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REVIEW

Brewing Nanochemistry with Green Tea: A Review with Sustainable Approaches

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The growth of the "green chemistry" has brought to the society a new prospects and broader picture of what mankind can achieve through sustainable manipulation at the chemical scale. Why nature is so important to human being and we must protect our environment. Nature preservation could be achieved by opting the fundamental concepts underlying the principles of green and sustainable chemistry. The use as well as generation of unwanted or harmful byproducts must be avoided by adopting simple, safer and authentic synthesis methodologies. To attain this goal, utilization of natural ecofriendly systems is highly crucial and desired. Among the available physical, chemical and other biogenic green procedures of fabrication for various metal-based nanoparticles, green tea extract application is relatively simple, quick in approach and safer way to generate these nanoparticles. In present review, the different reported metal nanoparticles synthetic methods using green tea is collectively emphasized. The literature precedents using mentioned reports has already been proved themselves cost effective, efficient and eco-friendly alternative for generating metal nanoparticles. Present work also provides the reported applications of generated nanoparticles, which are prepared by this benign procedure.

Keywords: Green tea, Nanoparticles, Biogenic synthesis, Green chemistry.

INTRODUCTION

In the current situation of pandemic (Covid-19), the importance of nature is now realized from cradle to grave. While spending time with the nature, we realized its benefits as well as trying to establish a link between such nature encounters and our mental, physical and economic well-being. Our appreciation of nature at this time of crisis is not without irony, we have to protect it for our future generations. For nature preservation, green chemistry is not only the choice but it's now become the necessity [1]. Green chemistry acts as the supporting mode of science for a future, where the field of chemistry and its chemicals makes our society and its surroundings healthful, renewable and degradable in contrast to toxic, nonrenewable and persistent chemicals [2-5]. The branch of sustainable chemistry are giving/provide us many options/ opportunity to replace the conventional chemical reactions with the ingredients of nature's recipe book. This concept is not only benign for environment but will also provide pleasingly yield/benefits to the industries [6].

The use of plant or the plant products is not at all, new in nanochemistry [7]. The utilization of plants or plants extracts in nanotechnology have gained a bulk of attention as a unpretentious, competent, economic and viable protocol and proved itself preferred choice for nanoparticle synthesis [8]. In contrast to the conventional methods, which entail energy inflation, utilization of noxious chemicals and as well as, high T/P (temperature, pressure) dependency often increases the cost, moreover ecologically expensive [9]. Henceforth, researchers are showing keen interest to utilize all plant fragments including leaves, fruits, roots, seeds and stems, bearing various biochemicals such as antioxidants or sugars in synthesizing nanoparticles [10,11]. The popularity of metal based nanoparticles is being very popular in many areas of the economic sectors. As it's known that metal at nanoscale dimensions shows different and unique properties as compared to their bulk material, as new surface has now exposed. The efficient metal nanoparticles are useful for electronics, photonics and even for medicinal purpose [12]. Therefore, there is also keen interest among the scientists for their synthesis using environmental safety measures. Basically, this approach follows main philosophy of "green synthesis" enlightened by numerous factors like minimization/control of waste [13], prevention of pollutant derivatives and practice of non-toxic auxiliaries [14] as well as reusable feedstock and remediation process, which further primarily help to boost the eco-friendliness [15-18].

'Green syntheses' of metallic nanoparticles have been implemented by choosing innumerable biological resources (such as fungi, bacteria, yeast, algae) and plant extracts (*e.g.*, tulsi leaves, bark of cinchona, black tea, oolong tea leaves *etc.*). Among numerous literature precedents, the synthesis of metal based nanoparticles using "Green Tea" is simple and straight procedure, which afford/yield nanoparticles from lab scale to industrial scale in comparison to aforementioned method of synthesis.

Following the green synthetic approaches undoubtedly is essential for our future existence on this planet. Specifying precisely in this review, we discuss the recent literature mentioned for the various metal nanoparticles synthesis using green tea. This review comprehensively summarized the comparison between different approaches such as conventional chemical synthesis, biogenies and the green tea route of synthesis. Apart of this, various reaction conditions for the preparation of these nanoparticles are also conversed. Different applications of prepared nanoparticles were also mentioned. The overview of this research theme will facilitate and stimulate researchers to fulfil their purposes from a single platform.

Why green tea?

Different approaches and "The green tea method": The conventional approaches of nanosynthesis are majorly including chemical and physical methods. These approaches are based on high energy consumption (high T/P conditions), utilization of non-greener compounds/solvents, generation of harmful byproducts is also a major concern, not only this, high economics with low yield also cannot be avoid. Apart the conventional methods for stable synthesis of the metal nanoparticles faces hurdles for nanoparticles aggregation and harsh reaction conditions [19-21]. The final product demands further purification steps as the leftover chemicals, byproducts or the reducing agents get adsorbed over the nanoparticles surface, further, adverse effects if these nanoparticles find application in treatment or medical applications. Prevention of agglomeration nanoparticles requires expensive chemical stabilizers. The other method, known as biogenic method involves bacteria, fungi, yeast and actinomycetes for the nanosynthesis [20-24]. Though this method is environmentally sound but it involves many factors to control including temperature, pH of the solution, strain of different microorganism, decontamination with other strain, media development, size control and above all special treatment to follow the procedure [8]. Hence, the finding cost-effective, safer, easily available and easy method for nanoparticle production is urgently needed [25]. The use of green tea as plant and plant product has emerged as new synthetic methods to synthesize these stable nanoparticles without toxicity concerns [17,19,26-33] and involve numerous benefits (Fig. 1).

