Plant mediated synthesis of Iron nanoparticles and their Applications: A Review

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ABSTRACT

Nanoparticles form the basis of nanoscience and nanotechnology which are considered as the most growing disciplines amongst various fields of science. Various methods for synthesis of nanoparticles include conventional methods like hydrothermal method, sol-gel method, laser-ablation, electrochemical techniques and thermal methods. However biogenic synthesis of iron nanoparticles is advantageous over conventional methods due to its eco-friendly, simple, cost-effective and non-toxic properties. Iron nanoparticles possess wide range of application from environmental remediation to magnetization of sediments and they are also known to possess anti-oxidant and anti-bacterial activity. Extracts of various plants like green tea, Amaranthus dubius, and Eichhornia Crassipes, Cynometra Ramiflora, Eucalyptus tereticornis and Melaleuca Nesophila Rosemarinus Officinalis are reported for synthesis of iron nanoparticles. Different environmental remediation applications of iron nanoparticles include degradation of dyes, removal of nitrate, hexavalent chromium, arsenate, arsenite, chemical oxygen demand and total phosphates. This review focuses on various plant extracts utilized for synthesis of iron nanoparticles and their potential applications. Different classes of phytochemicals responsible for conversion of precursor iron to nano-sized iron material, various characterization techniques for iron nanomaterials fabricated using plant extracts and optimum conditions for pollutant removal are also discussed.
1. Introduction

The prefix “nano” in the word Nanotechnology and Nanoparticles indicates one billionth or $10^{-9}$ units. Nanoscience which has been recently established as new interdisciplinary science is a whole knowledge on fundamental properties of nanosized objects [1]. The term “nanotechnology” was first presented in 1959 by Richard Feynman, an American Physicist who is known as Father of Nanotechnology and was first coined by Norio Taniguchi of Tokyo University of Science. Eric Drexler in his book named “Engines of Creation” explained nanotechnology in the context to nanometric scale and hence it is application of governing the properties of the substance at the molecular level [2-4]. Nanoparticles are the cluster of atoms in the size range 1-100 nm and possess properties between bulk materials and the atomic and molecular structures; thus the properties of nanoparticles differ from that of conventional solids [1, 4]. Shape, size and surface morphology of nanoparticles affect their chemical, physical and optical properties; these are all governed by the experimental conditions, methods of synthesis, reducing and stabilizing factors [3, 5]. Metallic nanoparticles due to their high surface to volume ratio shows considerably distinct physical, chemical and biological properties compared to their bulk materials and hence possess wide range of applications ranging from catalysts to sensing optics, anti-bacterial activity and data storage [1]. Iron nanoparticles find potential application as the catalyst for environmental decontamination, for degradation of ionic dyes, adsorbent for heavy metals/ions, as well as in the magnetization of sediments/cycling of iron of stratified marine environments; these are also known to exhibit anti-bacterial and anti-oxidant activity [6, 7]. Silver nanoparticles posses wide range of pharmacological applications due their potent anti-microbal, larvicidal, anti-cancer and wound healing properties. Silver nanoparticles are also known for sensing chromium ions in tap water and degradation of dyes like methylene blue and methyl orange [8]. Gold nanoparticles, silver nanoparticles or their combination functionalized with antibodies, peptides and/or DNA/RNA particularly target various cells. These nanoparticles functionalized with biocompatible polymers like polyethylene glycol are known for drug and gene delivery applications [9]. Various chemical and physical methods known for the synthesis of nanomaterials include electrochemical, hydrothermal, laser ablation, lithography, microwave and thermal decomposition [10]. But these methods have several limitations like requirement of specific experimental conditions in the terms of high energy, pressure and temperature requirements, discharge of toxic byproducts, and also they are expensive [11]. Biogenic synthesis of Nanoparticles involves synthesis of Nanoparticles using extract of plant leaves, fruit and other different parts of plants, various micro-organisms and other biological systems. Therefore, in order to overcome these limitations of conventional methods for synthesis of nanoparticles, a new approach of green synthesis of nanoparticles using extracts of different parts of plants, micro-organism and their metabolites and few other humic substances is gaining familiarity over conventional methods[12]. The advantage of green approach over conventional methods is due to their low cost, simplicity, and eco-friendly characteristic [13]. This review aims to summarize green methods for synthesis of iron nanoparticles using different plant extracts and their potential environmental applications.

