

Review Article

Plant-Mediated Green Synthesis of Iron Nanoparticles

Mihir Herlekar,¹ Siddhivinayak Barve,¹ and Rakesh Kumar²

¹ Department of Botany, KET's V.G. Vaze College of Arts, Science and Commerce, Mulund East, Mumbai, Maharashtra 400081, India

² National Environmental Engineering Research Institute, 89/B, Dr. Annie Besant Road, Worli, Mumbai, Maharashtra 400018, India

Correspondence should be addressed to Mihir Herlekar; herlekarm@gmail.com

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In the recent years, nanotechnology has emerged as a state-of-the-art and cutting edge technology with multifarious applications in a wide array of fields. It is a very broad area comprising of nanomaterials, nanotools, and nanodevices. Amongst nanomaterials, majority of the research has mainly focused on nanoparticles as they can be easily prepared and manipulated. Physical and chemical methods are conventionally used for the synthesis of nanoparticles; however, due to several limitations of these methods, research focus has recently shifted towards the development of clean and eco-friendly synthesis protocols. Magnetic nanoparticles constitute an important class of inorganic nanoparticles, which find applications in different areas by virtue of their several unique properties. Nevertheless, in comparison with biological synthesis protocols for noble metal nanoparticles, limited study has been carried out with respect to biological synthesis of magnetic nanoparticles. This review focuses on various studies outlining the novel routes for biosynthesis of these nanoparticles by plant resources along with outlining the future scope of work in this area.

1. Introduction

Nanotechnology can be defined as the manipulation of matter through certain chemical and/or physical processes to create materials with specific properties, which can be used in particular applications [1]. A nanoparticle can be defined as a microscopic particle that has at least one dimension less than 100 nanometers in size [2]. Unlike bulk materials, they have unique optical, thermal, electrical, chemical, and physical properties [3] and, hence, they find a variety of applications in the areas of medicine, chemistry, environment, energy, agriculture, information, and communication, heavy industry, and consumer goods [4].

Conventional nanoparticle synthesis methods like attrition and pyrolysis have drawbacks such as defective surface formation, low production rate, high cost of manufacturing, and large energy requirement [2]. Chemical synthesis methods (e.g., chemical reduction, sol gel technique, etc.) involve the usage of toxic chemicals, formation of hazardous byproducts, and contamination from precursor chemicals [2]. Hence, there is a growing need to develop clean, nontoxic, and environment-friendly procedures for nanoparticle synthesis. Some of the distinct advantages that

biological synthesis protocols have over the conventionally used physical and chemical methods are

- (a) clean and eco-friendly method, as toxic chemicals are not used [5];
- (b) the active biological component like enzyme itself acts as a reducing and capping agent, thereby reducing the overall cost of the synthesis process [5];
- (c) small nanoparticles can be produced even during large-scale production [6];
- (d) external experimental conditions like high energy and high pressure are not required, causing significant energy saving [7].

A very wide range of biological resources like microorganisms (bacteria, yeast, fungi, algae, and viruses) and plants can be used for nanoparticle synthesis [8]. While microbe-based protocols have been developed from the cumulative research efforts of several authors, plant-mediated biological synthesis of nanoparticles has gained importance only in the recent years [9]. Plant extracts reduce the metal ions in a shorter time as compared to microbes. Depending upon plant type and concentration of phytochemicals, nanoparticles

are synthesized within a few minutes or hours, whereas microorganism-based methods require a longer time [10]. The major drawback of microbe-mediated nanoparticle synthesis is the obligatory constraint of aseptic conditions, which requires trained staff, and raises the scaling-up cost [11]. All these reasons, along with the easy availability of plants in nature, make them more preferred biological resources than microbes.

Magnetic nanoparticles have emerged as a new class of important nanoparticles as they possess many exceptional properties like superparamagnetism, high coercivity, and so forth. These nanoparticles, when synthesized by conventional methods, have several limitations such as the following.

- (a) Nanoscale zero-valent iron particles (nZVI) synthesized by physical and chemical methods are highly reactive in nature and tend to form aggregates, which ultimately results in loss of reactivity [12, 13].
- (b) The magnetic nanoparticles synthesized by conventional methods cannot be used in biomedical applications wherein nonpolar organic solvents are used [14].
- (c) As-synthesized iron oxide nanoparticles lose their magnetism and dispersibility when exposed to air [15].