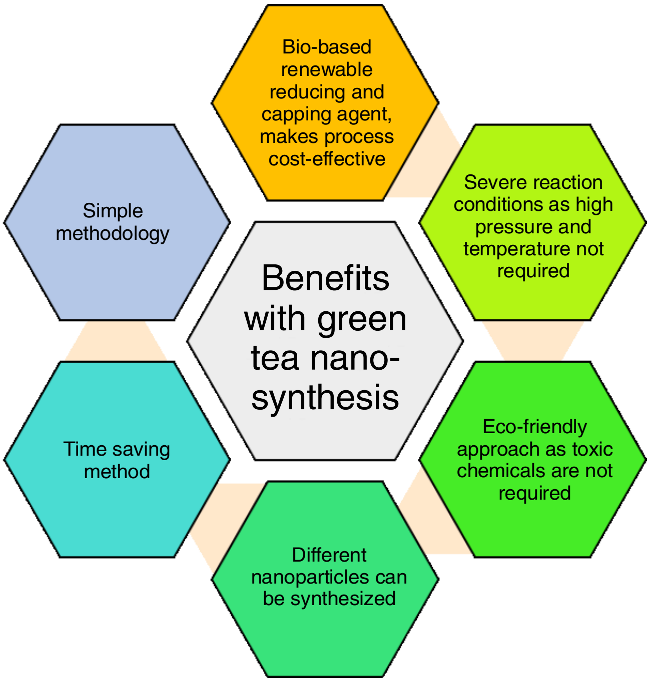

Fig. 1. Benefits with green tea nano-synthesis

Synthetic procedure and green tea extract

- The green tea extract performs as capping and reducing agent, that too in a single-step or one-pot synthesis. Therefore, abolishing multiple steps makes this process sustainable and economical by decreasing the use chemicals reagents and capital cost of the whole process.
- Bestowing to Sheldon, "the best solvent is no solvent and if a solvent is desirable then water is ideal". Using green extract in aqueous medium also replace the hazardous chemicals and organic solvent.
- In addition to this, it is a renewable resource derived from the natural sources.
- The usage of these extracts also eradicates the difficult microbial process of keeping cell cultures, which will lead lesser biohazard.

In this review, we will critically be analyzing the research activities on the sustainable and green production of metals (silver, gold, zinc and their oxides) as nanoparticles by adopting green tea. In addition, different reaction conditions and different applications were also discussed for the different metal ions prepared using green tea as well as various factor affecting the synthesis [7]. One of the major focus of the compiled efforts is to deliver comprehensive studies for the sustainable alternative.

Green tea's chemistry: Green tea is very famous drink after black tea and coffee. It has been consumed worldwide and growing in 30 countries. The history of green tea beverages has said to be discovered some 5000 years ago and initially it is used as a medicinal tonic. Later, green tea is formulated by taking extra cautions to prevent the oxidation of polyphenols present in green leaves. While the oxidation is promoted during black tea manufacturing, resultant many of these polyphenols are oxidized. Whereas, it has been kept partially oxidized product in oolong tea production [34].

Till yet, consumption of green tea provides various benefits to the drinker such as it improves the brain function, increases metabolism, decreases the risk of cancers, imparts anti-aging properties, reduces foul breath, forbid type-2 diabetes and other cardiovascular diseases [35]. It is well accepted by many findings of research that green tea have antitumor, bactericidal, anti-hyperglycemic, anti-inflammatory and body fat dissolving properties [36,37]. Without sugar, green tea is totally containing zero calories. However, it has found that the caffeine concentration in a cup of tea depends on the length of soaking or dipping time and on the amount of green tea present in one cup. In an average 20-45 mg of caffeine, there is 8 ounce in one cup.Thus, green tea is one of the safer and healthier drink today as it contains the greatest amounts of natural chemicals *e.g.* polyphenols [38] (Fig. 2) therefore, because of these benefits, dietitians and doctors suggests people to take green tea in diet regularly, as it represents an healthier way toward promoting human health [36].

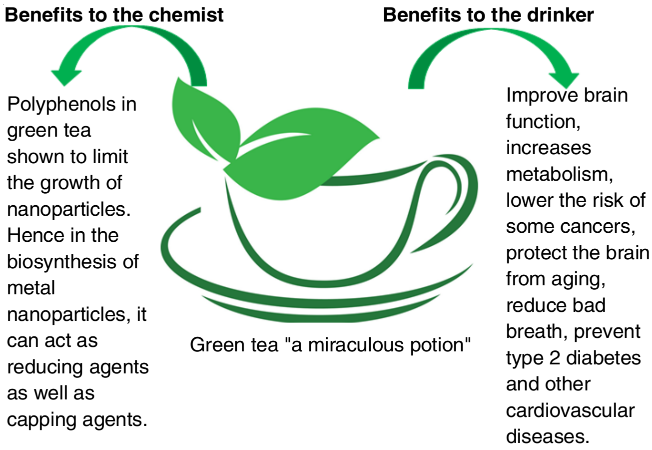

Fig. 2. Benefits of green tea to the chemist and to the drinker

Studies showed that dry green tea contains as much as 15 to 20% catechins, 2 to 3% caffeine and about 1 to 6% amino acids, vitamins, γ-amino butyric acid (GABA), chlorophyll, saponins and minerals. A group of polyphenols *e.g.* catechins are main astringency component in green tea. Its commonly named as tannins. Broadly of catechins are classified as: epicatechin, epigallo-catechin, epicatechin gallate, epigallocatechin gallate found in green tea leaves (Fig. 3) [39-43]. Presence of theobromine, methylxanthines and theophylline and amino acid theanine (5-nethylglutamine) in small amount imparts stringent properties to this tea. Apart of it, flavanols (quercetin, kaempferol and myricetin glycosides) and < 10% of total flavonoids are also present. The composition present in green tea is remained intact in fresh leaf, whereas after plucking limited enzymatically catalyzed variation has observed. During the enzymatic oxidations, various quinones are produced which further under-go condensation reactions to produce various chemical compounds such as bisflavanols, epitheaflavic acids, theaflavins and thearubigens. These are also responsible for imparting the distinctive colour and taste to it [34,44].

By using atomistic simulations, Botten *et al.* [45] have found the structural properties of (–)-epigallocatechin-3-gallate (most abundant), (–)-epicatechin-3-gallate, (–)-epigallocatechin-3-O-(3-O-methyl)-gallate and (–)-epigallocatechin in water and gas phase. In this work, the free energy conformational landscapes of these catechins as a function of the torsional degrees of freedom of polyphenolic rings at the ambient conditions were derived. The stable conformers and their connections were also determined. The free energy conformers are depend on the interactions of solvent and over the polyphenolic ring's structures. Furthermore, the position and number of hydroxyl groups and their absence or presence of the galloyl moiety have important role over the solvation shells of above mentioned catechins and its hydrogen bond capabilities. These all connected with interaction capacity and also affects its biological environment.

Recently, scientists discovered the role of polyphenols (catechins) found in green tea in the chemical reactions [46]. Scientist showed that a plethora of nanocompounds can be prepared by using this source from the multifunctional green chemical agents in nanochemistry, where polyphenols have been shown to limit the growth of nanoparticles. Thus, it can be used to achieve the stabilization as well as reduction of the metallic nanoparticles in "one-pot" synthesis procedure. The plant extracts work magical for the nanoparticles's synthesis. The reason behind this confirm that ingredients in extract act as stabilizing and reducing agents. In extract, epigallocatechin gallate (EGCG) is the major component, which reacts with the free radicals of hydrogen peroxide (H_2O_2), superoxide anion ($O_2^{\bullet-}$), hydroxyl ($HO^{\bullet}$), peroxyl, singlet oxygen and peroxynitrite [47]. Nune *et al.* [48] reported that one-electron reduction potential of EGCG is 550 mV, which is lower than that of glutathione (920 mV) and close to the α-tocopherol (480 mV) under standard conditions. These properties make this 'chemical cocktails' with full of health benefits.