![Fig. 1: Different method for synthesis of iron nanoparticles](image)

Muthukumar et. al. reported biogenic synthesis of iron nanoparticles using aqueous leaf extract of *Amaranthus dubius* possessing anti-oxidant capacity and catalytic activity. The comparative evaluation of catalytic activity of sodium borohydride mediated iron nanoparticles and *A. dubius* leaf extract mediated nanoparticles was carried out by analyzing decolourization efficiency of methyl orange on UV radiation and anti-oxidant capacity by 2,2′-diphenyl-1-picryl-hydrazyl (DPPH) radical scavenging assay.
Fig. 2: General process diagram of biogenic synthesis of Nanoparticles using plant extract

The characterization of *A. dubius* leaf extract mediated iron nanoparticles was carried out by UV-Vis spectrophotometer, X-ray diffraction(XRD), Fourier transform infrared spectroscopy(FTIR), Particle size analyzer(PSA) and Scanning electron microscope(SEM) and the results by the above mentioned characterization techniques revealed spherical shape of nanoparticles with cubic phase structure and diameter ranging from 43 to 220 nm. The experimental conditions were optimized to pH 6, time 90 min, temperature 37±1°C and ratio of *A. dubius* leaf extract to ferric chloride (4:5) to obtain high yield of *A. dubius* leaf extract mediated iron nanoparticles. XRD analysis of these nanoparticles revealed that they possessed rhombohedral crystalline nature. FTIR analysis of *A. dubius* leaf extract mediated iron nanoparticles showed peak at 3250 cm⁻¹ and 1500 cm⁻¹ corresponding to –OH functional group that can donate hydrogen and capable of binding to free Fe surface. The comparative investigation of catalytic activity of *A. dubius* leaf extract mediated iron nanoparticles and sodium borohydride mediated nanoparticles by decolourisation of methyl orange dye using UV radiation showed that *A. dubius* leaf extract mediated iron nanoparticles possess higher removal efficiency than sodium borohydride mediated iron nanoparticles due their surface constituent; under the experimental of 20 ppm methyl orange and 20 mg nanoparticles the colour removal efficiency observed was 90% and 81% for *A. dubius* leaf extract mediated iron nanoparticles and sodium borohydride mediated iron nanoparticles. The evaluation of anti-oxidant potential using DPPH assay showed inhibitory rate of 72% and 68% respectively by *A. dubius* leaf extract mediated iron nanoparticles and sodium borohydride mediated iron nanoparticles on scavenging effect of DPPH radical [7].

Fig. 3: Schematic diagram for synthesis of iron Nanoparticles using *A. dubius* leaf extract

