A Review on Facile Green of Magnetite Nanoparticles for Technological Applications

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Abstract*— In 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 the 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.

I. INTRODUCTION

Nanotechnology can be defined as the manipulation of matter through certain chemical and physical synthetic methods 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 nm in size [2]. Unlike bulk materials, they have unique thermal, optical, electrical, chemical, and physical properties and, hence, they find various applications in different areas like environment, medicine, agriculture, information, and communications in various industries and consumers goods [3]

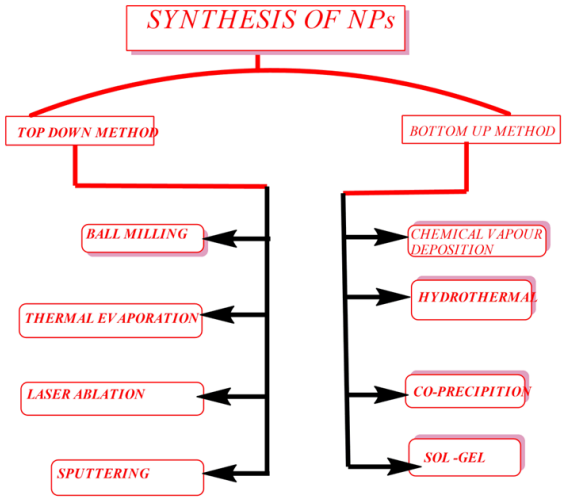

Figure 1: synthesis of nanomaterial's

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 [4]. Chemical synthesis methods (e.g., chemical reduction, sol-gel technique, etc) involve the use of toxic chemicals, formation of hazardous by products, and contamination from precursor chemicals [5].

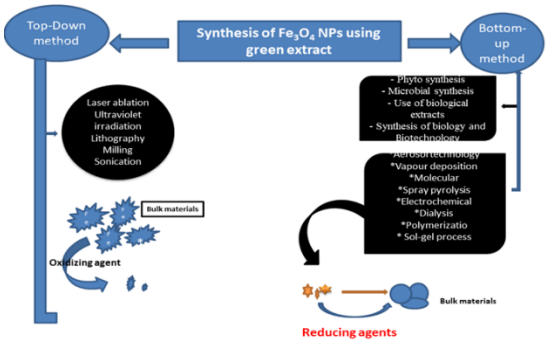

Figure2. Synthesis of Magnetite nanomaterials

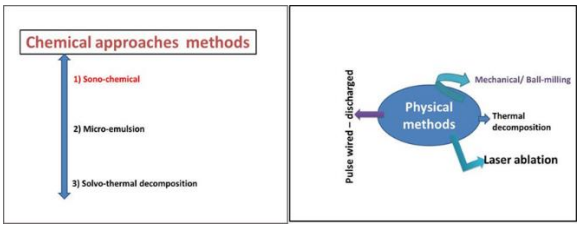

Figure 3: Chemical and physical methods for synthesis of nanomaterials.

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 clean and eco-friend method, as toxic chemicals are not used [6].

The active biological component like enzyme itself acts as a reducing and capping agent, thereby reducing the overall cost of the synthesis process [7]. Small nanoparticles can be produced even during large - scale production. External experimental conditions like high energy and high pressure are not required, causing significant energy saving [8]. A very wide range of biological resources like microorganisms (bacteria, yeast, fungi, algae, and viruses) and plants can be used for nanoparticles synthesis. While micro-based protocols have been developed from the cumulative research efforts of several authors, plant-mediated biological synthesis of nanoparticles has gained importance only in recent decades [9]. Plant extract reduces 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 microorganisms–based methods require a longer time [10]. The major drawback of microbes–mediated nanoparticles synthesis is the obligatory constraint of specific conditions, which requires trained staff, and raises the scanning-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.

Nanoscale zero-valent iron particles 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]

The magnetic nanoparticles synthesized by conventional methods cannot be used in biomedical applications wherein nonpolar organic solvents are used [14].As synthesized iron oxide nanoparticles lose their magnetism and dispersibility when exposed to air [15].

A review paper on the microbial synthesis of magnetic nanoparticles has been published by Abhilash et.al [16]. Two principle mechanisms, namely, biologically induced mineralization (BIM) and biologically controlled mineralization. Green synthesis of magnetite nanoparticles has remained a relatively unexplored research area with a majority of papers being published only in the last two decades. 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 the 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 a template.