Fig. 3 shows the structure of some important catechins present in the extract and the chemical reduction power of these army of chemicals is responsible for its activity.

Biosynthesis: Biosynthesis techniques employing green tea have gathered enormous recognition due to simple in procedure, effective in results, economical route and easily available method. It also considered to be admirable substitute to the conventional production methods for the nanoparticle synthesis.

Mechanism processes: The synthesis of nanoparticles using green tea extract comprises three main stages (Fig. 4) *viz.* (i) activation phase: The reduction of metal ions has been occurred in this stage, after reduction, the reduced metal species undergoes nucleation. (ii) Growth phase: In this phase, small nucleated nanoparticles coalesce together into larger size particles. Metal ion reduction in activation phase and growth phase together referred to as bottom-up approach, this phase is also responsible to increase the thermodynamic stability of synthesized nanoparticles; and (iii) termination phase: Nano-

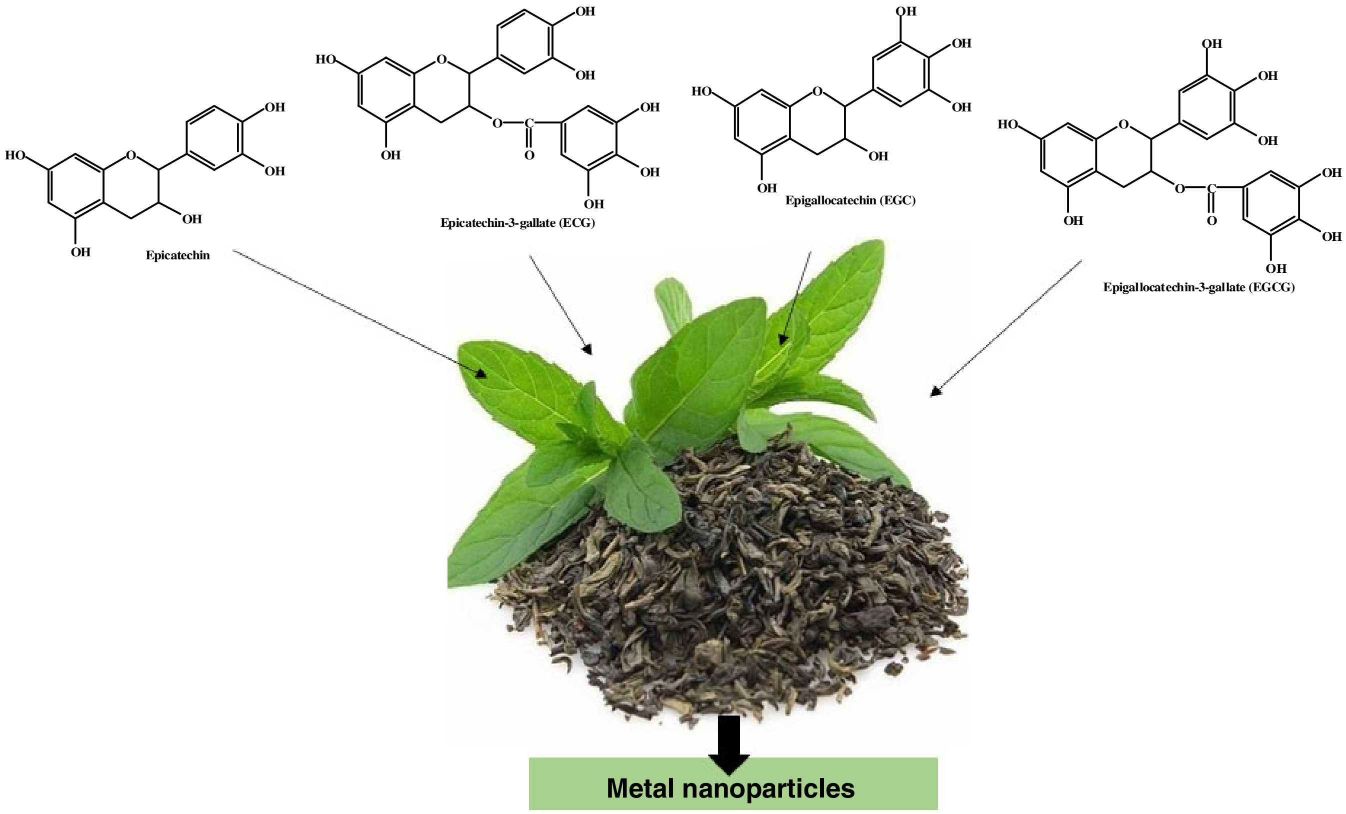

Fig. 3. Presence of various catechins in green tea

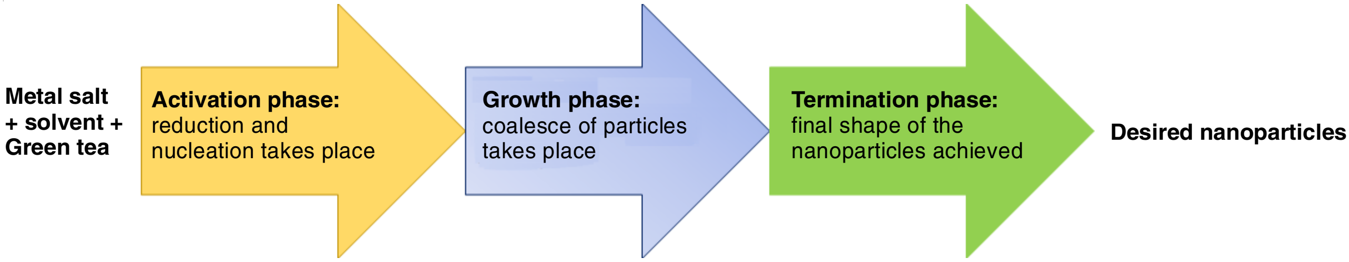

Fig. 4. Steps involved in mechanism for nanoparticles synthesis

particles in this phase acquire the most energetically favourable conformation as per the conditions in mother solutions. Hence, plant extract are having ability to synthesize and stabilize metal nanoparticles.