G. Jagathesan et al. synthesized iron oxide nanoparticles via eco-friendly pathway using aqueous *Eichhornia Crassipes* leaf extract possessing anti-bacterial activity against *S. aureus, P. fluorescens* and *E.coli*. Synthesis of iron oxide nanoparticles was done by 100 ml 50 % aqueous *Eichhornia Crassipes* leaf extract to 100 ml 0.1 M ferrous sulphate solution followed by addition of 10 ml 0.1 M sodium hydroxide solution; further after stirring the reaction mixture for 2 hours at 55°C the supernatant was discarded and dried pellet yield black brownish colored iron oxide nanoparticles. UV-Vis analysis of *Eichhornia* mediated iron nanoparticles showed broad spectrum at 379 nm and band gap value 3.27 eV. FTIR analysis of iron oxide nanoparticles showed peaks at 1400 and 1587 cm⁻¹ (N-H bending), 621 cm⁻¹ (C-H group), 2832 cm⁻¹ (nitrile group) and 1114 cm⁻¹ (C=O group). Also the FTIR analysis of plant extract showed the presence of similar functional group which indicates transfer of functional group of plant extract during synthesis. X-ray diffraction analysis of *Eichhornia* mediated iron nanoparticles revealed that obtained diffraction peak matched well with the standard magnetite XRD patterns. The composition of *Eichhornia* mediated iron nanoparticles 77.08 % of iron and 22.97 % of oxygen and rod shape of nanoparticles arranged without aggregation was proved by EDX and SEM analysis respectively. Evaluation of anti-bacterial activity showed that at the concentration of 100 μg/ml highest zone of inhibition was observed for *S. aureus, P. fluorescens* and *E.coli* due to the disruption of membrane by the formation of reactive oxygen species which may cause cell demise [14].

A. U. Mirza et al. fabricated iron oxide nanoparticles using aqueous leaf extract of *Agrewia optica* and *Prunus persica* followed by their evaluation of anti-bacterial and anti-oxidant activity.
UV-Vis analysis of *Agrewia optica* and *Prunus persica* leaf extract mediated iron nanoparticles exhibited peak around 248 nm, 278 nm and 284 nm respectively indicating capping of biomolecules on the surface of iron oxide nanoparticles with absence of surface Plasmon resonance. FTIR analysis of *Agrewia optica* mediated nanoparticles showed peak at 3313-3209 cm\(^{-1}\) (O-H stretching of phenol), 1628-1652 cm\(^{-1}\) (C=O stretching vibrations), 1036 cm\(^{-1}\) (C-O stretching), 1377 cm\(^{-1}\) (C-N stretching of aromatic amines), 846 (C-H bending of alkenes) and peaks at 484 and 538 cm\(^{-1}\) confirms the presence of Fe-O bond while *Prunus persica* mediated nanoparticles showed peak at 3314-3443 cm\(^{-1}\) (O-H stretching), 1629-1653 cm\(^{-1}\) (C=O stretching vibration coupled with C-N stretching and bending vibration of amido group), 1023 cm\(^{-1}\) (C=O-C vibration) and 410 and 683 cm\(^{-1}\) (Fe-O bonds). Cubic spinel structure of *Agrewia optica* and *Prunus persica* leaf extract mediated iron nanoparticles is confirmed by powder X-ray diffraction characterization and average crystalline size of these nanoparticles evaluated by Debye-Scherrer equation were found to be 15.43 and 18.13 nm respectively. The morphology of *Agrewia optica* and *Prunus persica* leaf extract mediated iron nanoparticles as confirmed by SEM analysis was found to be irregular clusters with rough surfaces, agglomerated, quasi-spherical, size ranging from 15-60 nm and spherical granular, agglomerated, size ranging from 13-70 nm respectively. The evaluation of anti-bacterial activity concludes that *Agrewia optica* and their mediated nanoparticles are more sensitive than *Prunus persica* and their mediated nanoparticles while on the other hand anti-oxidant potential evaluated by DPPH scavenging assay concludes that *Prunus persica* and their mediated nanoparticles possess more anti-oxidant potential than *Agrewia optica* and their mediated nanoparticles [5].

S. Groiss et. al. utilized aqueous leaf extract of *Cynometra Ramiflora* for phytomediated synthesis of iron oxide nanoparticles possessing anti-bacterial potential against E.coli and S. epidermidis as evaluated by standard Kirby-Bauer diffusion assay.