A review paper on microbial synthesis of magnetic nanoparticles has been published by Abhilash et al. [16]. Two principal mechanisms, *namely*, biologically induced mineralization (BIM) and biologically controlled mineralization (BCM), have been discussed, by which microbes synthesize iron oxide nanoparticles. However, plant-mediated synthesis of magnetic nanoparticles has remained a relatively unexplored research area with the majority of papers being published only in the last two years. To the best of our knowledge, a comprehensive review article summarizing the notable findings of researchers in this field has not been produced. This paper aims to fill this lacuna and provide an updated consolidation of the published literature regarding biosynthesis of magnetic nanoparticles by plant resources along with its advantages and future scope of work in this area. The paper is divided into three main sections depending upon the usage of plant resources for nanoparticle synthesis, *namely*, in the form of the extract, whole plant part (biomass), and as a template.

2. Plant Extract

Till now, iron nanoparticles (nZVI and iron oxide) have been mostly synthesized using different plant extracts. Plant extracts act as low-cost reducing and stabilizing agents. Magnetic nanoparticle synthesis is carried out at room temperature or by the hydrothermal route by mixing plant extract with metal salt solution in a fixed ratio.

2.1. Synthesis at Room Temperature

2.1.1. Commonly Used Plant Species. The most commonly used plant resource for iron nanoparticle synthesis is tea extract. nZVI were synthesized by Hoag et al. [17] by allowing

Camellia sinensis (green tea) extract to react with 0.1M FeCl₃ solution. These nanoparticles were synthesized at room temperature within a few minutes, and tea polyphenols acted as the reducing and capping agent. The activity of these nanoparticles was found to be higher when compared to two commonly used iron chelates for bromothymol blue degradation.

In another work, the synthesis was carried out at room temperature using different volumes of tea extract and Fe(NO₃)₃ solution to check the effect of tea extract concentration on size of the nanoparticle formed; it was found that particle size decreased with increase in the concentration. The size of the nanoparticles synthesized by borohydride reduction method was found to vary between 50 nm and 500 nm. The biocompatibility of nZVI synthesized using green tea and borohydride as the reducing agent was assessed using methyl tetrazolium (MTS) and lactate dehydrogenase (LDH) assay by exposing cell lines to nZVIs for 24 to 48 hours. LDH leakage increased with an increase in particle size, stressing the cellular membrane. Hence, nZVI synthesized using green tea being much smaller in size were shown to be nontoxic to human keratinocytes when compared to nanoparticles synthesized using the borohydride reduction process [18].

Shahwan et al. [19] synthesized iron nanoparticles, GT-Fe NPs (consisting mainly of iron oxide/oxohydroxide), using green tea extracts. These nanoparticles served as Fenton-like catalyst for the degradation of cationic dyes such as methylene blue (MB) and anionic dyes like methyl orange (MO). Almost complete removal of both dyes was achieved in 200 and 350 minutes for MB and MO, respectively. In the case of GT-Fe NPs, almost 100% removal of MB and MO was observed at an initial dye concentration of 10 mg/L and 100 mg/L. The efficiency was slightly lower for MB (96.3% for 10 mg/L and 86.6% for 100 mg/L) and significantly lower in the case of MO (61.6% for 10 mg/L and 47.1% for 100 mg/L) when iron nanoparticles were synthesized using the conventional borohydride reduction method.

Kuang et al. [20] used three different tea extracts, *namely*, green tea (GT), oolong tea (OT), and black tea (BT) to synthesize iron nanoparticles. These nanoparticles were tested for their capacity to act as a catalyst for Fenton-like oxidation of monochlorobenzene (MCB). GT-Fe NPs were able to remove 69% of MCB followed by 53% by OT-Fe NPs and 39% by BT-Fe NPs in 180 minutes. Under optimum experimental conditions, GT-Fe NPs were able to oxidatively degrade 81% of MCB along with a 31% reduction in chemical oxygen demand (COD). The surface area (5.82 m²/g) and percent Fe content (14.5%) of as-synthesized nanoparticles were low. Figure 1 displays the SEM image of irregular spherical iron nanoparticles indicating the chain-like structure.