II. PLANT EXTRACT

Till now magnetite nanoparticles (iron oxides) have been mostly synthesized using different plant extracts. Plant extract as low-cost reducing and capping agents. Iron nanoparticles synthesis is carried out at room temperature or by hydrothermal route by mixing plant extract with a metal salt solution in a fixed ratio.

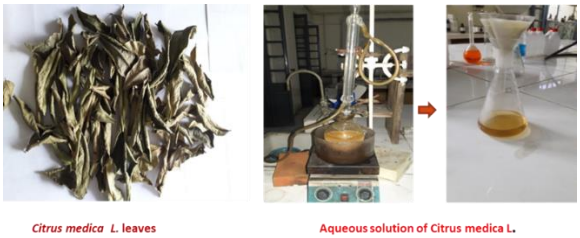

Fig 3: Preparation of an aqueous solution of leaf extracts

2.1 Synthesis of Magnetite (Fe_3O_4) nanomaterials

2.1.1 Commonly used plant species.

The most commonly used plant resource for iron nanoparticles synthesis is tea extract. Were synthesized by Hoag et al [17] by allowing Camellia sinensis (green tea) extract to react with 0.1 M $FeCl_3$ 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 $Fe(NO_3)_3$ solution to check the effect of tea extract concentration on the size of the nanoparticles formed; It was found that particle size decreased with increase in the concentration. The size of the nanoparticles synthesized by the borohydride reduction method was found to vary between 5 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) using assay by exposing cell lines to nZVI for 24 to 48hours. LDH leakage increased with an increase in particles size, stressing the cellular membrane. Hence, nZVI synthesized using green tea being much smaller in size were shown to be non-toxic to human keratinocytes when compared to nanoparticles synthesized using the borohydride reduction process[18].

Mebrahtu Hagos Kahsay et al (2018). facile synthesized of Magnetite nanoparticles (Fe_3O_4) using pod extract of *Dolichos Lablab L.* This nanoparticles are used to removes CV dye. Almost completely 200 min and temperature of 298 K.[19] displays the SEM images of spherical shape iron nanoparticles with particle size range of 8 to 60 nm.[19].

A.V Ramesh et al (2018) [20] Facile green synthesized Fe3O4 NPs using aqueous leaf extract of Zanthoxylum armatum DC. For efficient adsorption of Methylene Blue. This NPs are used to remove 96% of dye from contaminated water. Figure 2 depicts TEM image of the, it can be concluded that particles of iron exhibit a spherical shape with an average diameter of 38 nm.

Shahwan et al. [21] synthesized iron nanoparticles, GT-Fe NPs (consisting mainly of iron oxide/oxyhydroxide), using green tea extracts. These nanoparticles served as Fenton-like catalysts for the degradation of organic dyes such as methylene blue (MB) and 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. Susmitha lakshminarayana et al (2021). synthesized One-pot green synthesis of iron oxide nanoparticles from *Bauhinia tomentosa*: Characterization and application towards synthesis of 1, 3 diolein and they did various applications

Kuang et al. [19] used three different tea extracts, namely, green tea (GT), oolong tea (OT), and black tea (BT) to synthesize magnetite nanoparticles. These nanoparticles were tested for their capacity to act as a catalyst for Fenton-like oxidation of mono Chlorobenzene (MCB). GT-Fe NPs were able to remove 69% of MCB followed by 53% by OT-Fe NPs and 39% by BT-Fe NPs were able to oxidatively degrade 81% of MCB along with a 31% reduction in chemical oxygen demand (COD). The surface area (5.82m2/g) and percent Fe content (14.5%) of as-synthesized NPs were low. Figure1 displays the SEM image of irregular spherical iron NPs indicating the chain-like structure.

Huang et al. [23] 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 NPs were present. Due to the organic coating of biomolecules, as-synthesized NPs remained in a dispersed state and also showed good reactivity. Interestingly, oolong tea extract-mediated 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 Advantages of green synthesis

One of the major drawbacks of using plant resources for nanoparticles 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 agro-waste, which is otherwise a significant source of pollution. Some authors have used agro wastes as low-cost bio-reducing agents.