XRD pattern of *Cynometra Ramiflora* mediated iron nanoparticles indicate the presence of iron oxyhydroxide due to partial oxidation during synthesis. FTIR analysis of *Cynometra Ramiflora* mediated iron nanoparticles indicates the presence of –OH group which may act as metal chelators in the formation of iron nanoparticles. The existence of these nanoparticles as singular nanoparticles and small aggregated of spherical nanoparticles is confirmed by SEM analysis. EDS spectrum confirms the presence of Ca, Na, Si, Fe and O in *Cynometra Ramiflora* mediated iron nanoparticles. The optimum conditions for the removal of Rhodamine-B dye were concluded 2% hydrogen peroxide and 1.11 mM *Cynometra Ramiflora* mediated iron nanoparticles and equilibrium time 15 minutes leading to 100 % degradation of dye [12].
phenol complex. Photo catalytic activity of Cynometra Ramiflora aqueous fruit extract mediated magnetite iron nanoparticles has been evaluated by the degradation of methylene blue dye under sunlight which may be due to larger surface area and lesser band gap of iron oxide nanoparticles. Also the recovered nanoparticles were recovered for 5 consecutive batches of degradation with overall decrease in % degradation was less than 5% [13].

Wang et al. utilized green tea and eucalyptus leaves extract consisting polyphenols as capping agents to synthesize iron nanoparticles for nitrate removal from aqueous solutions and the mechanism of adsorption and co-precipitation along with subsequent reduction was proposed for nitrate removal [12, 17]. Poguberovic et al. synthesized zero-valent iron nanoparticles using oak, mulberry and cherry aqueous leaf extract for removal of trivalent arsenic and hexavalent chromium from aqueous solution. SEM and TEM measurements approved the formation of spherical nanoparticles within size range 10-30 nm and stable material with minimum agglomeration. Oak leaf extract mediated zero-valent iron nanoparticles exhibited higher adsorption capacities for trivalent arsenic removal than for hexavalent chromium and cherry leaf extract mediated zero-valent iron nanoparticles exhibited higher adsorption capacities for hexavalent chromium. The adsorption kinetics followed second order kinetics model and Freundlich adsorption isotherm well fitted to data [18].

C. P. Devatha et al. evaluated the aqueous leaf extracts of Mangifera Indica, Murraya Koenigii, Azadirachta Indica and Mangolia Champaca to synthesize iron nanoparticles for domestic waste water treatment. The potential of these nanoparticles for treatment of domestic water was evaluated for simultaneous removal of total phosphates, nitrates and chemical oxygen demand. Azadirachta Indica mediated iron nanoparticles showed the removal of 98.08 % of phosphate, 84.32 % of ammonia nitrogen and 82.35% of chemical oxygen demand compared to Mangifera Indica, Murraya Koenigii, and Mangolia Champaca mediated nanoparticles and hence may be considered as satisfactory for treatment of domestic water [19].

