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Plant Mediated Nanomaterials for Water Purification

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Abstract: Wastewater treatment has become a global concern issue of fundamental significance surrounding the most recent approaches that describe the techniques environmentalist and conservationist used. Recently, the development of green mediated nanomaterials for the water purification has turn out to be a major focus for researchers. This is due to the ecological friendly nature, cost effective and simple processing of the techniques. One of the most considered techniques is the fabrication of the metal and metal oxides nanomaterials using organisms. Amongst these organisms, plant is considered to be the best materials which can be biosynthesize in large scale for industrial application. Biosynthesis of the metal and metal oxide nanomaterials using plant is more stable and yield faster production than in the microorganisms. Rising preference in the investigation of biosynthesis materials using plants and plants derivatives by several researchers' to comprehend the mechanisms of metals and metal oxides uptake, formation and bioreduction in plants is as a result of the several merits shown by the plants. The present review highlighted the fundamental procedures and mechanisms of plants mediated biosynthesis techniques, particularly on the metal and metal oxides synthesis using plant extracts. Similarly, the functions of some of the biological components, that's the essential phytochemicals such as alkaloids, aldehydes, terpenoids, amides and flavonoids which serve as solvent systems and reducing agent has been discussed. The toxicity and stability of the nanomaterials and their related surface structural techniques to achieved biocompatibility are also highlighted. Lastly, several applications of the biosynthesized nanomaterials for the water and wastewater purification and the mechanisms prevailing green nanoparticles fabrication along with the interactions on degradation of dye and removal of heavy metals have been highlighted as well as their associated efficiency.

Keywords: Adsorption, Metals, Metal oxides, Nanomaterials, Plant synthesis, Wastewater.

I. Introduction

Water is a vital element of the ecosystem that plays a key role in the development of every society. Water covers 71% of the earth surfaces. However, 97% of the earth's water is found in the oceans which is too salty for consumption and other industrial activities, only about 3% is fresh water. Yet, the scarcity and contaminations of the freshwater have been increasing worldwide due to high population growth and industrial activities [1]. The reuse of wastewater has been regarded as alternative choice for conserving and increasing the available sources of the water. There are several applications of the reused wastewater which include artificial groundwater recharge, irrigation farming, aquaculture, consumptions, environmental practice and recreational activities [2]. The growing preference of reuse and recyclability by researchers towards water purification through the use of nanomaterials indicate the importance of extensive investigation in the purification processes so as to have economical, high effective, efficient decontamination and sustainable wastewater treatment [3] greater emphasis has been laid on the designing of nano-materials to improve the efficiency of treatment processes. Therefore, in the wake of technological improvement, a novel adsorbent humic acid-functionalized alumina (HAFA) [4]. This is because of their unique properties such as high adsorption capacity and high surface area, furthermore, the interaction between contaminant and nanoadsorbent materials may be physisorption or chemisorption depending on the functionalization of the nanomaterials [5]. However, among the different categories of water remediation and wastewater treatment, nanomaterials demonstrate greater potentials in achieving safe, qualitative and potable water supply, and furthermore involves less infrastructures requirement [6].

Removal of toxic metals and compounds that are found in low concentration is tedious and very challenging. Different remediation techniques have been fabricated and utilized for the elimination of contaminants like dyes, pesticides, heavy metals, organic acids, fertilizers, phenolic and halogenated compounds and so on [7]. Various techniques both conventional and modern have been used to get rid of these pollutants from wastewater and waters such as sedimentation, flocculation, precipitation, coagulation, membrane filtration, incineration, reverse osmosis, biological oxidation, ion exchange, oxidation using chemical oxidants (for example hydrogen peroxide, ozone, etc.), photocatalytic degradation and oxidation, photo-Fenton treatment, membrane processes, advanced oxidation processes (AOPs), electrochemical degradation and oxidation and adsorption methods [8] various methods for heavy metal removal from wastewater have been extensively studied. This paper reviews the current methods that have been used to treat heavy metal wastewater and evaluates these techniques. These technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods [9, 10].

