

Short Review Article



Plant-Mediated Iron Nanoparticles and their Applications as Adsorbents for Water Treatment–A Review

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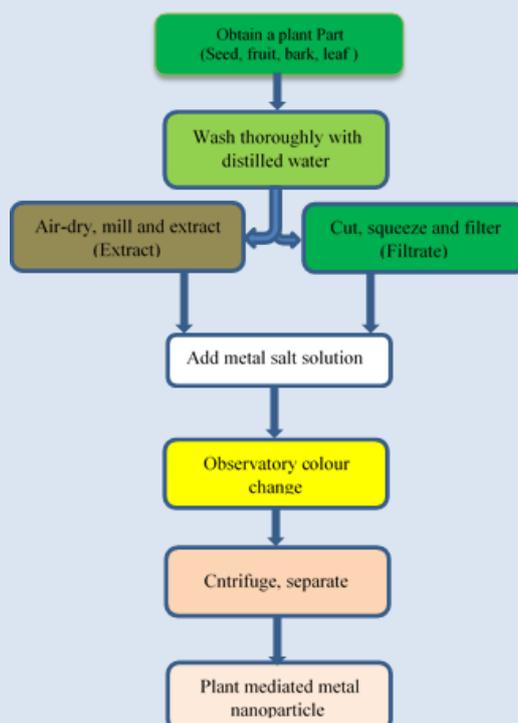
Abstract:

Plant-mediated synthesis of iron oxide nanoparticles has been increasingly drawing attention due to its eco-friendly nature and cost effectiveness. The biosynthesis technique engages plant secondary metabolites such as alkaloids, flavonoids, saponins, phenols, proteins, carbohydrates, glycosides, quinine, steroids, and tannins as reducers and/or stabilizers in the process of forming nanoparticles thereby replacing hazardous chemicals known with physical and chemical methods of nanomaterial synthesis. Biosynthesis method of nano particles has helped to a great extent to overcome some drawbacks, such as high energy and space requirement as well as high cost and hazard associated with various known physical and chemical methods. This work reviewed the biosynthesis of plant mediated iron oxide nanoparticles and their applications in water and wastewater treatment. Much work has been done to explore the effective, safe and cheap method for the dye removal in recent years. However, in future, more methods need to be explored to study and check the removal of dyes from wastewater using plant-mediated iron oxide nanoparticles for safer, cheaper and more efficient performance.

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Keywords: Biosynthesis; Nanoparticle; Magnetite; Wastewater

Graphical Abstract:



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Biography:



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1. Introduction

Over the years, aquatic communities have been extensively suffered due to rapid industrialization and this calls for a global concern. Textile, paper, paint, and printing industries are undeniable and the major sources of environmental pollution. Textile industries consume a lot of dye and generate large amounts of wastewater, containing both organic and inorganic pollutants. It is reported that about 15 % of 700,000 metric tonnes of over 10,000 commercially available dyes produced yearly are lost in textile effluents during production and processing operation [1-4]. The discharged wastewater in water bodies poses a potential risk to aquatic environment due to the bioaccumulation [4]. Generally, the presence of metal ions, aromatic ring, and halogen groups in dye molecules increases their toxicity, genotoxicity, mutagenic, carcinogenicity, and teratogenic property to living organisms [5-7]. Accumulation of dye in water bodies affects water turbidity, chemical oxygen demand and prevents light penetration through water. This disturbs photosynthesis to a large extent [8-12] and poses a great danger to aquatic animals and plants; therefore there is need for the dye removal before being discharged. The needs for environmental sustainability had led many researchers in the