The key reaction between metal ions with reducing metabolites and stabilizing agents present in green ta extract leads to the formation of reduced metal ion-reducing agent complex. These complexes interrelate further with the similar complexes and building small metal nanoparticle. Development and agglomeration of these small particles into bigger particles till it achieves stable size and shape.

Literature suggests that the large number of factors are also accountable for the nanosynthesis. First of all, the reduction process is been contingent on the concentration of green tea extract, which further activates biomolecules, pH, incubation time. Other important factors includes time of reaction, concentration of metal salts, temperature and metal electrochemical potential are also plays a significant role in the whole nanosynthesis process [49].

Gottimukkala *et al.* [50] used the green tea for the iron-oxide nanoparticles production with different morphology. Researchers reported around 4000 species are existing in the green tea extract. One-third of the total species includes polyphenols (mainly flavonoids and catechins). The epigallocatechin gallate (EGCG) catechin is the main active component having reduction potential of 0.57 V can change the ferrous to zero-valent iron as the reduction potential of the iron is -0.036 V. The plausible mechanism reported as per the authors are supposed to be taken in two main steps: step 1 involves the metal salt interaction and the formation of metal complex with present polyphenols in green tea extract. The complex formation often involves breaking of –OH bond present on catechins and side-by-side forming a partial bond with a metal ion, and step 2 involves the breakage of the above mentioned partial bond and transfer of electrons to reduce the metal ions to form nanoparticles and thus get oxidize to *ortho*-quinone.

Prospective applications: In the field of medical sciences, the simple size nanoparticles acted as probes to investigate in different places at cellular level without creating any disturbance. These nanoparticles have also been investigated for antimicrobial applications, biosensing, imaging and drug delivery [51]. Green tea having capacity to control the size-distribution during synthesis. Nune *et al*. [48] reported the synthesis of gold nanoparticles by using the combination of various bioactives such as thearubugins, theaflavins, catechins, *etc*. Numerous polyphenols present in green tea act as outstanding stabilizers on nanoparticles. Hence, green tea based reaction medium provide robust shielding from agglomeration. Further, cellular uptake and cytotoxic studies of T-AuNPs were also examined and reported in Human Prostate (PC-3) and breast cancer cells (MCF-7). Catechins coated T-AuNPs showed excellent affinity towards the receptors on prostate and breast tumor cells. The new avenues are opened by working on the collaborative advantages of utilizing green tea for playing duple roles involving gold nanoparticles production and stabilization in one-pot method.

Iron nanoparticles synthesized from green tea extract was utilized for the oxidation of monochlorobenzene and the removal of chemical oxygen demand (COD) [52]. The results were 81% and 31%, respectively. The prepared GT-Fe nanoparticles behave as a heterogeneous catalyst, which indicated that Fe^{2+} and Fe^{3+} leached from the green tea-Fe nanoparticles and consequently reduced the formation of iron sludge.

The formation of silver nanoparticles was achieved by using economical and sustainable biogenic approach by opting one-pot synthesis within a time period of 1 min by utilizing commercial green tea extract (*C. sinensis*) [46]. The surface modification of nanoparticles was carried by coating with polyethylene glycol (PEG), which improve the high dispersal and biocompatibility. Moreover, the cytotoxicity examination disclosed that the synthesized AgNPs from green tea extract did not showed noteworthy noxiousness to human keratinocyte (HaCaT) cells. Moreover, the amount of silver nanoparticles utilized to examine the antibacterial effect was not noxious to HaCaT mammalian corpuscle. Consequently, green tea fabricated AgNPs emerge as a potential candidate in the field of biomedical to combat with the infective microorganisms with lower toxicity to human cells.

Rajput *et al*. [53] observed that the desired crystallite AgNPs can be easily synthesized by differing the concentration of Ag^+ concentration, which is one of the essential parameters to influence/tune optoelectronic property and other applications of the nanomaterial.

Table-1 summarizes the fabrication and applications of different metal nanoparticles synthesized from green tea leaves.

Characterization: There are many techniques nowadays available which confirms the procedure and purity of these nanoparticles. The prepared nanoparticles can be characterized by UV-visible, SEM, TEM, XRD, Raman and FTIR spectroscopy [81-83]. The results from these techniques confirm the surface, nature, morphology (particles are irregular or regular, spherical, hexagonal, triangular and elongated shapes) and also help to understand the mechanisms of action and interactions of different polyphenols as reducing and capping agents at the molecular level.

Factors affecting the biosynthesis of metallic nanoparticles: Nevertheless, literature precedent provides several assumptions and factor which potentially help us to understand the complexity exhibit/persist in the synthesis of green nanoparticles (Fig. 5), the below mentioned points are worth to be consider during the biogenic synthesis [84,85]:

(i) Chemical configuration of plant extract: Antioxidants or polyphenols present in the plant extract act as the stabilizer, capping agent and prevent agglomeration [59]. Additionally, the polyphenol contents of tea leaves also provide stability to the metal nanoparticles during their biosynthesis in the aqueous medium [86]. Various reaction mechanism proposed by several researchers revealed that the nanocomposites can be easily attained by reduction of metal salts using tea leaf that consists highly polar and water-soluble EGCG, which function both as reducing and capping agent [86]. Furthermore, various evidence proposes that many biological species could accomplish both the role for the formation and prevent agglomeration of the naoparticles in water as solvent [53].

(ii) Plant extract concentration: Giri *et al.* [87] studied the effect of concentration of plant extract over the synthesis of nanoparticles, which represent an enhanced SPR signal during the synthesis of AgNPs over increasing the tea leave extract up to 4 mL volume due to production of more AgNPs which became saturated subsequently demonstraing ample transformation of Ag^+ into Ag^0. Additionally, a red shift in the wavelength for maximum absorbance (λ_{max}) was also reported