Huang et al. [21] used oolong tea extract for synthesizing iron nanoparticles. The polyphenol/caffeine content of the extract served as the reducing and capping agent. Characterization by XRD and FTIR indicated that zero valent iron, maghemite, and magnetite nanoparticles were present. Due to organic coating of biomolecules, as-synthesized nanoparticles remained in a dispersed state and also showed good reactivity. Interestingly, oolong tea extract-mediated

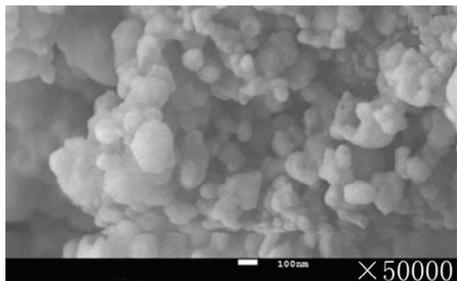


FIGURE 1: SEM image of green tea Fe NPs at 50,000 amplification.

iron nanoparticles displayed efficient degradation (75.5% in 60 minutes, at equilibrium) of the otherwise difficult-to-degrade dye malachite green, with a degradation rate of 0.045 min^{-1} . Malachite green degradation obeyed pseudo-first-order kinetics.

2.1.2. Plant Extract Derived from Agrowaste. One of the major drawbacks of using plant resources for nanoparticle synthesis is the destruction of plants and plant parts. A possible way to avoid this and to serve the additional purpose of pollution mitigation is to employ agrowaste, which is otherwise a significant source of pollution. Some authors have used agrowastes as low-cost bioreducing agents.

Njagi et al. [22] used aqueous *Sorghum* sp. (hybrid sorghum) bran extract for nZVI synthesis. The extract was prepared by obtaining sorghum bran powder in double-distilled water at different temperatures for half an hour. UV-visible spectra for these nanoparticles were similar to those for nZVI synthesized by tea polyphenols. Based on the XRD pattern, the nanoparticles were found to be amorphous in nature. The catalytic activity for the degradation of bromothymol blue was found to be higher for higher concentration of nanoparticles.

Eucalyptus globulus leaf extract was used by Madhavi et al. [23] as a bioreducing agent to synthesize nZVI. Polyphenol compounds in plant extract like oenothien B were identified to be responsible for the synthesis and stabilization of nZVI. The nanoparticles were found to be stable even after two months. 0.8 g/L of nZVI was sufficient to remove 98.1% of 400 mg/L hexavalent Cr within 30 minutes. Langmuir and Freundlich adsorption isotherm explained the adsorption process. Removal of Cr followed pseudo-second-order kinetic model. The sorption capacity of the adsorbent was found to be mainly influenced by reaction time and initial Cr (VI) concentration. More time was required for higher initial chromium concentration. 90 minutes were required for 71.9% removal of chromium when initial concentration in soil was 400 mg/L.

Wang [24] synthesized iron nanoparticles using eucalyptus leaf extract by adding 0.1 M FeCl_3 solution in a ratio of 1:2. The lack of any distinct diffraction peak indicated that the as-synthesized nanoparticles were amorphous in nature. An azo dye, acid black 194, was used to test

the adsorption-flocculation capacity of nanoparticles. As-synthesized nanoparticles exhibited very high adsorption-flocculation capacity and, at 25°C , 1 gm of nanoparticle removed 1.6 gm of the organic dye acid black 194. Polyphenol capping around the nanoparticles enabled its use in water purification and also in the remediation of groundwater.

Wang et al. [25] synthesized polydispersed iron nanoparticles employing eucalyptus leaf extract obtained from its leaf litter. nZVI, Fe_3O_4 , and Fe_2O_3 were the different forms of nanoparticles synthesized during the process. Due to the presence of different phytochemicals, each with varied reducing power in the extract form, the nanoparticles were polydispersed unlike in the case of nanoparticles synthesized using chemical reducing agent. For the first time, biologically synthesized nanoparticles were used for the treatment of eutrophic wastewater. After 21 days, percent removal of total N, total P, and COD was 71.7%, 30.4%, and 84.5%, respectively. The reason for very low P removal was assigned to the absence of calcium, magnesium, or aluminum, which act as precipitating agents. Figure 2(a) represents SEM image of polydispersed Fe nanoparticles synthesized using eucalyptus leaf extract.