development of several techniques for pollutant removal from wastewater. The techniques include the Fenton process [13]; degradation by photocatalytic processes [14-19], sono-chemical degradation [20]; photo-Fenton processes [21], chemical coagulation/flocculation, cloud point extraction, ozonation, oxidation, chemical precipitation, nano-filtration, ion exchange, reverse osmosis, and ultra-filtration[22-26], and modified methods such as those combining ultrasound with adsorption-desorption processes[27-30]. These methods proved to be effective; however, some revealed some limitations in the areas such as high cost of operation, a bulk of chemicals required, and disposal problems due to the accumulation of the bulk of sludge [17, 31-34]. Among these techniques, adsorption is considered as one of the most efficient method for wastewater treatment due to its design and operation simplicity, non-toxic, low cost of adsorbent and high efficiency [3,34]. Adsorption is the deposition of molecular species (atoms, ions or molecules) from a gas, liquid or dissolved solid onto the surface of a solid [35]. The method has been in existence from the early days of the decolorization of sugar solutions by bone char, to the later adoption of activated carbon for nerve gas removal from the battlefield, to today's several applications in various



fields. The adsorption method has been found as a useful tool in purification and separation processes. Adsorption techniques employ porous materials with large surface area, suitable surface charges, moderate mechanical strength and chemical interaction. Materials such as silica gel, clay, alumina, activated carbon, molecular sieve zeolites, synthetic resins, impregnated biomaterials, with the latest being nanoparticles have been extensively used as adsorbents for industrial applications in water and wastewater purifications.

Nanotechnology refers to a science engaging in the creation and applications of materials whose particles exist within the nanoscale; and, by convention, be between 1 and 100 nm in size [36]. Over the last few decades, nanotechnology has been a flourishing field of technology, creating novel ways of synthesizing particles of unique features and great importance. Nanotechnology provides the opportunities to manipulate the materials' properties by controlling their sizes and shapes, which have been the reason for numerous potential applications of nanomaterials. Nanomaterials have unique properties that distinguish them from a number of bulk materials, these include high surface energy, the large fraction of surface atoms, spatial confinement, and reduced imperfections [37]. Nanoscience is an important growing field with diverse applications in science and technology: environmental sustainability, medicine, food, drug, catalysis, material, energy, agriculture, telecommunication, among others [37,38]. For these purposes, different nanoparticles are available in different material sizes, shapes, morphologies, compositions, physical and chemical properties. The notably ones include carbon-based nanoparticles, metal nanoparticles, ceramic nanoparticles, semiconductor nanoparticles, lipid-based nanoparticles and polymeric nanoparticles. Among the nanoparticles commonly employed for the purposes mentioned earlier, the metallic nanoparticles have attracted a great deal of attention due to their remarkable properties including, mechanical strengths, thermal strength, high surface area, high ordered structure, magnetic properties, and optical properties [39]. Metal nanoparticles can generally be described as submicron scale entities consists of pure metals or their compounds [40]. The metallic nanoparticles are zero-dimension nanosized metals ranging between 1 nm and 100 nm [36]. Metallic nanoparticles are characterized by small size and large surface area. Their size, shape, and surface charge all influence their cellular uptake; hence the attributes for their wide applications and demand.

2. Synthesis of Bio Nanoparticles Using Plant Materials

Recently, scientists have found it economical to synthesize bio-nanoparticles from plants, fungus and algae as they are cost-effective, safe, efficient, and readily available. In achieving this feat, researchers have explored different techniques in developing nanomaterials. The techniques of producing nanoparticles can generally be classified as either top down approach or a bottom up approach. In the top down approach, nanoparticles are synthesized by size reduction from a suitable starting material [41]. This size reduction can be achieved through various physical and chemical manipulations. In a bottom up method of nano development, particles are built from smaller entities [42]. In a bottom up nano particle synthesizing method, the building blocks of the nanoparticles are first produced and then assembled to give the final desired product [43]. However, these methods, physical and chemical methods, can generally be considered to be expensive and unsafe due to the need for special equipment, high energy and chemical substances that are flammable, toxic and corrosive [44].