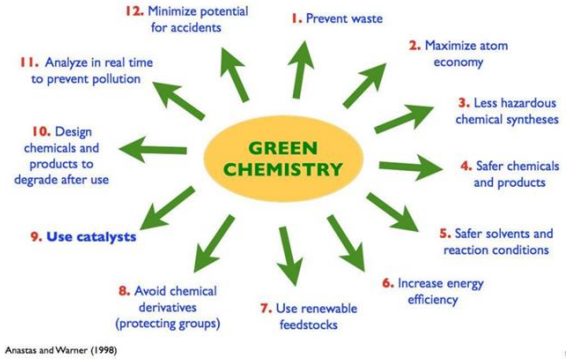

Figure 4. The 12 principles of green chemistry by Anastas and Warner.

Njai et al. [24] used an 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 NPs were similar to those for nZVI synthesized by tea polyphenols. Based on the XRD pattern, the NPs were found to be amorphous in nature. The catalytic activity for the degradation of bromothymol blue was found to be higher for higher concentrations of NPS Eucalyptus globulus leaf extract was used by Madhavi et al. [25] as a bioreducing agent to synthesize nZVI. Polyphenol compounds in plant extract like oenothein 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's adsorption isotherm explained the adsorption process. Removal of Cr followed by the 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 a higher initial chromium concentration. 90 minutes were required for 71.9% removal of chromium when the initial concentration in soil was 400 mg/L.

Wang [24] synthesized iron NPs using eucalyptus leaf extract by adding 0.1 m FeCl3 solution in a ratio of 1:2. The lack of any distinct diffraction peak indicated that the as-synthesized NPs were amorphous in nature. An azo dye, acid black 194, was used to test the adsorption flocculation capacity of nanoparticles. As-synthesized NPs exhibited very high adsorption-flocculation capacity and, at 25ºC, 1gm of NPS 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.

Vekateswarlu et al. [33] used Platina peel extract as a low-cost bioredcing agent for synthesizing magnetic nanoparticles. The 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 synthesize has been understood. The as-synthesized nanoparticles possess ample surface area (11.31m2/g) and high saturation magnetization (15.8emu/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 a TEM image of

nearly monodispersed magnetite nanoparticles synthesized using Platina peel extract.

Banana peel ash extract was used to synthesize iron oxide nanoparticles and an 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 62.05gm of iron oxide /reduced graphene oxide nanohybrids were able to remove 10 ppm of tetrabromobisphenol A in 30 minutes and lead and cadmium in 10 minutes at optimum experimental conditions. The nanohybrids showed good reusability with no significant decrease in efficiency even after the third cycle.

Kiruba Daniel et al. [29] used leaf extract of evergreen shrub D. Viscosa to synthesize iron nanoparticles. The effect of leaf extract concentration on nanoparticle synthesis was studied. Based on the FTIR study, flavonoids in D.viscosa leaf were identified to be responsible for the reduction of metal salts along with polyhydroxy groups in satin. Tannin and saponins were considered to be acting as capping agents. The antibacterial activity of synthesized nanoparticles was evaluated against human pathogens, namely E.coli, K. pneumonia, 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 NPs 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 NPs were effective against Pseudomonas aeruginsa. The zone of inhibition increased from 1 mm 2 mm when the concentration of NPs increased from 10uL to 40 uL.

Narayanan et al. [31] synthesized superparamagnetic magnetite/gold (Fe_3O_4/Au) hybrid nanoparticles at room temperature using grape seed proanthocyanidin (GSP) for the first time. These nanohybrids 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. The 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 an aqueous solution, at an 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, the 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 the time required for percolation. The combination of nZVI with Fenton reagents showed improved efficiency up to 95%. Priya, Naveen, Kamaljit_____Kaur and Amanpreet. KSidhu et al (2021) “Green Synthesis: An Eco-friendly Route for the Synthesis of Iron Oxide Nanoparticles” removal of organic dye pollutants. Kumar et al. [34] synthesized stable iron oxide

(Wuestite) using an 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 for up to 21 days. The phytochemicals in the extract acted as reducing and capping agents.

Mahmood M. S. AbdullahAyman M. AttaHamad A. AllohedanHamad Z. AlkhathlanM. Khan Abdelrahman O. Ezzat" Green Synthesis of Hydrophobic Magnetite Nanoparticles Coated with Plant Extract and Their Application as Petroleum Oil Spill Collectors".

Leaves of three plants native to Australia, namely, Eucalyptus tereticornis (A), Melaleuca nesophila(B), and Rosemary-inus 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 the nanoparticles synthesized. Complete decolorization 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 the 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 a 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. The 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 from aloe Vera, was considered as the reason for the decrease in saturation magnetization of Fe_3O_4 as compared to its bulk counterpart.