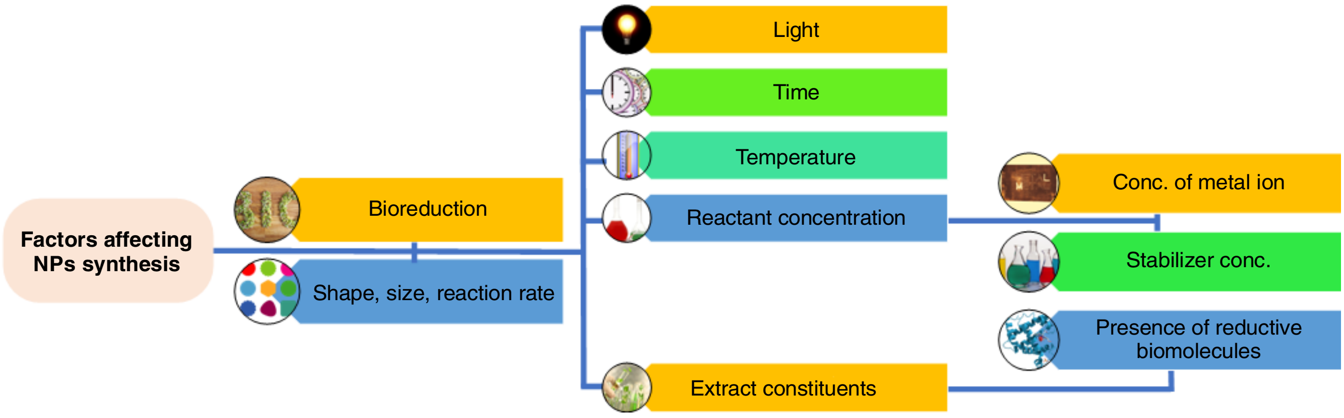

Fig. 5. Factors affecting the biosynthesis of metallic nanoparticles

TABLE-1
FABRICATION AND APPLICATIONS OF DIFFERENT METAL NANOPARTICLES SYNTHESIZED FROM GREEN TEA LEAVES

Conditions	Morphology and size	Applications	Ref.
Iron nanoparticles			
Tea leaves (60 g) were heated (80 °C), 1 h/1 L of water, followed by vacuum-filtered. Then, 0.1 M $FeSO_4$: tea extract were mixed in 1:2 ratio mixed for 1 h. Black nanoparticles obtained and separated.	Spherical, 20-40 nm 80-120 nm NPs obtained.	Fenton-like oxidation of monochlorobenzene	[52]
5 mL of plant extract and 5 mL of 0.001 M ferric chloride solution were stirred at 50-600 °C to furnish the synthesis of nanoparticles.	Nanospheres, 50-100 nm		[54]
Green tea extract: 20 g of green tea in 1 L of water heated at 80 °C, filtered. 0.1 M $FeCl_3$ solution: 16.2 g of $FeCl_3$ in 1 L water. Green tea extract + 0.1 M solution of Fe_3O_4 mixed in 2:1 ratio, stirring, green tea-nZVI obtained.	Spherical, 5 to 15 nm	Degradation of bromothymol blue	[55]
3.7 g ferric chloride + 9.54 g ferrous sulphate mixed in 500 mL distilled water. Both solutions were added and stirred, 80 °C, 10 min, 25 mL freshly prepared green tea extract, stirring, 20 mL ammonia added after a period of time.	–	The synthesized nanoparticles were utilized for photocatalytic degradation of Methyl orange dye. Numerous optimizations had been carried out by varying the conditions such as in absence of light, employing diverse type of light source: For example: UV light, artificial light and sunlight.	[56]
20 g green tea leaves, boiled in 1 L of water, 80 °C, 5 min, green tea extract + ferric ion solution, mixed in 1:2 ratio to obtain the targeted nanoparticles.	–	The nanoparticles were opted for removal of Cr(VI) from polluted groundwater flowing through the porous soil bed. Additionally, the authors have also carried out column tests to analyze flow rates.	[57]
0.01 M Ferric Chloride+ green tea leaves extract in equal proportion, colour change. Obtained NPs centrifuged, washed 2-3 times to eradicate the impurities and obtain pure NPs.	–	–	[50]
(1:1-1:4) green tea extract + iron salt precursor. Colour change from faint yellow to reddish brown further to finally black.	–	–	[58]
Green tea extract: 15 g of green tea in 250 mL of deionized water, 80 °C, 1 h. filteration, stored in freezer. Iron nanoparticles: green tea extract + 0.10 M $FeSO_4$ solution (2:1) at room temperature, agitated for 30 min. Black colour NPs of Fe^{2+} ions, filtered and washed with ethanol.	Quasi-spherical shaped, 20 to 80 nm	The author carried out batch experiment to display that 59.7% of nitrate can be eliminated by green tea-Fe NPs.	[59]
Zinc oxide nanoparticles			
Green tea extract: 5 g of powdered fresh green tea leaves, heating at 70 °C, 1 h in 100 mL of water, filtered, 0.3 M $Zn(CH_3COO)_2$ solution in 60 mL of distilled water, stirred for few minutes. Add 40 mL of this green tea extract to zinc solution, mixing and stirring. Dried at 80 °C overnight, pale-white ZnO NPs, calcinated at 100 °C, 2 h. NPs was confirmed by colour changes, SEM, UV-Vis and FT-IR.	–	Prepared ZnO material is the best suitable material for supercapacitor applications.	[60]
Green tea extract: 10 g dried leaves + 100 mL of waster, 80 °C, 2 h. ZnO NPs: 0.2 M $Zn(CH_3COO)_2\cdot(H_2O)_2$ (230 mL) + green tea leaves extract (100 mL), room temperature. ZnO NPs were dried out at 40 °C, 24 h and calcinated 100 °C, 1 h, Yield reported: 9.1 g of ZnO NPs.	Nanosheets, larger quantities of phytochemicals lead to nanoflowers	ZnO NPs for antimicrobial activity evaluated for selected pathogenic strains (*Staphylococcus aureus*, *Aspergillus niger*, *Escherichia coli*) using agar well diffusion method	[61]
$Zn(CH_3COO)_2\cdot(H_2O)_2$(0.2 M) stirred in distilled water (70 mL). Green tea extract: leaf powder (5 g) in distilled water (100 mL), mixing, 2 h, 80 °C, cool and filter. Extract (30 mL) + $Zn(CH_3COO)_2$ solution, desiccated at 60 °C, pale-white ZnO NPs, calcinated at 100 °C for 1 h.	–	Synthesized ZnO NPs displayed improved and comparable antimicrobial activities with respect to the activities of synthetic drugs: Regarding the antibacterial assay, the following pathogenic bacterial species were employed. Gram-negative bacteria: *Klebsiella pneumoniae, Pseudomonas aeruginosa, Escherichia coli* and Gram-positive bacteria: *Staphylococcus aureus.* In the antifungal assay, pathogenic fungi *Aspergillus fumigatus, Aspergillus flavus, Penicillium* sp. and *Aspergillus niger* were included.	[62]
Zinc nitrate solution (50 mL) + 5 mL of green tea leaf extract, agitated at 120 °C. ZnO NPs from the colour change (*i.e.* light brown to blackish brown), NPs separated by centrifugation and dried to yield yellow-coloured particles.	–	The green colour of the dye was removed up to 70% with the use of reducing agent sodium borohydrate. Removal of melachite green dye was performed.	[63]