However, Amongst the existing methods, adsorption is considered as the most effective and promising due to its low cost of operation, efficient treatment and simple designing process [11]. Thus, selection of appropriate materials (adsorbents) is the key factor in order to achieve the desire benefits of adsorption process [12]. Different categories of non-conventional materials such as activated carbon, clay minerals, waste from agricultural products, fly ash etc. have been comprehensively used for the elimination of different contaminants from wastewaters and water. Nevertheless, these categories of adsorbents exhibit some limitations such as weak adsorption capability, long time duration and weak regeneration capacity, production of high sewage sludge, expensive and energy inefficiency, release of toxic by-products, thereby adding more hazardous chemicals to the environment [13, 14]. Similarly, synthesis of nanoparticles via chemical route are usually expensive, because of the synthetic chemicals which are injurious to the human and other biota in the ecosystem [15]. On the other hand, synthesis via green routes from different microbes, enzymes, plants extract etc. are known to be simple, less toxic, cost effective and eco-friendly [16].

II. Plant-Mediated Green Synthesis

Different parts of plant can accumulate certain quantities of heavy metals, thus biosynthesis processes using extracts of plant have gained more consideration, due to its low cost, simple, viable methods, efficient as well as outstanding substitute to the conventional techniques for the generation of nanoparticle [7]. Several plants can be use as reducing and stabilizing agents for the synthesis of metallic nanoparticles. Lot of researchers have been exploring extracts of plant for the synthesis of green metal oxides and metal nanomaterials so to discover more application and mechanisms of action. Plants biomolecules such as proteins, coenzymes and carbohydrates have the potential of reducing metal salts to nanoparticles. The advantages of green synthesis using plant extract can never be overemphasize, this is because they are readily available, safe to handle, clean, eco-friendly and contains different active constituents which initiate the reduction process of the metals ions (Fig. 1). Nanoparticles synthesis with Alfalfa sprouts was among the earlier reported mediated plant synthesize nanoparticles [17]. The Alfalfa root absorbed silver from the growing nutrient agar media and transfer via same oxidation condition to the shoots. The shoots accumulate the translocated silver and organized in order to form nanoparticles. Thus, the nanoparticles generated along with plants provide higher rates of synthesis as compared to bacteria and fungi. For instance, extract of leaf of Geranium reach 90% completion of synthesizing nanoparticles in approximately 9 h as compare to the 24 to 124 h duration for other non-plant extract synthesis nanoparticles [18].