Table1: Size and morphology of iron nanoparticles synthesized by plant extracts.

Plant name	Part used	Type of NMs synthesized	Size (nm)	Shape	Application	Ref.
Dolichos lablab L.	Leaf	Fe_3O_4NPs	4-30	Spherical shape	Adsorption of organic des.	[19]
Zanthoxylum armatum Dc	Leaf	Fe_3O_4 NPs	5-38	Spherical	Adsorption of organic dyes and antioxidant (DPPH assay)	[20]
Azadirachta indica	Leaf	Fe_3O_4 NPs	3–8	Spherical	antioxidant activity (DPPH Assay)	[21]
Bauhinia tomentosa	Leaf	Fe_3O_4 NPs	31	Spherical		[22]
Cassia Occidentalis	Leaf	Fe_3O_4 NPs	20–30	Spherical	Adsorbent during photocatalytic degradation of 4-NP	[23]
Black tea		Fe3O4	20-40	Irregular shape	Removal dyes from contaminated water,	[24]

					Antioxidant.	
Eucalyptus	Leaf	Fe_3O_4	40-60	Cubic	Degrdations f dyes , antioxidant.	[25]
Murraya koenigii	Leaf	rGO/Fe_3O_4 nanocomposite	12	Hierarchy dimensio nal	Adsorbent forPb(II) removal	[26]
Sargassum thunbergii	Brown algae	rGO/Fe_3O_4 nanocomposite	7	Spherical	Dye degradation of MB	[27]
Shewanellaoneidensis	Bacteria	rGO/Fe_3O_4 nanocomposite	11	Spherical	Adsorption of MB, malachite green (MG) and CV	[28]
Banana	Peel	Fe_3O_4 nanocomposite	50-60	Spherical	Catalyst for reductionof 4-NP, Congo red (CR) and RhB	[29]

Ahmmad et al. [37] successfully synthesized highly pure hematite (α-Fe_2O_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 ($22.5m^2/g$) was four times higher, whereas the photocatalytic activity (capacity to generate OH radical when irradiated with visible light) was found to be about two times higher than commercially available hematite nanoparticles. The performance of the photoelectrochemical cell was enhanced when these nanoparticles were applied in the wet-type solar cells. Table 2 depicts the size and morphology of nanoparticles synthesized by the hydrothermal route.

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

Plant	Morphology	Size(nm)	Reference
Aloevera	Based reaction time	Around 7-30	[36] [38]
Green tea	Spherical	40-80	

III. PLANT SOURCES

As discussed earlier, iron oxide nanoparticles are prone to oxidation when exposed to air and also tend to form aggregates in an 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 pre-treatment. During the synthesis, plant biomass serves as the reducing agent as well as support for the as-synthesized nanoparticle.

Table3: Size and morphology of iron NPs synthesized by plant source

Plant	Morphology	Size(nm)	Reference
Alfafa biomass	Irregular rod	10	[40]
Orange peel	Rod like	20-40	[43]

Nanoparticle synthesis was carried out by exposing pre-treated 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 20 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 the microwave-assisted synthesis of magnetic nanocomposite using pine wood shavings and a spacer (saturated NaCl). Tannin was a renewable resource, and the microwaving process played an important role in the production of reduced iron oxide. Another nanocomposite 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. Media1. Figure 4 displays the SEM images of nanoparticles. Showed much-improved removal at a higher initial concentration as compared to Media. 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 an adsorption capacity of 43.7 mg/g, which was 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 Lo´pez-Tellez et al.[43] to synthesize iron oxide nanorods. The 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 the reduced form of metal and functional groups of cellulose and hemicellulose components. The effect of precursor iron salt and contact time were 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 nano biocomposites 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 the adsorption capacity of 1.9 mg/g achieved by only orange peel. Table 3 shows the variation in size and morphology when the biomass of different plant species was used for the synthesis of iron nanoparticles.

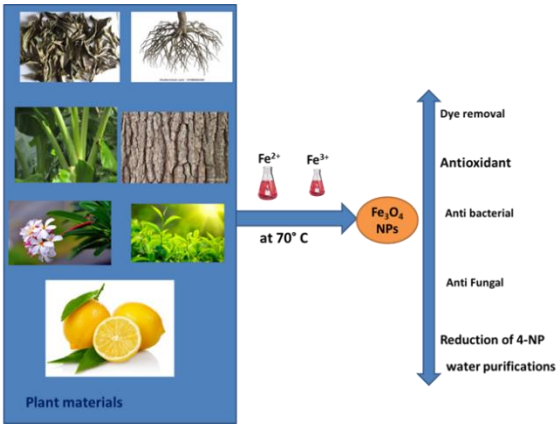

Fig 5 Various plant sources for synthesis of iron oxide nanoparticles

Low-cost magnetite nanoparticles were successfully synthesized using tea waste as a template by Lunge et al. [54]. 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),

IV. CONCLUSION

This review highlights the recent developments in iron nanoparticle synthesis by plants 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.

REFERENCES

[1] Usman. M, Byrne. J.M, Chaudary.A and Haderlein S.B “Magnetite and green rust: Synthesis: properties, and environmental applications of mixed–valent iron minerals. Chem.Rev.2018,11,87, 3251-3304, doi.org/10.1021/acs.chemrev.7b00224 (2021).

[2] Shakwat Hossen Bhuigan, Miah M.Y, Paul S.C, Aka.T.D, Habiba.O, Ashaduzzaman.Md "Green synthesis of iron oxide nanoparticle using *Carica papaya* leaf extract: application for photocatalytic degradation of remazol yellow RR dye and antibacterial activity" 2020 aug: 6(8)e04603, doi: 10.1016/j.heliyon.2020.e04603 (2020).

[3] Panigrahi.S, Kundu. S, Ghosh.S.K, Nath. S, and Pal.T "General method of synthesis for metal nanoparticles," Journal of Nanoparticle Research, vol. 6, no. 4, pp. 411–414, (2004).

[4] Sharma. R. K, Subham Yadav, Radhika Gupta and Gunjan Arora "Synthesis of Magnetic Nanoparticles Using Potato Extract for Dye Degradation: A Green Chemistry Experiment" 10.1021/acs.jchemed.9b00384 (2019).

[5] Qinzhang, yonggui Zhang and anbin Li Green synthesis of magnetite nanoparticle and its regulatory effect on fermentative hydrogen production from lignocellulosic hydrolysate by *Klebsiella* sp. Doi:10.1016.j.ijhydene.2021.03.142 (2021).

[6] Senapati. S, Ahmad. A. Khan. M. I. Sastry. M. and Kumar. R "Extracellular biosynthesis of bimetallic Au-Ag alloy nanoparticles," Small, vol. 1, no. 5, pp. 517–520, (2005)

[7] YenPin Yewkamayar Shameli, Miyakemikio, Xin Lee kar" Green biosynthesis of superparamagnetic magnetite Fe_3O_4 nanoparticles and biomedical applications in targeted anticancer drug delivery system. doi;10.1016/j.arabjc.2018.04.013 (2018).

[8] Kumar dhar .palash, Prianka saha Md. Kamrulhasin, Rezaul Haquae" Green synthesis of magnetite nanoparticles using lathus Sativus peel extract and evaluation of their Catalytic activity" doi.org/10.1016/j.clet 2021.100117(2021).

[9] Barzinjy Azeez A, Abdul Dalia A, Samir M. Hamad " Green synthesis of magnetite(Fe3O4) NPs using Rhuscoriaria extract: a reusable new 2-naphthol bis –Betti bases" doi.org/10.1080/247015562020.1723027 (2020).

[10] Bansal .V, Rautaray. D. Ahmad. A. and Sastry. M. "Biosynthesis of zirconia nanoparticles using the fungus Fusarium oxyspo- rum," Journal of Materials Chemistry, vol. 14, no. 22, pp. 3303–3305, (2004).

[11] Mohanpuria. P, Rana. N. K. and Yadav. S. K. "Biosynthesis of nanoparticles: technological concepts and future applications," Journal of Nanoparticle Research, vol. 10, no. 3, pp. 507–517, (2008).

[12] Gardea-Torresdey. J. L. Parsons. J. G. Gomez E. et al., "Formation and growth of Au nanoparticles inside live Alfalfa plants," Nano Letters, vol. 2, no. 4, pp. 397–401, (2002).

[13] Rai. M. Yadav. A. and Gade. A."CRC 675—current trends in photosynthesis of metal nanoparticles," Critical Reviews in (2003).

[14] Wu. W, He. Q. and Jiang. C. "Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies," Nanoscale Research Letters, vol. 3, no. 11, pp. 397–415,(2008).

[15] Abhilash, Revati. K, and Pandey. B. D. "Microbial synthesis of iron-based nanomaterials—a review," Bulletin of Materials Science, vol. 34, no. 2, pp. 191–198,(2011).

[16] Hoag. G. E. Collins. J. B. Holcomb. J. L, Hoag. J. R. Nad. M. N. - agouda, and Varma. R. S. "Degradation of bromothymol blue by "greener" nano-scale zero-valent iron synthesized using tea polyphenols," Journal of Materials Chemistry, vol. 19, no. 45, pp. 8671–8677,(2009).

[17] Nadagouda. M. N, Castle. A. B, Murdock. R. C. Hussain. S. M. and Varma. R. S. "In vitro biocompatibility of nanoscale zerovalent iron particles (NZVI) synthesized using tea polyphenols," Green Chemistry, vol. 12, no. 1, pp. 114–122, (2010).

[18] Shahwan. T. Abu Sirrah. S. Nairat. M. et al., "Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes," Chemical Engineering Journal, vol. 172, no. 1, pp. 258–266, (2011).

[19] Kuang. Y. Wang. Q. Chen. Z. Megharaj. M. and Naidu, R. "Heterogeneous Fenton-like oxidation of monochlorobenzene using a green synthesis of iron nanoparticles," Journal of Colloid and Interface Science, vol. 410, pp. 67–73, (2013).

[20] Huang. L., Weng. X. Chen. Z. Megharaj. M. and Naidu. R. "Synthesis of iron-based nanoparticles using oolong tea extract for the degradation of malachite green," Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 117, pp. 801–804,(2014).

[21] Njagi. E. C. Huang. H. Stafford. L. et al., "Biosynthesis of iron and silver nanoparticles at room temperature using aqueous sorghum bran extracts," Langmuir, vol. 27, no. 1, pp. 264–271, (2011).

[22] Mebrahtu Hagos Kahsay, Ramadevi Dharmasoth Basavaiah Keloth."facile synthesis of Magnetite nanoparticles using aqueous leaf extract of Dolichos Lablab for efficient adsorption of Crystal violet dye contaminated water," Emergent materials. /s42247-018-005-1, DOI:10.1007 Springer(2018).

[23] Ramesh. A.V. Ramadevi. D. Satish Mohan Botscha and Basavaiah. K. .Facile green synthesis of Fe3O4 NPs using aqueous leaf extract of Zanthoxylum Armatum. Dc for efficient adsorption of Methylene Blue, Journal of Asian ceramic societies. DOI: 10.1080/21870764.2018. 1459335(2018).

[24] Madhavi.V, Prasad. T. N. V. Reddy. K. V., A. V, Ravin- dra Reddy B. B., and Madhavi B. B., "Application of phytogenic zero- valent iron nanoparticles in the adsorption of hexavalent chro- mium," Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy, vol. 116, pp. 17–25, (2013).

[25] Sushmitha Lakshminarayanan, M. Furhana Shereen, K. L. Niraimathi, P. Brindha "One-pot green synthesis of iron oxide nanoparticles from *Bauhinia tomentosa*: Characterization and application towards synthesis of 1, 3 diolein" 8643 (2021).

[26] Wang. T, Jin. X, Chen. Z, Megharaj. M, and Naidu. R. "Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater," Science of the Total Environment, vol. 466-467, pp. 210–213, (2014)

[27] Sathishkumar. M, Sneh. K and Yun. Y.-S. "Immobilization of silver nanoparticles synthesized using Curcuma longa tuber powder and extract on cotton cloth for bactericidal activity," Bioresource Technology, vol. 101, no. 20, pp. 7958–7965, (2010).

[28] Song. H and Carraway. E. R, "Reduction of chlorinated ethanes by nanosized zero-valent iron: kinetics, pathways, and effects of reaction conditions," Environmental Science & Technology, vol. 39, no. 16, pp. 6237–6245, (2005).

[29] Kim. J. H. Tratnyek. P. G. and Chang. Y. S. "Rapid dechlorination of polychlorinated dibenzo-p-dioxins by bimetallic and nano-sized zerovalent iron," Environmental Science and Technology, vol. 42, no. 11, pp. 4106–4112, (2008).

[30] Mohammad A. Khalilzadeh, Somayeh Tajik,Hadi Beitolla and Richard A. Venditti* "Green Synthesis of Magnetic Nanocomposite with Iron Oxide Deposited on Cellulose Nanocrystals with Copper (Fe_3O_4@CNC/Cu): Investigation of Catalytic Activity for the Development of a Venlafaxine Electrochemical Sensor" *Ind. Eng. Chem. Res.* 2020, 59, 10, 4219–4228. doi.org/10.1021/acs.iecr.9b06214 (2021).

[31] Thuy Nguyen Thi DaoAnkireddy Seshadri Reddy, Fei Zhao, Huifang Liu, Bonhan Koo, Md. Moniruzzaman, Jongsung Kim* and Yong Shin" Green Synthesis-Based Magnetic Diatoms for Biological Applications" ACS sustainable chem.Eng.2021,9,9,3439-3451.doi.org/10.1021/acssuschemeng.007067.(2021)

[32] Journal of Contaminant Hydrology, vol. 146, pp. 63–73, (2013).

[33] Venkateswarlu S, Rao. Y. S. Balaji.T, Prathima.B and Jyothi. N.V. "Biogenic synthesis of Fe_3O_4 magnetic nanoparticles using plantain peel extract," Materials Letters, vol. 100, pp. 241– 244, (2013).

[34] Thakur. S. and Karak. N. "One-step approach to preparing magnetic iron oxide/reduced graphene oxide nanohybrid for efficient organic and inorganic pollutants removal," Materials Chemistry and Physics, vol. 144, no. 3, pp. 425–432, (2014).

[35] Kiruba Daniel. S. C. G. Vinothini. G. Subramanian. N. Nehru. K. and Sivakumar. M.

"Biosynthesis of Cu, ZVI, and Ag nanoparticles using Dodonaea viscosa extract for antibacterial activity against human pathogens," Journal of Nanoparticle Research, vol. 15, no. 1, article 1319,(2014)

[36] Senthil. M and Ramesh. C "Biogenic synthesis of Fe3O4 nano-particles using Tridax procumbens leaf extract and its antibacterial activity on Pseudomonas aeruginosa," Digest Journal of Nanomaterials & Biostructures, vol. 7, no. 4, pp. 1655–1661,(2012).

[37] Narayanan. S, Sathy. B. N. U. Mony, Koyakutty. M. Nair S. V. and Menon.D, "Biocompatible magnetite/gold nanohybrid contrast agents via green chemistry for MRI and CT bioimaging," ACS Applied Materials and Interfaces, vol. 4, no. 1, pp. 251–260, (2012).

[38] Machado. S, Pinto. S. L. Grosso. J. P. Nouws. H. P, Albergaria. J. T. and Delerue-Matos D, "Green production of zero-valent iron nanoparticles using tree leaf extracts," Science of the Total Environment, vol. 445-446, pp. 1–8, (2013).

[39] Machado. S, Stawin´ ski. W. Slonina. P. et al., "Application of green zero-valent iron nanoparticles to the remediation of soils contaminated with ibuprofen," Science of the Total Environment, vol. 461-462, pp. 323–329, (2013).

[40] Kumar. K. M, Mandal. B. K. Kumar. K. S. Reddy. P. S, and Sreedhar.B "Biobased green method to synthesize palladium and iron nanoparticles using Terminalia chebula aqueous extract," Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 102, pp. 128–133(2013).

[41] Wang. Z, Fang.C and Megharaj. M "Characterization of iron- polyphenol nanoparticles synthesized by three plant extracts and their Fenton oxidation of azo dye," ACS Sustainable Chemistry & Engineering, vol. 2, no. 4, pp. 1022–1025, (2014).

[42] Phumying. S, Labuayai. S. Thomas. C. V. Amornkitbamrung. C. Swatsitang. E. and Maensiri. S "Aloe vera plant-extracted solution hydrothermal synthesis and magnetic properties of magnetite (Fe_3O_4) nanoparticles," Applied Physics A, vol. 111, no. 4, pp. 1187–1193, (2013).

[43] Ahmmad. B. Leonard. K. Islam. M. S. et al., "Green synthesis of mesoporous hematite (α-Fe_2O_3) nanoparticles and their photocatalytic activity," Advanced Powder Technology, vol. 24, no. 1, pp. 160–167, (2013).

[44] Liu. J.-F, Zhao. Z.-S and Jiang. G.-B. "Coating Fe3O4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water," Environmental Science & Technology, vol. 42, no. 18, pp. 6949–6954, (2008).

[45] Yusefi M , Shameli K , Su Yee O, Teow SY , Hedayatnasab Z, Jahangirian H , Webster TJ , Kuča K "Green Synthesis of Fe_3O_4 Nanoparticles Stabilized by a *Garcinia mangostana* Fruit Peel Extract for Hyperthermia and Anticancer Activities" . https://doi.org/10.2147/IJN.S284134(2020)

[46] Herrera-Becerra. R. Zorrilla. C. Rius. J. L. and Ascencio. J. A. "Electron microscopy characterization of biosynthesized iron oxide nanoparticles," Applied Physics A, vol. 91, no. 2, pp. 241– 246, (2008).

[47] Ramasahayam. S. K. Gunawan. G. Finlay. C. and Viswa- Nathan. T. "Renewable resource-based magnetic nanocomposites for removal and recovery of phosphorous from contaminated waters," Water, Air & Soil Pollution, vol. 223, no. 8, pp. 4853– 4863,(2012).

[48] Zhou. H, Fan. T, and Zhang. D. "Biotemplated materials for sustainable energy and environment: current status and challenges," Chemistry and Sustainability Energy and Materials, vol. 4, no. 10, pp. 1344–1387, (2011).

[49] Cai.Y Shen. Y. Xie. A. Li. S. and Wang. X "Green synthesis of soya bean sprouts-mediated superparamagnetic Fe_3O_4 nano-particles," Journal of Magnetism and Magnetic Materials, vol. 322, no. 19, pp. 2938–2943, (2010).

[50] Lunge. S, Singh. S. and Sinha. A. "Magnetic iron oxide (Fe_3O_4) nanoparticles from tea waste for arsenic removal," Journal of Magnetism and magnetic materials, vol,356, pp.21-31,(2014).

[51] Belachew N, Ramadevi. D, Basavaiah .K J. Exp. Nanosci ,12,114-128(2017).

[52] Cong. H.P He. J.-J, Lu. Y. S- Yu. H. Small,6, 169-173. (2010)

[53] Bagherzadeh. M, Pirmoradian. M, Riahi. F Electrochemicaecta, 115, 573-580(2014).

[54] Kshama Parajuli, Aravind Kumar Sah, Hari Paudyal* "Green Synthesis of Magnetite Nanoparticles Using Aqueous Leaves Extracts of *Azadirachta indica* and Its Application for the Removal of As(V) from Water" DOI: 10.4236/gsc.2020.104009(2020)

[55] Hayasi. M. Karimi. M. polym. Bull., 2016,74, 1995-(2016).

[56] Srivastava.V, Agarwal. S.B, Mondal M.K, Environ. Sci. Pollut. Res. Int. 22,15386-154156. (2015)

[57] Hoan. N. T. V, Thu. N.T.V, .Due. H.V, Cuong. N.D. D.Q, Khieu. V. Vo, Journalof Chemistry, 24181721-10. (2016)

[58] Salleh. M.A. Mahmoud. M D.K, Wan Azlina Wan and Idris. A. Desalination,280,1-13(2011).

[59] Ali. I, Peng .C, Naz. I, Khan. Z.M, sultan. M., Islam. T. abbasi. I.A RSC Adv.7, 40158-40178(2017).

[60] Bai H, Shi GQ Gas sensors based on conducting polymers. Sensors 7:267–307(2007).

[61] Anastas. P.T, Warner. J.C. Green Chemistry: Theory and Practice, Oxford University Press, USA, (2000).

[62] Shubhangi Mane-Gavade,Arihant Malgave, Gurunath Nikam,Amruta Koli,Amit Supale,Sandip Sabale" Green synthesis of magnetite nanoparticles (Fe_3O_4 NPs) using *Acacia concinna* fruit extract and their antibacterial activity" https://doi.org/10.1002/masy.202100140(2021)

[63] Gupta AK, Gupta M (2005) Synthesis and surface engineering of iron oxide nanoparticles for applications. Biomaterials 26:3995–4021

[64] Jeong U, Teng XW, Wang Y, Yang H, Xia YN (2007) Superpara- magnetic colloids: controlled synthesis and niche applications. Adv Mater 19:33–60.

[65] Wilson JL, Poddar P, Frey NA, Srikanth H, Mohomed K, Harmon JP (2004) Synthesis and magnetic properties of polymer nanocom-posites with embedded iron nanoparticles. J Appl Phys 95:1439–1443

[66] K.Basavaiah, Y.pavan kumar, A.V. Prasad Rao., "A facile one-pot synthesis of polyaniline/magnetite nanocomposites by micelles-assisted method", Appl. Nanoscience (2013)