$\text{Fe}^0/\text{Fe}_3\text{O}_4$ nanoparticles were successfully synthesized using pomegranate leaf extract by Rao et al. [26]. These nanoparticles were coated on two strains (NCIM 3589 and NCIM 3590) of heat-killed yeast cells *Yarrowia lipolytica*, which is considered a good biosorbent itself. The bio-nanocomposite was evaluated for its capacity to remove hexavalent chromium. The sorption capacity of magnetically modified yeast cells was three times more than that of unmodified yeast cells. At initial chromium concentration of 1000 mg/L and under optimum conditions, modified NCIM 3589 showed better adsorption capacity (186.32 mg/g) than modified NCIM 3590 (137.31 mg/g).

Venkateswarlu et al. [27] used plantain peel extract as a low-cost bioreducing agent for synthesizing magnetite nanoparticles. Iron salt solution was hydrolyzed, resulting in the formation of ferric hydroxide, which was subsequently reduced by various biomolecules to form Fe_3O_4 nanoparticles. Based on FTIR results, the possible involvement of polyphenols and other biomolecules in nanoparticle synthesis has been understood. The as-synthesized nanoparticles possess ample surface area ($11.31 \text{ m}^2/\text{g}$) and high saturation magnetization (15.8 emu/g). Based on the results obtained for BET surface area and pore volume, the structure of nanoparticles was assigned to be mesoporous. By virtue of this property, the as-synthesized nanoparticles can be used in the field of environmental remediation for the removal of toxic metals and dyes. Figure 2(b) depicts TEM image of nearly monodispersed magnetite nanoparticles synthesized using plantain peel extract.

Banana peel ash extract was used to synthesize iron oxide nanoparticles, and aqueous extract of *Colocasia esculenta* leaves was used to reduce graphene oxide by Thakur and Karak [28]. The formation of iron oxide was confirmed using XRD (peaks at 30.15, 36.2, 43.32, 53.89, and 29) and FTIR (stretching Fe-O vibration at 576 nm). 57.13 and 62.05 gm of iron oxide/reduced graphene oxide nanohybrids were able to

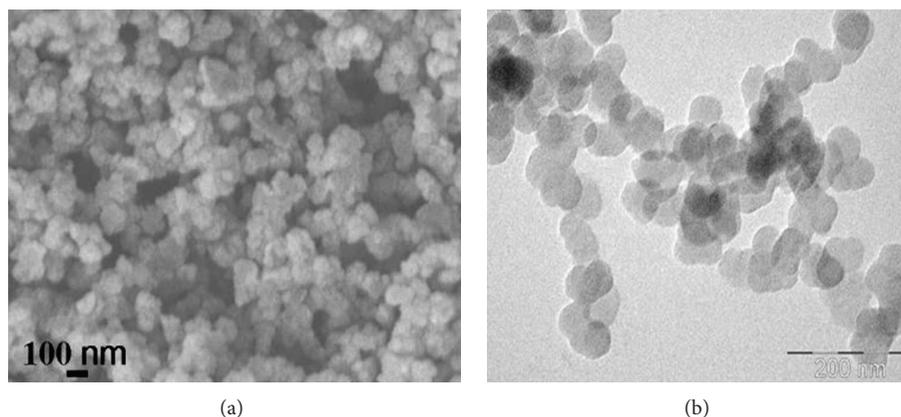


FIGURE 2: High magnification SEM (a) image of EL-Fe NPs and TEM (b) image of PP-Fe NPs.

remove 10 ppm of tetrabromobisphenol A in 30 minutes and lead and cadmium in 10 minutes at optimum experimental conditions. The nano hybrids showed good reusability with no significant decrease in efficiency even after the third cycle.

Kiruba Daniel et al. [29] used leaf extract of the evergreen shrub *Dodonaea viscosa* to synthesize iron nanoparticles. The effect of leaf extract concentration on nanoparticle synthesis was studied. Based on FTIR study, flavonoids in *D. viscosa* leaf were identified to be responsible for the reduction of metal salt along with polyhydroxy groups in santin. Tannin and saponins were considered to be acting as capping agents. The antimicrobial activity of synthesized nanoparticles was evaluated against human pathogens, namely, *E. coli*, *K. pneumoniae*, *P. fluorescens*, *S. aureus*, and *B. subtilis*. A very low concentration of as-synthesized nanoparticles was sufficient to display effective antimicrobial activity as compared to earlier reports.