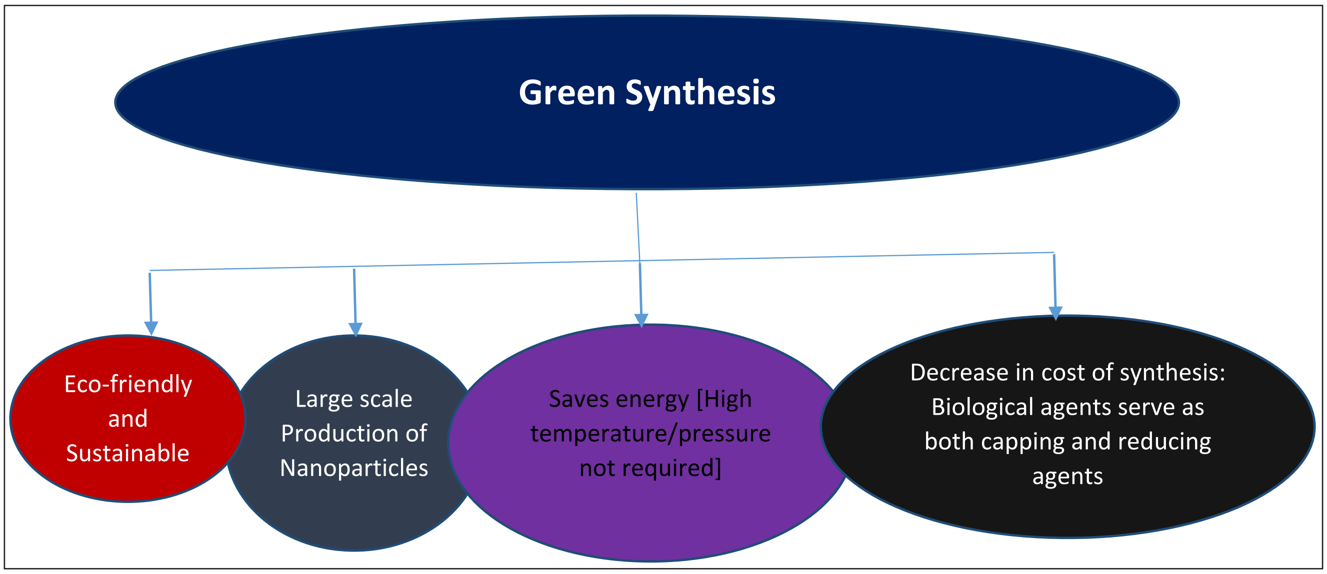

Fig. 1: Main Advantages of Green Synthesis Technique [19]

Therefore, the use of plant extracts for synthesizing of nanoparticles have been increasing rapidly resulting to a novel age in green synthesis. Scores of researchers have established that the synthesis of nanoparticles using extract of plant may be achieved within few minutes at room temperature in the metal salt solution. However, the nature of the plants extracts determine the rate of the synthesis [20, 21, 22, 23]. Different factors like type of metal salt, pH, concentration of plant extract and temperature influence the nanoparticle's green synthesis [24]. Nearly, all parts of plant like leaves, roots, flowers, seeds, stem and latex have been utilized for synthesizing nanoparticles [25]. The phytochemical compounds in plant extract serve as both capping and reducing agents which stabilize and modify the morphology of the nanoparticles [13]. Some of the phytochemical compounds involve in the bio-reduction and capping of the metals nanoparticles include; proteins, flavonoids, alkaloids, phenols, enzymes, alcoholic compounds, terpenoids, amino acids and polysaccharides. Similarly, reports indicated that chlorophyll pigments, ascorbic acid, methyl chavicol, quinol, eugenol, theophylline, vitamins, linalool and caffeine behave as reducing and capping agents for the metallic salts in the nanoparticle synthesis [26, 27]. These abovementioned phytochemicals have the capability to reduce, stabilize, capping and prevent accumulation of nanoparticles. The carboxyl and hydroxyl group of phenolic compounds attach to the metal surface [28]. The synthesis of nanoparticle via chemical route is usually costly because of the utilization of synthetic chemicals which are hazardous to the environment [15]. On the contrary, nanoparticle synthesis via green route is easy, non-hazardous, cost-effective and environmentally friendly using different extracts of enzymes, microbes, plants, etc. [16]. Some researches related to synthesis of nanoparticles via green route and their utilization in the treatment of wastewater has been carried out [29, 30].