Zinc oxide NPs: $Zn(NO_3)_2$ and extract of green tea mixed (1:3) exposed to microwave rays (540 W) for 7 min, brownish black NPs obtained. Filtration, dried at hot air oven, 4-5 h.	Spherical, 20 and 50 nm	The current-voltage (I-V) characteristics of thin film of ZnO/NG nanocomposite were investigated. JSC (short-circuit photocurrent), VOC (open-circuit photovoltage), FF (fill factor) and η (efficiency of the solar cell) were recorded for ZnO/NG nanocomposite. Captivatingly, the cell exhibit a virtuous power conversion efficiency of 3.54% with high stability.	[64]
Silver nanoparticles			
Ag NPs synthesized by opting green tea grown at distinct elevations such as 86 m, 1700 m and 2000 m above sea level in eastern Nepal. The NPs synthesized by green tea leaves grown at height of 1700 m were found to be homogeneously dispersed and smaller in size, in contrast to Ag NPs fabricated with tea leaves from the other two heights.	T1-AgNPs and T3-AgNPs: Variable shapes, with size ranging from 10 to 60 nm; T2-AgNPs: spherical shaped with size ranging from 10 to 20 nm	Synthesized AgNPs from tea leaves were more utilized to detect presence of Hg^{2+}. Ag NPs fabricated from the tea leaves from 1700 m elevation showed better Hg^{2+} ion sensing having a detection limit of 9.79 ?M. Remarkably enhanced detection limit of mercury ions (0.71 μM) was observed over stabilizing the NPs with cationic surfactant *i.e.* aqueous trimethyloctylammonium bromide and the nanoparticles can detect the Hg^{2+} ion in lower concentration.	[65]
$AgNO_3$ solution (0.025 mol, 2 mL) drop-wise mixed in green tea extract (9 mL), constant stirring for overnight. Ag NPs were separated by centrifugation, washed 2-3 times with water and ethanol. NPs were dried in an oven for a time period of 2 h, 60 °C, grinded to powder.	Spherical, 6.13 to 8.46 nm	*In vitro* cytotoxicity activity was examined for four cancer cell lines which were human breast adenocarcinoma (MCF-7), cervical (HeLa), epithelioma (Hep-2) and lung (A549) as well as normal human dermal fibroblasts (NHDF) cell line. The antioxidant property was evaluated with ABTS, DPPH, p-NDA, H_2O_2 and DMSO scavenging assays. Here, the green tea based Ag NPs disclosed notable results in parallel to the standard antioxidants ascorbic acid and rutin.	[66]
Tea leaves (10 g) boiled in distilled water (100 mL), 60 °C, 10 min., filtered and stored. Ag NPs: 100 mL of silver nitrate (1 mM) + tea extract (12 mL), room temperature, colour change of reaction mixture.	Spherical, average 4.06 nm	The green synthesized nanoparticles can be effectively employed in many fields such as cosmetics, foods and medicine.	[67]
$AgNO_3$ (10 mM, 750 mL) + tea extract (25 mL) mixing, 30-50 °C, 20 min. brown colour NPs formed. NPs separated by centrifugation, later washed and dried.	The author reported a method to manipulate and control the NPs size. The nanoparticles were spherical and to some extent cubic i) 25 nm, ii) 45 nm and iii) 75 nm sizes	Activity of Ag nanoparticles were investigated to explore the suitable antibacterial application.	[68]
Extract: green tea (2 g) in deionized water (100 mL), magnetically agitated at 60 °C, the resultant mixture was filtered. Silver nitrate (0.1 M, 75 mL) and green tea extract (75 mL), mixing, pH of 10.5 by dropwise adding of NaOH (1 mol/L), further agitated for 15 min. NPs separated by centrifugation and rinsed twice and freeze dried by employing a lyophilizer. Afterwards, surface modification of biogenically synthesized nanoparticles was attained by polyethylene glycol (PEG) to improve their distribution and biocompatibility.	Spherical, 34.68 ± 4.95 nm, Average PDI value: 0.28 ± 0.01 Average zeta potential: 35.5 ± 3.32 mV AgNPs (3.9 ± 1.6 nm) and PEG-AgNPs (4.2 ± 1.3 nm)	The prepared nanoparticles are not noxious to human keratinocyte (HaCaT) cells. The antimicrobial efficacy of the biogenic nanoparticles was examined in contrary to Gram-positive *Staphylococcus aureus* (ATCC 29213), Gram-negative *Pseudomonas aeruginosa* (ATCC 27853), *Klebsiella pneumoniae* (ATCC 700603), *Escherichia coli* (ATCC 25922) and *Salmonella enterica* (ATCC 14028) bacterial strains. *Salmonella enterica* act as highly sensitive strain and can detect with a minimum inhibitory concentration and minimum bactericidal concentration of 7 and 15 µg/mL, respectively. Remarkably, the silver nanoparticles does not exhibit any toxicity for HaCaT mammalian cells in the optimum concentration in which Ag NPs behave as efficient antibacterial. Consequently, biogenically prepared Ag NPs stand as potential candidate in the field pf biomedical applications to prevent from pathogenic bacteria with minimal cytotoxicity to normal cells.	[46]
Silver nitrate + tea extract, agitated for 2 h.	Spherical, 20 to 90 nm	Antibacterial property of AgNPs was studied by examining the growth curve and also by the Kirby-Bauer disk diffusion approach. Low antibacterial activity against *Escherichia coli* was observed with green tea based Ag NPs, which could be accredited to their large size and low release of silver ion.	[69]
Methanol extract of green tea obtained in 90 min at 70 °C. NPs checked by SEM and particle size analyzer.	Morphology is not uniform, tends to aggregate and the size distribution of silver nanoparticles is 82.33-740.89 nm with an average diameter of 157.8 nm.		[70]