2.1.3. Other Plant Species. Senthil and Ramesh [30] reported the green synthesis of Fe_3O_4 nanoparticles at room temperature using leaf extract of *Tridax procumbens*. Carbohydrates present in the plant extract were responsible for nanoparticle synthesis. XRD showed clearly distinguishable peaks, which could be perfectly indexed to crystalline Fe_3O_4 . As-synthesized nanoparticles were effective against *Pseudomonas aeruginosa*. The zone of inhibition increased from 1 mm to 2 mm when the concentration of nanoparticles increased from 10 μL to 40 μL .

Narayanan et al. [31] synthesized superparamagnetic magnetite/gold ($\text{Fe}_3\text{O}_4/\text{Au}$) hybrid nanoparticles at room temperature using grape seed proanthocyanidin (GSP) for the first time. These nano hybrids were used as better CT contrast agents than conventionally used iodine-contrast agents. The long-term biocompatibility even at higher doses warranted its use in medical applications.

Machado et al. [32] screened leaf extracts of 26 plants for the production of nZVI. Importance of synthesis variables like extraction temperature, time, and leaf mass to solvent volume ratio was checked. 80°C was identified as the optimum temperature, whereas in extraction time and leaf mass, solvent volume ratio varied as per leaf type. The quality

of the extracts prepared was assessed by determining their antioxidant activity using the ferric reducing antioxidant power (FRAP) method. Plant polyphenols play a vital role in conferring antioxidant property and, hence, the total polyphenol content (TPC) of the extract was estimated using the Folin-Ciocalteu method. On the basis of results obtained from FRAP assay and TPC content, pomegranate, mulberry, and cherry extracts were used for nZVI synthesis. Iron nanoparticles formed by mixing plant extract and Fe (III) solution were characterized by TEM.

In another study, Machado et al. [33] synthesized nZVI using grape marc, black tea, and vine leaf extract. The degradation efficiency of the synthesized nanoparticles was tested against the commonly used anti-inflammatory drug ibuprofen. In aqueous solution, at initial concentration of 10 mg/L and pH 7, iron nanoparticles synthesized using black tea showed degradation efficiency of 51 to 66%. At pH 3, efficiency of nZVI synthesized using black tea extract decreased by 30%. The efficiency was 32% and 42% for grape marc and vine leaf extract nZVI, respectively. In degradation experiments conducted for sandy soil contaminated with ibuprofen (2.8 mg/kg), vine leaf extract nZVI showed maximum efficiency (62%) whereas black tea extract nZVI was the least efficient (36%). The degradation process in sandy soil was slower than that in aqueous solution due to time required for percolation. The combination of nZVI with Fenton reagents showed improved efficiency up to 95%.

Kumar et al. [34] synthesized stable iron oxide (Wuestite) using aqueous extract of *Terminalia chebula* dry fruit pericarp. The as-synthesized nanoparticles were pure iron oxide (confirmed by energy dispersive X-ray spectroscopy (EDS)) and stable up to 21 days. The phytochemicals in the extract acted as reducing and capping agent.

Leaves of three plants native to Australia, namely, *Eucalyptus tereticornis* (A), *Melaleuca nesophila* (B), and *Rosmarinus officinalis* (C) were explored by Wang et al. [35] for their efficiency in synthesizing iron nanoparticles and used as heterogeneous Fenton-like catalyst for decolorization of azo dye (Acid black 194) and total organic carbon (TOC). Fe-P NPs A showed maximum removal capacity of dye followed by Fe-P NPs B and Fe-P NPs C, depending on the size of

TABLE 1: Size and morphology of iron nanoparticles synthesized by plant extracts.

Plant	Morphology	Size (nm)	Reference
Green tea	Spherical	5–15	[17]
Tea powder	Differs according to the quantity of tea extract		[18]
Green tea	Irregular clusters	40–60	[19]
Green tea, oolong tea, and black tea	Irregular spherical	20–40	[20]
Oolong tea	Spherical	40–50	[21]
Sorghum bran	Spherical	40–50	[22]
Eucalyptus	Spherical	50–80	[23]
Eucalyptus	Cubic	40–60	[24]
Eucalyptus	Spherical	20–80	[25]
Pomegranate	ND	100–200 nm	[26]
Plantain peel	Spherical	Less than 50 nm	[27]
Banana peel	ND	10–25	[28]
<i>Dodonaea viscosa</i>	Spherical	50–60	[29]
<i>Tridax procumbens</i>	Irregular spheres	80–100	[30]
GSP	ND	Around 30	[31]
Pomegranate, mulberry, and cherry	Spherical	10–30	[32]
Vine leaves, black tea leaves, and grape marc	ND	15–45	[33]
<i>Terminalia chebula</i>	Chain-like	Less than 80 nm	[34]
<i>Eucalyptus tereticornis</i> (A)	Spherical (A and B) Aggregates like grapes (C)	40–60 (A & B)	[35]
<i>Melaleuca nesophila</i> (B)			
<i>Rosmarinus officinalis</i> (C)			

Note. ND: not done.

the nanoparticles synthesized. Complete decolourization was achieved in 200 minutes without any pH adjustment and at an initial concentration of 50 ppm. As-synthesized nanoparticles were also able to remove over 87% of TOC within four days.