Madhavi et al. manifested the use of aqueous extract of Eucalyptus Globules to synthesize zero-valent iron nanoparticles for adsorption of hexavalent chromium. FTIR analysis of Eucalyptus Globules mediated zero-valent iron nanoparticles reveals phenolic –OH group (3346.39 cm⁻¹) were involved in the reduction of Fe²⁺ to Fe⁰. The SEM analysis shows the fabricated material to be polydisperse with varied sizes and spherical shape ranging from 50 to 80 nm. The zeta potential of Eucalyptus Globules mediated zero-valent iron nanoparticles was found to be -77 mV which indicates the repulsion among the nanoparticles and hence confirms their stability. The effective adsorption of hexavalent chromium by Eucalyptus Globules mediated zero-valent iron nanoparticles is due to stabilization of fabricated material by a macro cyclic phenolic Oenothein B. which would also effectively aid in chromium adsorption. The experimental conditions were optimized to 0.8 g/L of Eucalyptus Globules mediated zero-valent iron nanoparticles for contact time of 30 min for removal of 400 mg/L of hexavalent chromium. Also Eucalyptus Globules mediated zero-valent iron nanoparticles follows Langmuir and Freundlich adsorption isotherms for removal of hexavalent chromium and is also consistent with pseudo second order kinetic model [16].
Wei et al. used aqueous peel extracts of *Citrus Maxima* to fabricate iron nanoparticles for removal of hexavalent chromium from aqueous media. The mechanism proposed for removal of hexavalent chromium was adsorption and reduction. TEM images confirmed the size of nanoparticles ranging from 10 to 100 nm with irregular shape [20]. K.S. Prasad et al. employed aqueous leaf extract of *Mentha Spicata* L. to synthesize polydisperse, crystalline and face centered cubic type iron nanoparticles and studied the applicability of *Mentha Spicata* L. mediated iron nanoparticles-chitosan beads in removal of arsenate and arsenite from aqueous medium [21]. Wang et al. fabricated iron polyphenol nanoparticles using aqueous extract of *Eucalyptus tereticornis*, *Melaleuca Nesophila* and *Rosemarinus Officinalis* leaves and assessed their potential of Fenton like oxidation of azo dye using acid black 194. Addition of 110 μL of these plant mediated iron nanoparticles to 50 mL of acid black 194 solution of concentration 50 mg/L containing 10 mL of hydrogen peroxide, 100% decolorization was achieved after contact time of 200 min along with 87% of total organic carbon removal after 4 days and data well fitted to pseudo to pseudo first order kinetic model [22].

Kuang et al. green tea, oolong tea and black tea extracts to synthesize iron nanoparticles for heterogeneous Fenton like oxidation of monochlorobenzenes. Amongst all green tea mediated iron nanoparticles possessed highest degradation efficiency 69% due to its rich polyphenol content. Also green tea mediated iron nanoparticles demonstrated 31% removal of COD under optimum conditions of 0.6 g/L GT nanoparticles, initial pH 3 and 0.045 mol/L of hydrogen peroxide [23]. Mahadavi et al. utilized aqueous leaf extract of *Saragassum Muticum* containing sulphated polysaccharides to fabricate magnetic iron oxide nanoparticles with crystalline nature and cubic shape [24]. T. Shahwan et al. synthesized iron nanoparticles using polyphenol rich *green tea* leaves extract and demonstrated their applicability as fenton like catalysts to decolorize aqueous solutions of methylene blue and methyl orange. The study concluded more effectiveness of GT-iron nanoparticles as effective fenton like catalysts compared to conventional sodium borohydride mediated iron nanoparticles in terms of kinetics and removal efficiency [25]. T. Wang et al. reported *eucalyptus* leaf extract containing mainly epicatechin and quercetin glucuronide for synthesis of iron nanoparticles and their utility in removal of 71.7% of total N and 84.5% COD in eutrotropic waste water treatment [26]. Various plants extracts used for synthesis of nanoparticles and their applications are shown in Table 1.