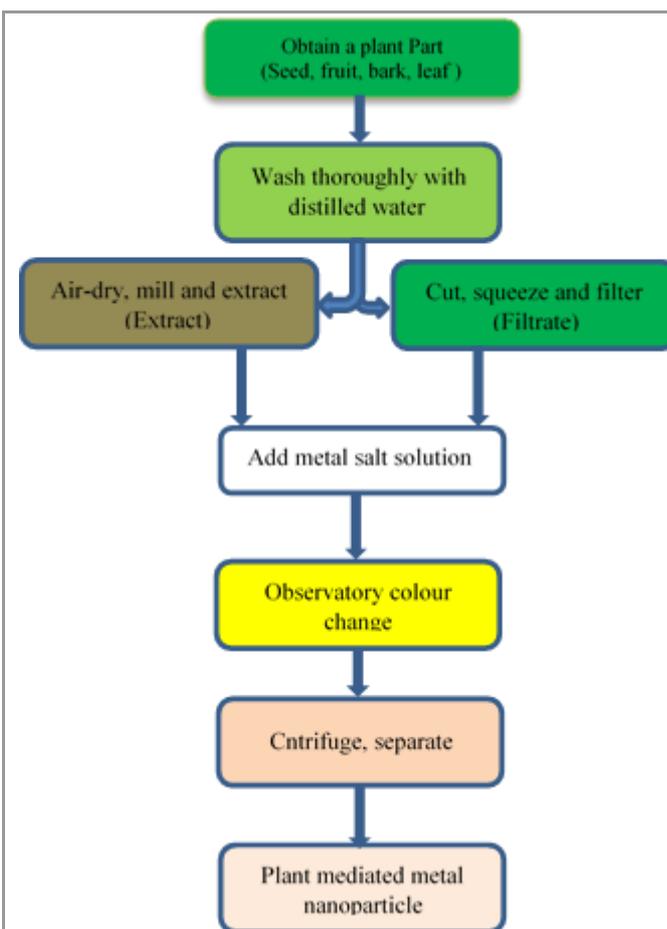


Figure 1. Schematic protocol for green synthesis of plant mediated nanoparticle.

Therefore, the green synthesis method using biological specimens has emerged as a simple, economical and environmentally friendly. Of the biological methods of nanoparticles synthesis, the techniques based on using

plant parts have been widely reported [45-48]. The green approach is the preferred method for metal and metal oxide nanoparticles synthesis because of its feasibility, low toxicity, environmental friendliness, and safety to human health when compared with physical and chemical methods. In recent times, plant mediated nanoparticle synthesis using plant part extract or living plant has been reported in literatures [49,50]. Fresh or dried plant materials; leaf, fruit, bark, seed, peel, and root extracts perform well in the green synthesis of plant mediated nanoparticles under normal experimental conditions [46, 51-56] and replacing hazardous chemicals by plant phytochemicals.

Several applications of bio synthesized metal nanoparticles for wastewater treatment have including, silver nanoparticle [57], iron oxide nanoparticle [58-60], and zinc oxide nanoparticle [61,62] have been reported.

3. Plant as source of bioactive materials for metallic nanoparticles

Application of the biological systems such as plants and microorganisms has found as an alternative procedure for preparation of nanoparticles [63-65]. Biosynthesis method of nanoparticles has provided a great help to overcome some drawbacks, such as high energy and space requirement as well as high cost associated with physical and chemical methods [59, 66, 67]. More importantly, the biosynthesized nanoparticles are free of hazardous material on the surface nano-sized materials. Biosynthesis of NPs are

eco-friendly, time affordable, and cost effective [68]. The utilization of plant materials in the synthesis of nanoparticles engages the secondary metabolites such as alkaloids, flavonoids, saponins, phenols, proteins, carbohydrates, glycosides, quinine, steroids, and tannins [69,70]. Biological agents act as reducers and/or stabilizers in the process of forming nanoparticles [71]. Although the exact mechanism involved in nanoparticles biosynthesis using extracts of various plants is ambiguous, it has been reported that the biomolecules in plant extract such as phenol, protein, and flavonoids play important roles in the reduction of metal ions and capping the biosynthesized nanoparticles [72]. The biosynthesis of plant mediated iron nanoparticles have been carried out by many researchers using a number of plants. Extracts of Neem leaves [58], Tangerine peel [60], *Acacia nilotica* pods [73], *Albizia lebbbeck* leaves [74], *L.camara* fruit [75]; *Eriobotrya japonica* leaves [56]; orange peel [15]; *Mangifera indica* [76], *Murraya Koenigii* [76], Oolong tea [77], *Zanthoxylum armatum* leaves [78], green tea leaves [44, 79], *Eucalyptus* leaves [45], and *Lantana camara* leaves [80].