Green synthesis of nanomaterials utilizing extracts of plant has been prominence in the last few decades [31] we report on the uptake of silver by living alfalfa plants. X-ray absorption spectroscopy and transmission electron microscopy (TEM. Phumying *et al*. [32] reported the nanoparticles synthesis of Fe_3O_4 using extract from Aloe vera plant, in which XRD reveal formation of high purity nanoparticles. Temperature and pressure directly affect the transitional/intermediate size of the particle which was calculated using XRD. With an increase in pressure and temperature, the intermediate particle size also increases. It was inferred from the correctivity that the nano-particles were super-magnetic. By the use of stabilizing agents and reductants gotten from the extracts of the leaf of *Ocimum sanctum* and from a solution of Nickle nitrate $\{Ni(NO_3)_2.6H_2O\}$ which was aqueous in nature as the precursor. Pandian *et al*. [33] was able to synthesize nanoparticles of Ni. The hydrated electrons from the aqueous plant extract was able to reduce the ions of Ni(II) to Ni atoms. Furthermore, these atoms aggregate subsequently thereby forming Ni nanoparticles. The formation of nanoparticles of Ni were confirmed by the use of the spectrum of ultraviolet, Visible (UV/Vis) in which the sample showed a peak which corresponds to nanoparticles of Ni at 395 nm. Using the Debye-Scherrerformular, the intermediate size of particle was 30 nm and a confronted cantered cubic structure was registered by the pattern of XRD for the synthesized nanoparticles of Ni. Also, through the reduction of manganese acetate using eco-friendly natural products i.e. turmeric curcumin serving as a stabilizing agent while lemon extracts served as a reducing agent, nanoparticles of MnO were synthesized by Jayandran *et al*. [34], using solvent extraction technique, for the stabilization of the synthesized MnO nanoparticles, curcumin was extracted from turmeric. A change in colour was noticed after an aqueous solution of Pd $(OAc)_2$ was stirred using *Catharanthusroseous* (which is a mixture of 8 -OH group compounds) extracted by methanol at a temperature of 60 ^oC over a period of 60 mins. A UV/Vis absorption peak in the range of 360 to 400 nm which is corresponding to about 40 nm nanoparticles of palladium spherical in nature was observed. On another development, Velmurugan *et al*. [35] documented the use of palladium nanoparticles as photocatalytic mediator through its synthesis, characterization and subsequent application. Utilizing aqueous extracts from the leaf of the plant *Hippophaerhamnoides*, nanoparticles of palladium were synthesized as documented by Nasrollahzadeh *et al*. [22]. Furthermore, the biosynthesis of the nanoparticles of Pt from the extracts of *Azadirachtaindica* was also reported by Thirumurugan *et al*. [36]. Development small to large spheres nanoparticles ranging from 5-5 nm which are poly-dispersed was shown by the TEM analysis. The synthesis rate of the nanoparticles was temperature dependant, hence, with an increase in temperature of the reaction system, the rate of the formation of the nanoparticles of Pt also increased. Various FTIR peaks shows that it corresponds to the existence of aliphatic amines (1219.01 cm^{-1}) carbonyls (1728.22 cm^{-1}) and alkanes (1365.60 cm^{-1}) groups respectively. The leaf the plant *Azardirachtaindica* contains the phytochemical terpenoids. This terpenoid serves a dual purpose of a stabilizing agent as well as a reducing agent for the synthesized NPs. Owing to the fact that banana is considered as one of the favourite foods globally, statistically, greater than a hundred million tons are globally consumed annually while the peel is always discarded as trash. The peel comprises of different biopolymers ranging from lignin, cellulose, proteins, hemicellulose, and pectin which could all be utilized efficiently in nanoparticles synthesis. A very good example of nanoparticles which were synthesized using the skin of banana are the Hydroxyapatite nanoparticles. The existence of pectin in the skin of the banana plant performs a significant part or role in modulating the surface of the nanoparticles. Nanoparticles of Mn_3O_4 possessing super-capacitive properties were successfully synthesized using extracts from the skin of banana. One of the most stable oxides of Mn which poses a wide range of fascinating properties such as high-density magnetic storage standard and catalysis is the Mn_3O_4 [30]. Agglomerated particles consisting of 20 to 50 nm diameter were depicted by the SEM analysis. Also, by the use of zinc acetate dehydrate as the precursor and extracts from the leaf of corriandrumsativum, nanoparticles of zinc oxide were synthesized and subsequently utilized in the degradation of anthracene photo-catalytically. A 96% degradation of a 100 µg/L of anthracene was achieved at optimum conditions of 25 ^{o}C temperature, adsorbent dose of 1000 µg/L, UV radiation of 240 nm, and neutral pH (7). The result of the kinetic studies showed that it fitted well to the pseudo-first order rate constants and the Langmuir adsorption isotherm. GCMS and HPLC analysis were used to confirm the formation of anthraquinone as a major product of the degradation. Hence, the noxiousness of the pollutant anthracene has been reduced by the photocatalytic degradation reaction [37]. The green synthesis of different nanoparticles using extracts of plants such as Lemon grass (*Cymbopogonflexuosus*), Alfalfa (*Medicagosativa*), Tulsi (*Osimum sanctum*), Neem (*Azadirachtaindica*), Aloe vera Aloe (*barbadensis Miller*), Mustard (*Brassica juncea*), Lemon (*Citrus limon*) and Coriander (*Coriandrumsativum*) as depicted in (Table I). Basically, while nanoparticles of metallic nature can be formed in vivo (in plants) by the reducing ions of metallic salts which were initially absorbed as soluble salts, such research has investigated the in vivo nanoparticles synthesis. The synthesis (in vivo) of nanoparticles such as nickel, copper, zinc, and cobalt in Brassica juncea, Helianthus annuus, and Medicagosativa have been studied [38]. Likewise, using different plants leaf extracts like "*Calotropis gigantean* [39], *Hibiscus rosa-sinensis* [40], *Aloe barbadensis* Miller [41], *Coriandrumsativum*, *Camellia sinensis* [42] and *Acalyphaindica* [43]" nanoparticles of ZnO were synthesized.