Silver precursor + discarded product of tea leaves (*Camellia sinensis*).	Circular, hexagonal, triangular nanoparticles, 40 to 60 nm	The prepared silver nanoparticles exhibit high antibacterial activity. The order of antibacterial activity: *K. pneumonia* > *E. coli* > *C. diptheriae*. Additionally, the NPs reveals noteworthy impact on the development of *Vigna radiata* seeds at 50% concentration of nanoparticles. The NPs grafted over cotton cloth also exhibit high antibacterial activity for Gram-positive organisms. The fabricated nanoparticles were successfully employed for the degradation of phenol red and blue textile dye.	[53]
10 g of discarded tea was added in double distilled water (100 mL), boiled, 60 °C, 5 min. 20 mL (decanted extract) + $AgNO_3$ (1 mmolL^{-1}, 80 mL), stirred, 60 °C, 30 min. Colour change from yellow to brown, centrifugation, washed with water for 3 times, dried in a vacuum oven, 50 °C, overnight.	Torispherical, average size 45 nm	This work focused on the degradation of methylene blue (MB) and ethyl violet (EV) in aqueous solution with AgNPs as catalyst in the absence and presence of H_2O_2. The AgNPs exhibit fast, efficient and stable catalytic activity in the degradation of cationic organic dyes, but it is no catalytic degradation of anionic organic dyes at room temperature. The fabricated Ag NPs exhibit high antimicrobial activity against pathogenic bacteria. Additionally, the fabricated Ag NPs can further be employed as highly active and efficient catalyst in industries and water purification.	[71]
Silver nitrate solution (0.025 mol, 2 mL) + aqueous extract green tea (9 mL), mixing, overnight. Ag NPs centrifugation, water and ethanol washed, dried in oven, 2 h at 60 °C. Ag NPs crushed o fine powder. (Phytochemical studies reveals that the presence of high quantity of biochemicals in green tea leaves are responsible for the reduction and stabilization of silver salt to silver nanoparticles).	Spherical, 6.13 to 8.46 nm	The antioxidant activity was evaluated by ABTS, DPPH, *p*-NDA, H_2O_2 and DMSO scavenging assays. The results revealed that the AgNPs prepared by adopting green method exhibited remarkable activity with respect to the standard antioxidants ascorbic acid and rutin. Later on, the *In vitro* cytotoxicity activity was established on 4 cancer cell lines such as human breast adenocarcinoma (MCF-7), cervical (HeLa), epithelioma (Hep-2) and lung (A549) along with one normal human dermal fibroblasts (NHDF) cell line.	[66]
$AgNO_3$ (10 mM, 750 mL) + green tea extract (25 mL) agitated, 10 min, 30 °C. brown coloured NPs separated by centrifugation, washed and dried. Green tea extract (80 µg/mL) in water used. Ag NPs confirmed by dynamic light scattering, UV-visible (UV-Vis) spectroscopy and scanning electron microscopy.	30 to 80 nm	AgNPs were evaluated for antimicrobial activity and photocatalytic dye degradation. The AgNPs showed antibacterial activity against E. coli, S. aureus and S. pyogenes with 6, 5 and 8 mm zone of inhibition, respectively. The fabricated nanoparticles were further utilized for degradation of methylene blue (65%).	[72]
Gold nanoparticles			
Initially, tea leaves (100 mg) in double distilled water (6 mL) was stirred, -40 °C, 5 min. $NaAuCl_4$ (0.1 M, 100 ?L) +tea extract, sudden transformation of pale yellow solution to purple-red colour, stirring, 5 min. Gold nanoparticles filtered, checked by UV absorption spectroscopy and TEM analysis.	Spherical, 14-45 nm	The group have carried out cytotoxicity studies of nanoparticles. The phytochemical coated Au NPs revealed remarkable efficiency toward prostate (PC-3) and breast (MCF-7) cancer cells and realiazed to be non-noxious by MTT assay.	[52]
Distilled water (2 L) and green tea leaves (200 g), sonication, 1 h, ambient temperature, filtered extract (having final concentration of 0.03%)+ $HAuCl_4·3H_2O$ (0.5 mM) + NaOH (1 mM), mixed and water was added to make up the volume of 2 mL, incubated in an oven, 80 °C, 2 h. SPR of the nanospheres also recorded by the aid of UV-Vis spectroscopy.	Nanospheres, 8.7 ± 1.7 nm, Nanostars 99.0 ± 47.0 nm Nanorods length and width were 60.4 nm and 16.4 nm	The cellular uptake of each type of AuNP was quantitatively measured using HepG2 cells. On 24-well plates, the cells were seeded at a density of 5.0 × 10^4 cells/well and incubation was conducted for 24 h in an oven at 37 °C under a CO_2 (5%) atmosphere. Subsequently, excess Au NPs were removed from the incubated 5 ?M Au NPs and the cells were exposed with trypsin. Finally, the concentration of Au uptake by the trypsinized cells was quantitatively determined with ICP-OES and LA-ICP-MS.	[73]
200 mg of green tea in 12 mL of distilled water, stirred, 15 min., filtered. 6 mL of extract, 0.1 mL of chloroauric acid trihydrate solution (0.1 M) dropwise, stirred, 5 min. colour change from pale yellow to purple red confirm the synthesis of gold nanoparticles. Continue stirring for an additional 15 min.	–	The experiment can be conducted in a typical laboratory session and is suitable for incorporation into the undergraduate introductory chemistry laboratory curriculum and constitutes an influential example sustainable synthesis.	[74]
Initially, 0.2 mL of green tea extract in 1.0 mL of double distilled water+ 0.3 mL aqueous solution of Gold (III) chloride hydrate ($HAuCl_4$) (25.8 mM), agitated, room temperature.	74% irregular spherical, 10% hexagonal, 8% triangular and 8% elongated shapes with size range ~ 2.94 to 45.58 nm Size range of ~2.94 to 45.58 nm with an average of 13.14 nm		[75]