Table 1 describes the size and morphology of magnetic nanoparticles synthesized by using extracts of the plants.

2.2. Hydrothermal Synthesis. Hydrothermal synthesis involves the preparation of the plant extract and dissolution of the desired molarity of the metal salt in it. The mixture is then allowed to react in a Teflon-lined autoclave under atmospheric pressure at different temperatures for a fixed interval of time. This process requires lower temperature than the calcination process to convert the precursor into crystalline materials.

Phumying et al. [36] synthesized Fe_3O_4 nanoparticles by the hydrothermal method using aloe vera plant extract. High purity of synthesized nanoparticles was confirmed with XRD. The average particle size calculated from XRD increased with an increase in temperature and time. Based on the coercivity, it was concluded that the nanoparticles were superparamagnetic in nature. The authors observed that increasing the reaction temperature and time resulted in magnetite nanoparticles with enhanced crystallinity and saturated magnetization. The coating of glycoproteins, namely, aloin, aloe-emodin, barbaloin, and isobarbaloin, originating

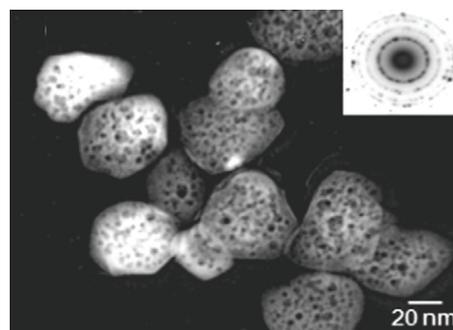


FIGURE 3: TEM image of $\alpha\text{-Fe}_2\text{O}_3$ NPs synthesized by green tea leaves.

from aloe vera, was considered as the reason for the decrease in saturation magnetization of Fe_3O_4 as compared to its bulk counterpart.

Ahmmad et al. [37] successfully synthesized highly pure hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles by the hydrothermal synthesis method using green tea (*Camellia sinensis*) leaf extract. Figure 3 shows the TEM image of somewhat spherical and highly porous particles. The surface area of as-synthesized nanoparticles ($22.5\text{ m}^2/\text{g}$) was four times higher, whereas the photocatalytic activity (capacity to generate OH radical when irradiated with visible light) was found to be

TABLE 2: Size and morphology of iron nanoparticles synthesized by the hydrothermal method.

Plant	Morphology	Size (nm)	Reference
Aloe vera	Depends on reaction temperature and time	Around 6–30	[36]
Green tea	Somewhat spherical	40–80	[37]

about two times higher than commercially available hematite nanoparticles. The performance of the photoelectrochemical cell was enhanced when these nanoparticles were applied in wet-type solar cell. Table 2 depicts size and morphology of nanoparticles synthesized by the hydrothermal route.

3. Plant Biomass

As discussed earlier, iron oxide nanoparticles are prone to oxidation when exposed to air and also tend to form aggregates in aqueous solution [12, 13, 15]. To avoid this, nanoparticles should be coated or mixed with supporting materials such as humic acid and carbon [38]. Plant biomass can serve as a highly economical, renewable, and rich source of carbon. It can be used to synthesize nanoparticles with little or no pretreatment. During the synthesis, plant biomass serves as the reducing agent as well as support for the as-synthesized nanoparticles.

Nanoparticle synthesis was carried out by exposing pretreated and milled powder of *Medicago sativa* (alfalfa) to the salt solution of ferrous ammonium sulfate. A reaction time of 48 hours was given for nanoparticle synthesis. In this study, the focus was also on determining the role of pH as a size-limiting parameter. It was found that the optimum pH to obtain nanoparticles of size less than 10 nm was 10 [39]. In the second study, more emphasis was laid on electron microscopy-based characterization of the above-mentioned iron oxide nanoparticles. Advanced techniques like high angle annular dark field (HAADF) Z contrast was used to locate the nanoparticles in alfalfa biomass. Energy dispersive spectroscopy (EDS) and high resolution transmission electron microscopy (HRTEM) were used for further characterization of the synthesized nanoparticles [40].