4. Characterization of Iron Nanoparticles

Identification and evaluation of the physical and chemical properties of nanomaterials are as important as their synthesis. Nanoparticles properties dictate their reactions and applications providing an opportunity to engineer materials for desired unique properties.

Table 1. Characterization techniques for nanoparticle properties.

Entry	Parameters	Importance	Techniques	Ref.
1	Size and dispersion	Size reveals the external dimensions of a particle while dispersion gives the degree to which particles clump together into weakly bound agglomerates or strongly bound aggregates	SEM, AFM, XRD, DLS, and Back-calculation from surface area measurements	[81], [82]
2	Shape	Material shape as well as its surface topography with the presence of ridges, cracks or pores defines its morphology. It influences dispersion, functionality and toxicity.	TEM, SEM, AFM	[83], [81]
3	Surface area, charge and chemistry	Surface properties influence reactivity and surface interactions with ligands.	Adsorption of gases, BET, EMA, AES	[84]
4	Chemical composition and crystal structure	Chemical composition reveals the atomic elements which a nanoparticle is composed. Crystal structure determination reveals the arrangement of nano structure which could be crystal, amorphous or intermediate between the two. Crystal structure influences physical and chemical properties.	AAS, ICPMS, NAA, XRD, XRF, XRF, XRF, EDX	[85], [82]
5	Solubility	This is done to measure the degree to which materials dissolve from a nanoparticle.	AAS, ICPMS	[86]



Table 2. Plant-Iron nanoparticles, size, morphology and applications.

Entry	Plant	Size (nm)	Morphology	Adsorbate	Adsorption capacity (mg/g) / Percentage efficiency (%)	Ref.
1	Neem leaf	21.03	Spherical	DDT	--/90.20	[58]
2	Tangerine peel	50 – 20	Spherical	Cd	10.90/90.00	[60]
3	<i>Eriobotrya japonica</i>	89.00	Spherical	Cr(VI)	312.5/--	[91]
4	Acacia nilotica pods	230	Irregular	Methyl Orange	19/--	[73]
5	Albizia lebbeck leaf	--	--	Crystal violet	--/96.59	[74]
6	Albizia lebbeck leaf	--	--	Congo red	--/96.59	[74]
7	<i>L.camara</i> fruit	1.9	Spherical	Ni (II)	227.20/--	[75]
8	<i>Eriobotrya japonica</i> leaf	171.2	Irregular spherical	Basic Red 46		[56]
9	Orange peel	500	Spherical	Cd	--/71.43	[3]
10	<i>Mangifera indica</i>	100-150	Spherical	Total phosphates	--/91.89	[76]
11	<i>Murraya Koenigii</i>	100-150	Spherical	Phosphates	--/97.68	[76]
12	<i>Murraya Koenigii</i>	100-150	Spherical	Ammonia nitrogen	--/87.08	[76]
13	<i>Murraya Koenigii</i>	100-150	Spherical	COD	--/88.24	[76]
14	<i>Azadirachta Indica</i>	96-110	Spherical	Phosphates	--/98.08	[76]
15	<i>Azadirachta Indica</i>	96-110	Spherical	Ammonia nitrogen	--/84.32	[76]
16	<i>Azadirachta Indica</i>	96-110	Spherical	COD	--/82.35	[76]
17	<i>Magnolia Champaca</i>	99-129	Spherical	Phosphates	--/98.84	[76]
18	<i>Magnolia Champaca</i>	99-129	Spherical	Ammonia nitrogen	--/74.78	[76]
19	<i>Magnolia Champaca</i>	99-129	Spherical	COD	--/88.23	[76]
20	<i>Magnolia Champaca</i>	99-129	Spherical	BOD	--/88.23	[76]
21	Oolong tea extract	40 – 50	Spherical	Malachite green	--/75.5	[77]
22	<i>Zanthoxylum armatum</i> leaf	17	Spherical	Methylene blue	0.4712 /--	[78]
23	Green tea leaf	5 – 15	Spherical	Degradation of bromothymol blue	Effective	[79]
24	Green tea leaf	40 -60	Irregular clusters	Methylene blue	--/99	[44]
25	Green tea leaf	40 – 60	Irregular clusters	Methyl orange	--/99	[44]
26	Eucalyptus leaf extract	20 – 80	Spherical	Total N	--/71.7	[45]
27	Eucalyptus leaf extract	20 – 80	Spherical	COD	--/84.5	[45]