**Table 1:** Different plant extracts used for the synthesis of iron Nanoparticles and their environmental applications

<table>
<thead>
<tr>
<th>No.</th>
<th>Extract of plant used</th>
<th>Application of plant mediated nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aqueous leaf extract of <em>Amaranthus dubius</em></td>
<td>Anti-oxidant activity and photocatalytic activity for degradation of methyl orange</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous leaf extract of <em>Eichhornia Crassipes</em></td>
<td>Anti-bacterial activity</td>
</tr>
<tr>
<td>3</td>
<td>Aqueous leaf extract of <em>Agrowia optica</em> and <em>Prunus persica</em></td>
<td>Anti-oxidant and anti-bacterial activity</td>
</tr>
<tr>
<td>4</td>
<td>Aqueous leaf extract of <em>Cynometra Ramiflora</em></td>
<td>Anti-oxidant and anti-bacterial activity</td>
</tr>
<tr>
<td>5</td>
<td>Polypenol rich extract of <em>Green tea</em></td>
<td>Hydrogen peroxide catalyzed degradation of bromothymol blue</td>
</tr>
<tr>
<td>6</td>
<td>Aqueous extract of <em>Eucalyptus Globules</em></td>
<td>Adsorption of hexavalent chromium</td>
</tr>
<tr>
<td>7</td>
<td>Green tea and <em>Eucalyptus leaves</em> extract</td>
<td>Nitrate removal from aqueous solution</td>
</tr>
<tr>
<td>8</td>
<td>Aqueous leaf extracts of oak, cherry, and mulberry</td>
<td>Trivalent arsenic and hexavalent chromium removal from aqueous solution</td>
</tr>
<tr>
<td>9</td>
<td>Aqueous leaf extracts of <em>Mangifera Indica</em>, <em>Murraya Koenigii</em>, <em>Azadirachta Indica</em> and <em>Mangolia Champaca</em></td>
<td>Removal of total phosphates, nitrates and chemical oxygen demand (COD)</td>
</tr>
<tr>
<td>10</td>
<td>Aqueous peel extracts of <em>Citrus Maxima</em></td>
<td>Hexavalent chromium removal from aqueous solution</td>
</tr>
<tr>
<td>11</td>
<td>Aqueous leaf extract of <em>Mentha Spicata</em> L.</td>
<td>Arsenate and arsenite removal from aqueous solution</td>
</tr>
<tr>
<td>12</td>
<td>Aqueous extract of <em>Eucalyptus tereticornis</em>, <em>Melaleuca Nesophila</em> and <em>Rosemarinus Officinalis</em> leaves</td>
<td>Fenton like oxidation of acid black 194 and total organic removal</td>
</tr>
<tr>
<td>13</td>
<td>Aqueous extracts of <em>green tea, black tea and oolong tea</em></td>
<td>Fenton like oxidation of monochlorobenzenes and chemical oxygen demand removal</td>
</tr>
<tr>
<td>14</td>
<td>Polyphenol rich <em>green tea leaves</em> extract</td>
<td>Decolorization of aqueous solution of methylene blue and methyl orange</td>
</tr>
<tr>
<td>15</td>
<td><em>Eucalyptus leaf</em> extract</td>
<td>Removal of total N and chemical oxygen demand in eutrotic waste water treatment</td>
</tr>
<tr>
<td>16</td>
<td>Leaf extract of <em>Camellia Senensis</em></td>
<td>Degradation of bromothymol blue</td>
</tr>
<tr>
<td>17</td>
<td>Leaf extract of <em>Tridax Plocymbens</em></td>
<td>Anti-bacterial activity</td>
</tr>
<tr>
<td>18</td>
<td>Leaf extract of <em>Punica Granatum</em></td>
<td>Removal of hexavalent chromium</td>
</tr>
<tr>
<td>19</td>
<td>Leaf extract of <em>green tea</em></td>
<td>Degradation of trichloroethylene</td>
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</table>
Conclusion:
This review summarizes various plants and their extracts used for phytomediated synthesis of iron nanoparticles and their potential environmental applications. Various applications of iron nanoparticles in environmental remediation includes degradation of bromothymol blue, Rhodamine-B, trichloroethylene, fenton-like oxidation of acid black-194 and monoclorobenzenes, removal of hexavalent chromium, arsenite, arsenate, nitrate and total phosphates from aqueous solutions. This review also focuses on various plant extracts and classes of phytochemicals present in them to synthesize iron nanoparticles. Also optimum conditions for removal of pollutant in aqueous medium are highlighted. Various kinetic models and adsorption isotherms fitted to data of pollutant removal and some molecules for responsible for removal of pollutant and formation of nano-sized iron material, characterization data of fabricated material, comparison between potential of plant mediated fabricated iron nanoparticles and those synthesized by conventional methods are also discussed. Thus phytomediated synthesis of iron nanoparticles is effective, simpler, low-cost, eco-friendly and non-hazardous technique for synthesis of nanosized iron materials.

References:


