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Review Article

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Plant-Extract Mediated Synthesis of Copper- and Iron-Based Nanoparticles for Various Applications

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Abstract

Green synthesis has attracted wide attention as a trustworthy and environmentally friendly approach for synthesising a broad variety of nanomaterials, including metal nanoparticles NPs and metal oxide NPs. It is considered an advanced tool for reducing the harsh effects related to the conventional methods of NPs synthesis, which are generally used in the laboratory and industry. The current review article focuses on investigations indicating the new processes to produce copper (Cu) and iron (Fe)-based NPs by using extracts of plant parts, particularly, flower, stem, seeds, whole plant, and fruit extracts, followed by the future opportunity of work in this area.

Keywords

Green synthesis, Nanomaterials, Plant extracts, Copper, Iron-based

Introduction

In recent years, nanotechnology has appeared as a modern and revolutionary technology with applicability in a wide range of fields [1-6]. Amongst nanomaterials, current research focus is mainly on the synthesis of NPs since they can be easily produced and manipulated. Magnetic NPs come under the category of inorganic NPs, which can be applied in different areas due to their numerous exceptional characteristics. Since the last decade, new approaches for the synthesis of nanomaterials have been an exciting area of exploration in nanoscience and nanotechnology [7-10]. Several chemical and physical methods are reported in the literature for NPs preparation [11-13] but these methods suffer from various drawbacks, hence research attention has recently moved in the direction of developing clean and eco-pleasant synthetic approaches [14-16]. Keeping in view of the disadvantages related to physical and chemical methods of NPs synthesis (toxicity, recyclability, stability requirements, etc.), green synthetic approaches have been invented, which may utilize plant extracts, bacteria, fungi, algae, etc. Among the available green methodologies for NPs synthesis, employment of extracts of different plant parts is quite simple for large scale production in comparison with bacteria or fungi-mediated synthesis. This may be due to the valuable phytochemicals present in various natural plant extracts, which have the ability to reduce metal salts into metal NPs. There are excellent review articles published since last 2-3 years regarding the preparation of Fe and Cu-based NPs by applying green methods [17-19]. In continuation, we would like to report the current findings and progress in this particular area. As a result of the limitations associated with chemical and physical methods of NPs synthesis, we decided to provide a brief overview of recent developments rather than a comprehensive review. In this review article, green synthetic approaches for Fe and Cu-based NPs using natural extracts of plants have been summarized.

Green Production of Copper-Based Nanoparticles

NPs possess a broad application in different areas of recent research significance, including environmental, pharmaceutical, biomedical, energy, and catalytic applications, etc. [20-22]. Among transition-metal based NPs, copper nanoparticles (CuNPs) are of great concern because they are cheap and easily available [23, 24]. They can be utilized in heat transfer systems, sensors, as catalysts for chemical reactions, and as antimicrobial agents [25-32]. There are many reported methods for metal NPs synthesis [33, 34] which cause production of pure and well-defined NPs, yet they are neither profitable nor environmentally pleasant due to the toxic nature of chemicals. Hence, biosynthesis of nanoparticles is one of the important tools of green chemistry, which makes use of a diverse range of plants, fungus, bacteria, yeast, and viruses [35, 36].

