolyphenolic compounds	**[81]**
$AgNo_3$ 0.001M	Lippianodiflora (Aerial extract)	95˚c 10 minutes	Antioxidant, antibacterial and cytotoxic activity	2, 7-dioxatricyclo [4.3.1.0 (3, 8)] decan-4-one (35.75%), stigmasterol (16.86%), benzoic acid, 4-etoxy-, ethyl ester (13.73%), azacyclotridecan-2-one (11.86%) and n-hexadecanoic acid (10.12%)	**[82]**
$AgNo_3$ 0.001M	Tecomellaundulata (Leaf extract)	60˚c 2 hours		cirsimaritin and cirsili,rutin, quercetin, luteolin-7-glycoside and β-sitosterol	**[83]**
$AgNo_3$ 0.003M	aloe vera (plant extract)	200˚c 6 hours	Antibacterial activity	caffeic and chlorogenic acids,aloesin and isoaloeresin D,aloin A/B and emodin,orientin and	**[84]**

				isovitexin	
$AgNo_3$ 0.003M	ayapanatriplinervis	60˚c 3 hours	Antibacterial activity	hexadecanoic acid (14.65%), 2,6,10-trimethyl,14-ethylene-14-pentadecne (9.84%), Bicyclo[4.1.0] heptane, 7-butyl- (2.38%), Decanoic acid, 8-methyl-, methyl ester (3.86%), 1-undecanol (7.82%), 1-hexyl-1-nitrocyclohexane (2.09%), 1,14-tetradecanediol (6.78%), Octadecanoic acid, 2-hydroxy- 1,3-propanediyl ester.	**[85]**
$AgNo_3$ 0.01M	Phlomis (leaf extract)	25˚c 24 hours	Antibacterial activity	α-pinene (12.40%), γ-cadinene (10.92%), and γ-elemene (6.46%). Hexadecane (8.97%), 2-dodecnenal (6.57%), and heptadecane (6.32%)	**[86]**

3. Zinc nanoparticles

Zinc the last element of 3d transition series is post transition metal. It shows only one normal oxidation state of +2 similar to that of manganese. Zinc is an essential mineral, including to prenatal and postnatal development [87]. Zinc deficiency causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea. Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans [88]. Consumption of excess zinc can cause ataxia, lethargy, and copper deficiency. Applications of zinc are in electrical batteries, small non-structural castings, and alloys such as brass. A variety of zinc compounds are commonly used, such as zinc carbonate and zinc gluconate (asdietary supplement),zinc chloride (in deodorants), zinc pyrithione (anti-dandruff shampoos), zinc sulfide (in luminescent paints), and zinc methyl or zinc diethyl in the organic laboratory.

Research and development are mainly oriented to control the shape, size, structure and compositions of nanomaterials. Each of these factors is a key factor in determining the properties of nanomaterials that lead to different technological applications. Nano zinc oxide is a multifunctional material with its unique physical and chemical properties such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo-stability [89]. ZnO nanoparticles are synthesized by different methods. It is confirmed that the various applications of ZnO nanoparticles depend upon the control of both physical and chemical properties such as size, shape, crystal structure, size-distribution, dispersion, surface-state, and expendability. It has led to the development of imposing variety of techniques for synthesizing the nanomaterials. Some researchers used a controlled precipitation method. The process of precipitating zinc oxide was carried out using zinc acetate: Zn (CH3COO) 2·H2O and ammonium carbonate: $(NH4)_2CO_3$ [90, 91]. A simple precipitation process for the synthesis of zinc oxide was carried out. The single step process for the large scale production without unwanted impurities is desirable for the cost-effective preparation of ZnO nanoparticles [92, 93]. Among all the methods of preparation zinc nanoparticles green method is widely used method these days.