Ramasahayam et al. [41] developed a protocol for microwave-assisted synthesis of magnetic nanocomposite using pine wood shavings and a spacer (saturated NaCl), which they denoted as Media 1. Figure 4 displays the SEM image of nanoparticles embedded in a woody matrix in a highly dispersed state. Tannin was the renewable resource, and the microwaving process played an important role in the production of reduced iron oxide. Another nanocomposite (Media 2) prepared during the study employed oven-drying instead of microwaving and was without any spacer. This reduced iron oxide nanocomposite was used to remove phosphorus from water. Media 1 showed much improved P removal at higher initial concentration as compared to Media 2. Phosphorus was removed completely when the initial concentration was 1 mg/L. At an initial concentration of 500 mg/L, this renewable resource-based nanocomposite showed the adsorption capacity of 43.7 mg/g, which was

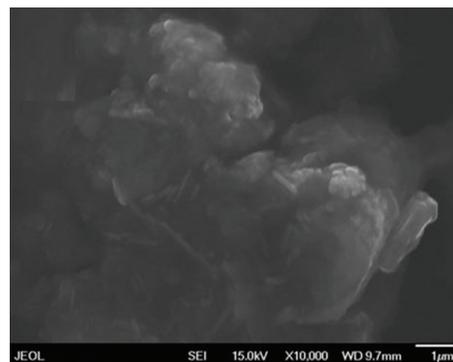


FIGURE 4: SEM image of reduced iron oxide NPs in pine wood shaving at 10,000 magnifications.

TABLE 3: Size and morphology of iron nanoparticles synthesized by plant biomass.

Plant	Morphology	Size (nm)	Reference
Alfalfa biomass	ND	3.1 Nm	[39]
Alfalfa biomass	ND	1–10 nm	[40]
Pine wood shavings	Irregular rod like and spherical	10 (rod like) 100 nm (spherical)	[41]
Orange peel	Rod like	20–40	[43]

Note. ND: not done.

much higher than the earlier reported cases. Also, the low-cost nanocomposite was regenerated four times without significant loss of sorption capacity.

Cellulosic materials can also be used to synthesize and stabilize metal nanoparticles. Orange peel mainly consists of starch, cellulose, hemicelluloses, and lignin [42]. Ethanol-treated orange peel powder was used by López-Téllez et al. [43] to synthesize iron oxide nanorods. Cellulose content of orange peel reduced Fe (II) metal ions and nanoparticles formed were stabilized on the surface of the orange peel by the means of electrostatic and weak van der Waals interactions between reduced form of metal and functional groups of cellulose and hemicellulose components. Effect of precursor iron salt and contact time was studied to understand their effect on the formation of nanorods. Amongst the precursor salt solutions screened, 0.01 M iron acetate resulted in well-dispersed iron nanoparticles after a contact time of six hours. Iron was deposited on the surface of the biomass and it mainly existed in the form of iron, iron (II) oxide, and magnetite. The nanobiocomposite removed 96% and 76% of 10 mg/L and 50 mg/L chromium, respectively. The adsorption capacity of this novel nanocomposite was found to be 7.44 mg/g as compared to adsorption capacity of 1.9 mg/g achieved by only orange peel. Table 3 shows the variation in size and morphology when biomass of different plant species were used for synthesis of iron nanoparticles.

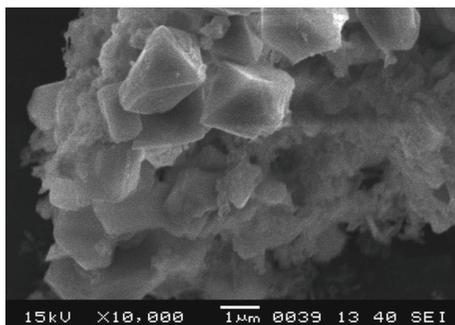


FIGURE 5: Cuboid/pyramid-shaped crystal structure of magnetite (Fe_3O_4) nanoparticles by tea waste.