It is well-known that different plant parts can be used for the preparation of Cu-based NPs using different precursor salts under varying reaction conditions. In this regard, Nasrollahzadeh et al. [37] caused immobilization of CuNPs on a natrolite zeolite surface by using *Anthemis xylopoda* flower aqueous extract, which acts as a reducing and stabilising agent. The performance of the catalyst was examined for N-formylation of amines under eco-friendly reaction conditions. It was observed that the catalyst could be reused at least five times without significant loss of activity. Further, *Punica granatum* seeds extract arbitrated CuNPs were prepared by Nazar et al. [38]. The CuNPs displayed excellent photocatalytic activity for the methylene blue (MB) degradation under irradiation of solar light. Another study reported by Ismail [39] revealed inexpensive and ecological method for CuNPs production using fruit extract of sumaq (*Rhus coriaria* L.) as a stabilizing agent. CuNPs showed excellent activity against Gram-positive bacteria. It was established that *Citrofortunella microcarpa* leaves extract synthesized CuO NPs were employed as photocatalyst for the purification of rhodamine B dye polluted water [40]. Further, *Ailanthus altissima* leaf aqueous extract prepared CuO NPs demonstrated significant inhibitory activity against *Staphylococcus aureus* and *Escherichia coli* [41]. *Jatropha curcas* leaf extract utilized green synthesis of CuNPs was described by Ghosh et al. [42]. It was illustrated that the flavonoids, glycosides, tannins, and alkaloids present in the plant extract were used as reducing, stabilizing, and capping agents. CuNPs synthesized by using *Hagenia abyssinica (Brace) JF. Gmel* leaf extract appear to be more crystalline in nature as reported by Ananda Murthy et al. [43]. Asemani M and Anarjan N [44] synthesized CuO NPs (mean particle size of 80 nm) using walnut leaf extract. Another study by Sinha et al. [45] described the biogenic synthesis of spherical CuNPs (22 - 27 nm) by using the peel extracts of *Citrus grandis*. As revealed by X-ray diffraction (XRD) data, the average crystallite size was 18 nm. Further, Mohamed et al. [46] reported a simple, beneficial, and environment-friendly method using seedless dates' extract rich in phenolics and flavonoids for synthesizing Cu/CuO NPs. Furthermore, Akhter et al. [47] prepared CuNPs from stem extract of holoparasitic plants (*Orobanche aegyptiaca*) which were found to be active against *E. coli* and *S. aureus* and exhibit nematicidal activity. Another report by Sukumar et al. [48] showed that *Caesalpinia bonducella* seed extract synthesized CuO NPs could be used as a graphite electrode surface modifier and also possesses high antibacterial activity. Sarker et al. [49] prepared spherical, mono-disperse, and highly stable CuO NPs in a unique and economical way by using *Adiantum lunulatum* whole plant extract.

Another literature report by Rabiee et al. [50] demonstrated CuO NPs synthesis by using leaf extracts of *Achillea millefolium*. Investigation of the catalytic activity of CuO NPs for azide-alkyne cycloaddition and A^3 coupling reaction, and also the photocatalytic activity was examined for the degradation of MB dye. Ethanolic and aqueous extracts of hawthorn fruit were chosen to prepare monodispersed and stable CuNPs by Długosz et al. [51]. Recently, Nieto-Maldonado et al. [52] synthesized CuNPs using extracts of fresh petals of *Rosa* 'double delight' or fresh leaves of *Gardenia jasminoides* Ellis as stabilizing agents. A simple, clean, and efficient process for synthesizing CuNPs was further developed by Shubhashree et al. [53] by using *Hyptis suaveolens* (L.) extracts. Furthermore, Tamil Elakkiya et al. [54] synthesized CuO NPs using *Sesbania aculeate* leaf extract, which increased the growth of *Brassica nigra* and exhibited powerful antimicrobial activity. Table 1 indicates synthesis of Cu-based NPs using various plant extracts.

Green Production of Iron-Based Nanoparticles

Iron oxide nanoparticles (IONPs) synthesis is in progress due to their unique properties including super-paramagnetism, biocompatibility, non-toxic nature, as well as biodegradability, cost-effective production, etc. [55, 56]. Investigations into the Fe-based NPs preparation via plant extracts have been thoroughly examined by many authors [57-60].

FeNPs are commonly synthesized using sodium borohydride ($NaBH_4$) , which is quite expensive and not eco-compatible. Hence, different tea extracts were used for FeNPs synthesis via the green route [61, 62]. The polyphenols present in tea catalysed the synthesis of Fe NPs. Furthermore, IONPs functionalized bio-nanocomposite prepared by using pomegranate leaf extract [63] was found to be efficient in removing hexavalent chromium. Additional application of FeNPs synthesised from *Eucalyptus* leaf extracts includes its use in wastewater treatment [64]. It is well known that fruit peels discarded in the production of fruit juice cause environmental pollution. These peels can be utilized for the production of FeNPs for various applications. In this regard, *Citrus maxima* peel extracts synthesized FeNPs are used for the reduction of Fe (III) in aqueous solution [65]. Further, *Hibiscus sabdariffa* Roselle flower synthesized FeNPs catalysed the oxidative degradation of rhodamine B [66]. A simple and fast procedure for the synthesis of spherical Fe_2O_3 NPs using fruit extracts of Cornelian cherry was reported by Rostamizadeh et al. [67]. These Fe_2O_3 NPs are found to be more effective in stimulating

Table 1: Synthesis of copper-based nanoparticles using plant extracts.