Table 3: list of some plants used in the preparation of Zinc nanoparticles

Type of Zn used	Plant material used	Reaction conditions i.e. temperature and time duration	Applications	chemical composition (plant extract)	References
CH_3COOZn 0.01M	Nyctanthesarbor-tristis (Flower extract)	25˚c 2 hours	Anti-fungal activity	yclohexylethanoid, rengyolone (1 1 1 1 1); a new iridoidglucoside, 6-O-trans-cinnamoyl-7-O-acetyl-6b-hydroxyloganin (2 2 2 2 2); and three known iridoidglucosides, arborside C (4 (4 (4 (4 (4), 6b-hydroxyloganin (6 6 6 6 6) and nyctanthoside (7 7 7 7 7)	[94]
CH_3COOZn 0.2M	Camellia sinensis (Leaf extract)	60˚c 24 hours	Anti-microbial activity	epigallocatechingallate (EGCG) ranged from 117 to 442 mg/l, epicatechin 3-gallate (EGC) from 203 to 471 mg/l, epigallocatechin (ECG) from 16.9 to 150 mg/l, epicatechin (EC) from 25 to 81 mg/l and catechin (C) from 9.03 to 115 mg/l.	[95]
CH_3COOZn 0.091M	Hibiscus subdariffa (Leaf extract)	50˚c 30 minutes	Anti-diabetic,anti-bacterial activity	Tannins (17.0%), saponnins (0.96%), phenols (1.1%), glycosides (0.13%), alkaloids (2.14%) and flavonoids 20.08%).	[96]
$ZnNO_3$ 5gm	Punicagranatum (Peels extract)	60˚c 2 hours	Anti-microbial activity	12 hydroxycinnamic acids, 14 hydrolysable tannins, 9 hydroxybenzoic acids, 5 hydroxybutanedioicacids, 11 hydroxy-cyclohexanecarboxylic acids and 8 hydroxyphenyls ,illogic acid, gallic acids, punicalin, and punicalagin	[97]
$ZnNO_3$ 0.01M	Lycopersicumesculentum extract	80˚c 5 minutes	Photo-voltaic activity	Ascorbic acid,Beta carotene, gallic acid, chlorogenic acid, ferulic acid, cafeic acid, rutin, and quercetin,lycopene.	[98]

$(Zn(NO_3)_2.6H_2O)$ 0.1M	Costuspictus d. don (Leaf extract)	80˚c 4 hours	Antimicrobial And anticancer activities	carbohydrates, triterpenoids, proteins, alkaloids, tannins, saponins, flavonoids, sterols	**[99]**
$Zn(NO_3)_2{\cdot}6H_2O$ 0.01M	Albizialebbeck (Stem bark)	45˚c 24 hours	Antimicrobial, antioxidant, and cytotoxic activities	lupenone (1), freidelin (2), lupeol (3), sapiol (4), mixture of β-sitosterol&stigmasterol (5), β sitosterol- 3-O-glucoside &stigmasterol -3-O-glucoside mixture (6), stigmasterol -3-O-glucoside (7), luteolin (8) and rutin (9)	**[100]**
Ch_3ooZn 1M	Ulvalactuca (seaweed extract)	70˚c 3-4 hours	photocatalytic, antibiofilm and insecticidal activity	fibres (54.0%), minerals (19.6%), proteins (8.5%) and lipids (7.9%),hemicellulose (20.6%), cellulose (9.0%) and lignin (1.7%),oleic acid (16.0%)	**[101]**
CH_3COOZn .2M	Pentatropiscapen sis	60˚c 3 hours	Anti-proliferative activity		**[102]**
$Zn(CH_3COO)_2{\cdot}2H_2O$ (2.1g)	Moringaoleifera (Leaf extract)	24˚c 1 hours	Photocatalytic and antibacterial activity	9-octadecenoic acid (20.89%), L-(+)-ascorbic acid- 2,6-dihexadecanoate(19.66%), 14–methyl-8-hexadecenal (8.11%), 4- hydroxyl-4-methyl-2-pentanone (7.01%), 3-ethyl-2, 4-dimethylpentane (6.14%), phytol (4.24%), octadecamethyl-cyclononasiloxane (1.23%), 1, 2-benzene dicarboxylic acid (2.46%), 3, 4-epoxyethanone comprising (1.78%), N-(-1-methylethyllidene)-benzene ethanamine (1.54%), 4, 8, 12, 16-tetramethylheptadecan-4-olide (2.77%), 3-5-bis (1, 1-dimethylethyl)-phenol (2.55%), 1-hexadecanol (1.23%), 3, 7, 11, 15-tetramethyl-2 hexadecene-1-ol (1.17%), hexadecanoic acid (2.03%) and 1, 2, 3-propanetriyl ester-9 octadecenoic acid(1.23%)	**[103]**
CH_3COOZn 0.2M	Calotropis (Leaf Extract)	60˚c 24 hours	Seedling growth activity	methyl β-carboline-1-carboxylate , (+)-dehydrovomifoliol, pleurone , calotropagenin and calotoxin	**[104]**

Zn(NO3)2. 5H2O (0.005M)	Momordicacharantia (Leaf extract)	25˚c 24 hours	Acaricidal, pediculicidal and larvicidal activity	Momordicin I, Momordicin IV , Aglycone of Momordicoside, Aglycone of Momordicoside L and Karavilagenin D	[105]

Conclusion

This review summarizes green synthesis of three metal nanoparticles; copper, silver, and zinc. We discussed different approaches that have been defined in the last few years. Researchers have focused their attention on understanding the nanoparticle biosynthesis as well as detection and characterization of biomolecules involved in the synthesis of metallic nanoparticles. On the basis of the depth literature study one can say that the green method is cost-effective, simple and eco-friendly compared to other methods.

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