4. Using Plant Biomass as Template

Template-assisted synthesis is a method in which the template serves as a structure within or surrounding which a nanostructure is generated; herein, the nanostructure develops morphology complimentary to the template. Biotemplates, also called as soft templates, have distinct advantages over other templates in being low-cost, renewable, eco-friendly, and also easily removable [44]. In the case of plant material as biotemplate, the biomolecules sometimes aid in nanoparticle synthesis.

Synthesis of superparamagnetic Fe_3O_4 nanoparticles at room temperature and atmospheric pressure using soya bean sprout as biotemplate was first reported by Cai et al. [45]. This was a first of its kind study in which plant template was used for magnetite nanoparticle synthesis at room temperature. It served as the nucleation site during nanoparticle synthesis and controlled the size and morphology of nanoparticles. The nanoparticles were simultaneously formed on the epidermal surface and also in the interior stem wall when the template was immersed in Fe^{2+} and Fe^{3+} solutions for four hours, later allowing it to react with an alkali (NaOH). The nanoparticles were recovered from the template by the processes of milling, magnetic separation, washing, and drying. By means of FTIR analysis, the role of soya bean sprout proteins and other biomolecules in nanoparticle synthesis was confirmed. As-synthesized nanoparticles had a saturation magnetization value of 37.1 emu/g.

Low-cost magnetite nanoparticles were successfully synthesized using tea waste as template by Lunge et al. [46]. Figure 5 depicts cuboid/pyramid-shaped crystal structure of magnetite nanoparticles. The cost of synthesis was estimated to be Rs. 136 per kg whereas cost of treatment was as low as Rs. 140 for treating 100 liter water. As-synthesized nanoparticles were evaluated for arsenic (As (III) and (V)) removal and showed much higher adsorption capacity than adsorbents reported till date. The adsorption capacity for As (III) was reported to be 188.69 mg/g and that for As (V) was 153.8 mg/g. The adsorption data fitted well with the Langmuir adsorption model. Equilibrium was achieved within 10 hours at the initial concentration of 2 mg/L As (III), adsorbent dose of 1 g/L, and at neutral pH. At higher initial concentration, the sorption

TABLE 4: Size and morphology of iron nanoparticles synthesized by plant biotemplate.

Plant	Morphology	Size (nm)	Reference
Soya bean sprout	Spherical	8	[45]
Tea waste	Cuboid/pyramid	5–25	[46]

process followed pseudo-first-order kinetics whereas pseudo-second-order kinetics was observed at low concentration of As (III).

Thermodynamic study revealed endothermic nature of reaction. The effect of operational parameters on arsenic removal showed that percent removal increased with the increase in the dose of adsorbent but decreased with the increasing initial concentration of solute. The adsorbent performed best in pH range of 7.0 to 8.0 which indicates that no pH adjustment is required when adsorbent is used for arsenic removal from drinking water. Amongst the coexisting anions, sulfates interfered the most and nitrate the least in arsenic removal. The removal efficiency of the adsorbent decreased when the initial concentration of interfering anions increased from 100 to 800 mg/L. The adsorbent could be successfully regenerated using NaOH and reused for five successive cycles.

Table 4 shows size and morphology of magnetic nanoparticles when plant material was used as bio-template.

5. Conclusion

This review highlights the recent developments in iron nanoparticle synthesis by plant either in the form of extracts or as it is. While physical and chemical methods of synthesis are more common, several eco-friendly and economically feasible synthesis protocols have also been developed, in some cases even by employing unused plant parts such as peels and leaves. As-synthesized nanoparticles have been successfully implemented in the fields of medicine and environmental remediation. However, the enormity of future research scope in this field cannot be accentuated enough.

6. Future Scope of Work

- (i) There is a clear need to explore plant resources other than tea and eucalyptus, which have been commonly used in contemporary research.
- (ii) The experimental conditions for the preparation of plant extract, *namely*, plant mass: solvent ratio, extraction temperature, and time, along with the mixing ratio of plant extract and metal salt solution, should always be optimized.
- (iii) Research efforts must also concentrate on the improvement of monodispersity and surface area of as-synthesized nanoparticles.
- (iv) For magnetic nanoparticle synthesis using plant biomass, research must focus on shortening the contact time to compete with the conventional chemical synthesis methods.

- (v) More emphasis should be accorded to employing plant waste for nanoparticle synthesis, considering that it serves the dual purpose of waste management.
- (vi) Ultimately, the application of these biologically synthesized nanoparticles in different fields should be promoted.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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