The synthesis of nanoparticles via green synthetic route have been reported in various studies. The decontamination of Pb^{2+} from industrial wastewater using green synthesized of TiO_2 by extracts of *Syzgiumcumini* have been reported by Sethy *et al*. [13]. Also, the cytotoxic activities, adsorption efficiency for dye and heavy metals, as well as antioxidant, antibacterial of Fe_3O_4 nanoparticles, which was synthesized through a green route by using extracts of *Cinnamomumtamala* and *Jatropha curcas*, and the effect of green synthesis coated Magnetite (*Jatropha curcas* -Fe_3O_4 and *Cinnamomumtamala* -Fe_3O_4) for the treatment of wastewater including dye adsorption, metals detoxification as well as antioxidant, antibacterial and cytotoxic activities were reported by Das *et al*. Bahal *et al*. [44] investigated the photodegradation of industrial dye using bionanocomposite of Amphoteric Chitosan and TiO_2. Gautam *et al*. [46] reported adsorption and reusability of lead from aqueous solution synthesized by using leaf extract of Moringa oleifera coated with magnetic nanoparticles. However, there is need to explore more green synthesized nanocomposites for effective and eco-friendly water remediation. Nyankson *et al*. [47] zeolite (Z reported the maximum adsorption of 2.57 mg/g at 25 °C [i.e. 97.5%] of organic molecules from wastewater using green synthesis nanocomposites of Zeolite A/Fe_3O_4. Similarly, effective degradation of remazol yellow RR dye and antibacterial activity of bionanocomposites comprising of *Carica papaya* leaf extract capped iron oxide nanoparticles was reported by Bhuiyan *et al*. [48], in which peak degradation of 76.6% using a catalyst dose of 0.8 g/l under pH 6 at 2 hours was reported.

Table I: Application of Green Synthesize Nanomaterials from Different Parts of Plant Used for Water Purification

Nanomaterial	*Plant Species*	*Part Used*	*Size and Morphology*	*Adsorption Process*	*Reference*
Fe0/Fe_3O_4 nanoparticles	Punicagranatum	Leaf	100–200 nm	Hexavalent chromium removal	[49]
Iron nanoparticles	AzadirachtaIndica	Leaf	50–100 nm Spherical	Azo dyes example, acid Orange	[50]
Fe_3O_4 nanoparticles	Tridaxprocumbens	Leaf	80–100 nm crystalline irregular sphere shapes	Antibacterial	[51]
Magnetite nanoparticles	Carob	Leaf	5–8 nm crystalline mono dispersed	Azo dyes example acid Orange	[52]
Iron-polyphenol nanoparticles	Eucalyptus tereticornis, Rosemarinus officinalis and Melaleuca nesophila	Leaf	50–80 nm spherical	Catalyst for decolourisation of azo dyes	[53]
Iron complex nanoparticles	Eucalyptus Tereticornis	Leaf	40–60 nm	Cubic Adsorption of azo dyes	[30]
Iron-based nanoparticles	Grape	Leaf	15–100 nm quasi-spherical shape	Amorphous Azo dyes like acid orange	[54]
Iron nanoparticles	Azadirachtaindica	Leaf	~100 nm	-	[55]
Iron oxide nanoparticles	Green tea	Leaf	70 nm spherical crystalline	-	[56]