This makes their characterization a crucial step to fully understand the origin of nanoparticle behaviour, and subsequently translate their laboratory performances to specific real world applications. To fully comprehend the features of nanoparticles, investigations are necessary on particle size and distributions, particle shape, chemical composition and crystal structure, surface area, surface chemistry and charge and solubility. The investigations can be conducted given the large number of existing techniques, including the combination of different methods and different approaches to data analysis for a same technique. Some parameters, characterization techniques, and their importance are presented in Table 1.

5. Iron Nanoparticles

Iron nanoparticles are the iron oxide particles with diameters ≤ 100 nm. Iron oxide nanoparticles consist of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and/or magnetite (Fe_3O_4) particles. Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ display ferromagnetic behaviour and both crystallize in the inverse spinel cubic structure [87-90]. The major difference between the two structures is the presence of Fe^{2+} and Fe^{3+} ions in Fe_3O_4 , while $\gamma\text{-Fe}_2\text{O}_3$ contains only Fe^{3+} ions and vacancies in their sub-lattices [87]. Also, while the temperature above which a material loses its magnetic properties known as Curie temperature (TC) is 900 K for maghemite, magnetite has a Curie temperature (TC) of 860 K [88-90]. Recently, iron oxide nanoparticles have attracted much interest due to their unique properties including, superparamagnetism, surface-to-volume ratio, greater surface area, and easy separation methodology. Iron oxide nanoparticles have great potential for their applications as wastewater treatment adsorbents, catalytic materials, pigments, gas sensors, coatings, ion exchangers, magnetic data storage devices, magnetic recording devices, magnetic resonance imaging, and bioseparation [87].

It is a well-established fact that iron and iron oxide nanoparticles show greater catalytic activities for dye reduction and removal. Recently, there has been a great interest in using the plant extract in synthesizing the metal nanoparticles such as iron, silver, gold, magnesium, and platinum for industrial applications. The iron oxide nanoparticle is safer and cheaper. Iron oxide nanoparticles have been synthesized using biological methods. These include the use of extract of different plants. Table 2 contains some reports of earlier research works.

6. Justification of using Nanoparticles

The iron nanoparticles can be produced by one of the cheapest, simplest and most effective method [92]. Nanosized iron oxides are potential materials for efficient binding metal ions in water and wastewater

treatment. Its small size gives a high surface-area-to-volume ratio that allows good interaction with various chemical species, both aqueous and gaseous [93]. Material manipulation such as changing the shape and size of iron oxide during activation expose the materials' most active catalytic sites, thereby making it an efficient and cheaper catalyst for various reactions [92,94-96]. Also, adjustment of iron oxide compositions can be made for the selective adsorption of different metal ions. Iron oxide nanoparticles are now seen to be attractive for the adsorption or recovery of metal ions from the natural water streams or industrial wastes [97].

7. Conclusion

This review discussed the recent growing interest in the use of plant mediated iron nanoparticles for water and wastewater treatment. Various cost effective and environmentally friendly green synthesis techniques have been developed using biological specimens and taking over from the well-known physical and chemical methods of nano synthesis which are considered toxic and not cost-effective. With the continual deployment of nanosized iron oxide particles for environmental sustainability as environmental mediators, there is a need to search for suitable plants to sustain the goal without jeopardizing the existing functions of medicinal plants.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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