Green tea (1.5 g) and deionized water (100 mL), mixed, boiled. chloroauric acid trihydrate (5 mL, 10-3 M) taken in aliquot part (1-4 mL) of green tea extract and appropriate amount of de-ionized was mixed to adjust the volume of 10 mL. NH_4OH (2.5 mL)+silver nitrate (5 mL, 10-3 M) + green tea extract (1-10 mL) + followed by addition of de-ionized to 50 mL. Rapid colour change observed. i). For Au NPs: yellow solution into pink, grey-blue and pale violet. ii). For Ag NPs, yellow to bright yellow and to dark brown.	Anisotropic nanotriangles and nanoparticles (40 nm)	Colloidal systems of Ag and Au NPs possess remarkable single photon mediated luminescence. This photophysical properties can be altered by varying the concentrations of metal ions as well as the amount of reducing agent, which majorly effect the development, progress and luminescence property of these NPs.	[76]
Ag or Au NPs: silver nitrate or chloroauric acid trihydrate + aqueous solution of sodium bicarbonate + tea extract under ambient reaction conditions.	The nanoparticles were stable at room temperature and had a uniform particle size (Au: ~10 nm, Ag: ~30 nm). Ag: Spherical (8.5 ± 2.5 nm) Au: 11.0 ± 4.2 nm Ag: 34.4 ± 9.6 nm	The prepared NPs displayed high antibacterial activity and a characteristic colour, thereby showing potential application as antimicrobial pigments.	[77]
Miscellaneous action			
The natural extracts of green tea leaves were used for the surface functionalization of a titanium alloy (Ti6Al4V), which has been chemically pre-treated. The chemical pre-treatment enriches the surface of the titanium alloy in hydroxyl groups, which allow surface functionalization and induces a bioactive behaviour (spontaneous precipitation of hydroxyapatite from inorganic body fluids)	–	This treatment is designed for dental implants and osteo-integrable joint prosthetic components. In this work, the effects of functionalization with polyphenols were tested on mesenchymal stem cells, KUSA A1.	[78]
Titanium dioxide nanotubes used as an solid phase adsorbent to extract the suspended and soluble chromium species such as Cr(III) and Cr(VI) present in the tea leaves and tea infusion and quantified it with help of inductively coupled plasma mass spectrometry,	–	This method was applied for the analysis of chromium and its distribution and content in tea leaves and tea infusion.	[79]
This work showed that green tea extract which consist high amount of epigallocatechin gallate (EGCG) stand as a potential candidate to eradicate the problem of bone loss (For *e.g.*, osteoporosis and periodontal disease). The group studies the effect of green tea on bone metabolism of ovariectomized rats after experimental periodontal disease (EPD) by histologic, morphologic and microtomographic factors.	–	Microtomographic results showed that trabecular thickness and bone surface density values in alveolar bone interradicular septum of the OVX + EPD + GTE groups were similar to the Sham group. The outcomes reveals that green tea extract have capability to recover from the bone related problem in osteoporotic rats with periodontic ailment.	[80]

by the group over increasing the tea leave extract volume [87]. Yu *et al.* [88] also investigated the result of various quantity of plant extract on the AgNPs synthesis efficiency, which reveals that the dilution of tea extract leads to decrease in the nanoparticle production efficiency.

(iii) Concentration of metal salt: Studies confirms that the biological assisted methods synthesized nanoparticles have many crystallite shapes. These are considered to be reliant on the reactant-metal ion concentration in solution, different kinds and number of enzymes released by the plant extract and consequent pH of the resultant matrix. Generally, the green tea based nanosynthesis confirmed the resultant change in colour from colourless to particular colour of the solution. This concomitant colour is owed by the surface plasma resonance (SPR) phenomenon of nanoparticles. Increasing metal nitrate concentration has significant enhancement in SPR absorbance, owing to the improved hydroxyl groups oxidation by the polyphenols present in the tea extract [87].

(4) Effect of pH: Since the effectiveness of adsorption is typically thought to depend on the pH of the solution, a change in pH might stimulate differences in the adsorbate's degree of ionization and the properties of the adsorbent's surface [89].

(5) Reaction time: The resultant dimensions of the obtained nanoparticles were dependent over the incubation time or interaction time between two main phases *i.e.*, drops of metal nitrate and green tea leaves extract. Moreover, the slower addition rate of metal nitrate, the larger size nanoparticles were obtained.

(6) Reaction temperature: The studies also suggested that the synthetic procedure of nanoparticles by tea extract get enhanced over increasing the temperature. Yu *et al.* [88] investigated the synthesis of AgNPs formation using 5% (v/v) tea extract over different temperatures *i.e.* at 25, 40 and 55 ºC. However, it is analyzed that no noteworthy effect on the synthesis efficiency was observed but to the delight an increase in size was observed, which is a average hydrate particle sizes of AgNPs were 91, 129 and 175 nm, respectively. This could be attributed towards the improved reaction rates of metal nanoparticles synthesis over increasing the temperature consequently increase the size of the nanoparticles.

Interestingly, the temperature plays an important part for the extraction procedure [90]. During extraction procedure, the vital enzymes persisting in different parts of plants are liable for the reducing and capping actions, got released and activated over boiling [91]. Far ahead, the obtained extract has capability to synthesize the nanoparticles at ambient temperature. This confirms the capability and competence of the biogenic synthetic procedure of nanoparticles.

Synthetic techniques: Researchers also check the effect of microwave for the efficient synthesis of metal nanoparticles. The results revealed that the over irradiation with microwave augmented procedures and the reactions was accomplished quite rapidly (7 min) in comparison to the conventional method (4-5 h at room temperature). However, according to Zhang *et al*. [92], a microwave-assisted method enhanced the synthesis of nanoparticles with more effectiveness, less time and lower temperatures. The traditional approach, however, resulted in the more stable nanoparticles with greater mean sizes.

Challenges: Several challenges are persisting in the field which need to be answered [11], such as:

(i) Regulated distribution and reproducibility of nanoparticle size.

(ii) Stability and cytotoxicity profile: There is a necessity to concern about the long-standing consequences of the nanoparticles on animal and human as well as their accumulation in the ecosystem.

(iii) Design and methodology of the reaction conditions and altering the results for the production of high amounts of proteins, enzymes and biomolecules, which are responsible for the biosynthesis and stabilization of the metal nanoparticles to regulate morphologies and other features.

(iv) The bioreduction of metal nanoparticles by blends of bioactive ubiquitous motifs present in tea leaves extracts is environmentally benign, yet chemically complex. Henceforth, researchers show keen interest to unveil the mode of action of biological motifs and enzymatic action involved behind nanoparticles biosynthesis as well as the detection of biological derivatives involved in reduction, formation or stabilization of metal nanoparticles.

(v) Quantitative investigation for phytonutrients existing in the green tea extract.

Conclusion

Green tea assisted procedure for the synthesis of different metals nanoparticles has substantial ability along with numerous benefits in contrast to old conventional methods. Keeping the benefits in mind, this procedure can easily replace the conventional physical and chemical methods. But, scaling of these methods and developing the schemes for the nanosynthesis will be the next achievement. However, in terms of the environmental advantages, this biogenic method doesn't require any additional/external toxic chemicals for the reduction, capping and stabilizing agent. Polyphenols-catechins existing in green tea are seemingly accountable for the structuring of a strong coating on the metal nanoparticles and consequently, offering the steadiness from aggregation. The forthcoming generation will consider the challenges prevail in the conventional methods and encompass the sustainable approach of green tea mediated synthesis of materials/nanoparticle and practically move the field from laboratory to a higher scale by accepting the current issues, specifically well-being and environmental factors.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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