Nanomaterial	*Plant Species*	*Part Used*	*Size and Morphology*	*Adsorption Process*	*Reference*
Iron oxide nanoparticles	*Hordeumvulgare* and *Rumexacetosa*	Leaf	10–40 nm amorphous	-	[56]
Zerovalent iron particles [nZVI]	Tea	Tea powder	40–50 nm spherical	-	[57]
Iron oxide nanoparticles	*GarlicVine* (Mansoaalliacea)	Leaf	13.82 nm–15.45 nm crystalline	-	[58]
Iron nanoparticles	Green tea	Leaf	40–60 nm	Amorphous Degradation of aqueous anionic and cationic dyes	[59]
Fe_3O_4 spherical magnetic nanoparticles	Syzygiumcumini	Seed	9–20 nm spherical crystalline	-	[60]
Zero-valent iron	Camelliasinensis	Leaf	5–15 nm Spherical crystalline	Bromothymol blue degradation (organic contamination)	[61]
Mesoporous hematite [α-Fe_2O_3] nanoparticles	Green tea	Leaf	40–80 nm crystalline	Photo catalytic activity	[62]
Iron nanoparticles	Terminaliachebula	Fruit	<80 nm amorphous chain-like morphology	-	[63]
Iron oxide nanoparticles	Alfalfa	-	1–10 nm	-	[64]
Iron oxide nanoparticles	Alfalfa	-	<5 nm	-	[65]
Iron nanoparticles	Green tea	Leaf	20–120 nm	Degradation of monochlorobenzene	[66]
Iron oxide nanoparticles	Passifloratripartitavar	Fruit	18.23–24.65 nm spherical crystalline	-	[67]
Iron oxide nanoparticles	Green tea	Leaf	70–80 nm spherical amorphous	Degradation of dye (malachite green)	[68]
Iron oxide nanoparticles	Sorghum	Bran	40–50 nm spherical amorphous	Degradation of bromothymol blue	[69]
Cu, ZVI, and Ag nanoparticles	Dodonaeaviscose	Leaf	50–60 nm Spherical	Antibacterial	[70]
Hexavalent chromium with polyphenol-coated nano zero-valent iron	Green tea	Leaf	5–10 nm Spherical	Removal of hexavalent chromium	[71]
Zerovalent iron nanoparticles	Eucalyptusglobules	Leaf	50 to 80 nm spherical	Adsorption of hexavalent chromium	[72]
Fe_3O_4 magnetic nanoparticles	Orange extract	Peel	30–50 nm crystalline cubic	-	[60]
Active iron nanoparticles	*S. jambos* (L.) *Oolong* tea, A. *Moluccana* (L.), etc.	Leaf	-	Removal of chromium	[73]
Magnetite (Fe_3O_4) nanoparticles	Aloe vera	-	6–30 nm cubic spinel structure crystalline	-	[74]
Fe nanoparticles	Eucalyptus	Leaf	20–80 nm amorphous	Treatment of eutrophic wastewater	[53]
Iron–polyphenol complex nanoparticles	Salvia officinalis	Leaf	5–25 nm spherical	-	[75]

Nanomaterial	*Plant Species*	*Part Used*	*Size and Morphology*	*Adsorption Process*	*Reference*
Zero valent iron	Green-Tea	Leaf	-	Soil mineralogy	[76]
Iron-based nanoparticles	Oolong tea	Leaf	40–50 nm spherical	Degradation of malachite green	[77]
Iron nanoparticles	Green tea and eucalyptus	Leaf	20–80 nm quasi-spherical	Nitrates removal	[78]
Polyphenol-coated nanoiron	Green tea	Leaf	-	Transport properties of nano zero-valent iron [nZVI] through soil	[79]
Iron oxide Nanoparticles	Eucalyptusglobulus	Leaf	Chitosan	Removal of arsenic	[80]
Nano iron Particles [GnIP]	*Menthaspicata* L. Leaf	20-45 nm poly dispersed cubic crystalline	Chitosan	Removal of arsenic	[81]
Fe and Fe/Pd Bimetallic Nanoparticles	Green tea	Leaf	20–30 nm aggregates	Degradation of organic trichloroethylene [TCE] pollutant	[82]