S. No.	Plant	Reducing or capping agent	Size (nm)	Structure /Shape	References
1.	*Punica granatum*	Seed extract	43.9	Semi-spherical	[38]
2.	*Rhuscoriaria L.*	Fruit extract	22	Semi-spherical	[39]
3.	*Citrofortunella macrocarpa*	Leaf extract	54 - 68	Spherical	[40]
4.	*Citrus grandis*	Peel extract	22 - 27	Spherical	[45]
5.	*Ailanthus altissima*	Leaf extract	20	Spherical	[41]
6.	*Hagenia abyssinica*	Leaf extract	34.76	Mix. of spherical hexagonal, triangular cylindrical and irregular	[43]
7.	*Adiantum lunulatum*	Plant extract	1.5 - 20	Spherical	[49]
8.	*Achillea millefolium*	Leaf extracts	28	Semi-spherical	[50]
9.	*Hawthorn berries*	Fruit extract	200	Spherical	[51]
10.	*Rosa* 'double delight'	Fresh petals	11.7	Spherical	[52]
11.	*Gardenia jasminoides* Ellis	Fresh leaves	3	Spherical	[52]

the growth of barley than its bulk. Another catalytic application of the magnetic NPs synthesized by Prasad et al. using watermelon rinds includes the preparation of bioactive tetrahydro-pyrimidine derivatives [68]. This is eco-friendly green method for the synthesis of tetrahydro-pyrimidine derivatives in high yield (94%) with only 5 mmol of Fe_3O_4 NPs as catalyst without the requirement of additional reductant or surfactant. Furthermore, Yew et al. reported the preparation of magnetite NPs by using seaweed, *Kappaphycus alvarezii* [69]. In one more study, Ardakani et al. [70] synthesized spherical FeNPs using aqueous leaf extract of *Chlorophytum comosum,* which can be utilized to control the removal of methyl orange from the aqueous solution.

Nanoscience plays a very important role in controlling air pollution and in the degradation of dyes. In this perspective, Karpagavinayagam and Vedhi [71] developed a non-toxic and clean method for the synthesis of IONPs using *Avicennia marina* flower extract. Table 2 indicates synthesis of various iron-based NPs using natural plant extracts.

Future Perspectives

This review highlighted current developments in the green synthetic protocols using plant extracts for Fe and Cu-based NPs and their modifications with respect to particular application in catalysis ranging from organic transformations to electrocatalysis, photocatalysis, and so on. Cu-based NPs synthesized by using various plant extracts exhibit excellent photocatalytic activity for the degradation of methylene blue and for the purification of rhodamine B dye polluted water and CuNPs were found to be active against *S. aureus* and *E coli*. They also exhibit nematicidal activity and could be used as a graphite electrode surface modifier. Fe-based NPs are efficient in removing hexavalent chromium and can be used for wastewater treatment. Further, they can be used to catalyse the oxidative degradation of rhodamine B, removal of methyl orange from the aqueous solution, preparation of bioactive tetrahydro-pyrimidine derivatives and to control air pollution. These investigations suggest that Fe and Cu-based nanomaterials are promising candidates for environmental, biomedical, and catalytic applications. Further, more studies are required regarding the synthesis and functionalization

Table 2: Synthesis of iron-based nanoparticles using plant extracts.

S. No.	Plant	Reducing or capping agent	Size (nm)	Structure /Shape	References
1.	*Hibiscus sabdariffa*	Flower extract	18	Spherical	[66]
2.	*Citrullus lanatus*	Rind extract	2 - 20	Spherical	[68]
3.	*Kappaphycus alvarezii*	Seaweed extract	14.7	Spherical	[69]
4.	*Chlorophytum comosum*	Leaf extract	Below 100	Spherical	[70]
5.	*Avicennia marina*	Flower extract	10 - 40	Honeycomb	[71]

of Cu and Fe-based nanoparticles for particular application.

Conflict of Interest

Authors declare that they have no conflict of interest.

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