III. Plant Extracts as Capping Agents

Plant extracts demonstrate a vital role as capping agents in the synthesis of nanoparticles. Functionalization and stabilisation of nanoparticles can be achieved by controlling the scale, morphology, and surface protection to prevent agglomeration using capping agents to pass on useful properties [83]. Several surfactants have been documented to be used to modify the desired shape and size of the nanoparticles as capping agents, but these are hard to extract and do not degrade simply. Therefore, commercial surfactants are environmentally harmful [84, 85]. As far as the limitations of these chemicals are concerned, there is a critical requirement for the synthesis of nanoparticles to utilize capping agents which are eco-friendly and to devise eco-friendly biochemical routes at laboratory and industrial levels. There are various kinds of molecules that may function or be utilized as capping agents, but with their potential position, few of the narrowly defined green capping agents have been discussed below.

IV. Nanoparticles Toxicity and Stability

The transportation and environmental distribution of the liberated nanoparticles is related to their capacity to form metastable aerosols in environmental fluids or aqueous suspensions. As a result, the strength of nanoparticles in the atmosphere can be measured by assessing their proclivity to mix or interact with nearby media. Agglomeration is a time-dependent process related to particle collision rates, whereas suspension stability is mainly determined by particle size and affinity to other environmental constituents. The green synthesis of Ag NPs from tea leaf extraction was found to be stable after entering the aquatic environment [86]. Similarly, the stability of AgNPs (in aqueous medium) produced using plant extracts and plant metabolites was reported from the resulting material [87]. Complexation of the surface is also confirmed to influence nanoparticles' intrinsic stability via controlling their colloidal stability. The nature and stability of nanoparticles can be predicted theoretically using a mechanistic understanding of surface complexation processes [88]. The rate of dissolution or colloidal stability of nanoparticles can be controlled by regulating particle size and surface capping, or by using functionalization techniques [89, 90]. When determining their environmental effects or toxicity, the transformation of nanoparticles is an important property to consider. Sulfurization of AgNPs, for example, greatly decreased their toxicity due to the lower solubility of silver sulphide [91] which modifies their properties and alters their transport, fate, and toxicity. It is essential to consider such transformations when assessing the potential environmental impact of Ag-NPs. This review discusses the major transformation processes of Ag-NPs in various aqueous environments, particularly transformations of the metallic Ag cores caused by reactions with (in). The utilization of biocompatible stabilising agents like biodegradable copolymers and polymers has opened up a "greener" possibility for surface engineering of nanomaterials for similar purposes. Such techniques may provide remarkable stability, such as in situ AuNP synthesis capped with Korean red ginseng root [92]. In addition to surface chemistry, the structure, size and shape of the nanomaterials are other primary structural features that determine nanomaterial toxicity [93]. Toxicity testing of synthesised AgNP using plant leaf extracts indicated that the chemical activation treatment of AgNP resulted in higher seed germination rates than the control treatments [94].

V. Characterization of Nanoparticles

Nanoparticles characterization is significant in terms of controlling synthesis of nanoparticles and applications. Characterization of nanoparticles is carried out utilizing a range of various techniques like X-ray Diffractometry (XRD), FTIR, SEM, TEM, AFM, UV– Vis spectroscopy, DLS and XPS. These techniques are helps in resolving various parameters like crystallinity, size of particle, fractal dimensions, shape, surface area and pore size. Moreover, these techniques determines the dispersion, orientation and intercalation of nanotubes and nanoparticles nanocomposite materials. SEM, TEM, and AFM can be used to estimate particle morphology and scale. The benefit of AFM over SEM and TEM is that it uses three-dimensional imaging to assess particle volume and height. In addition, DLS is used to measure particle size distributions. Furthermore, X-ray diffraction is used to assess crystallinity, and UV– Vis spectroscopy is used to check sample formation by demonstrating the Plasmon resonance [95, 96] as well as in the construction of sensors and biosensors, are reviewed here. In particular, subsequent to brief surveys of the most-commonly used methods of preparation and arraying of materials with localized surface plasmon resonance (LSPR, 97, 98, 99, 100].

VI. Mechanism of Plant Extract

Green nanoparticles synthesis using mediated plant extract involves the mixing of metal precursor solutions at different reaction conditions with the plant extract [18]. Some of the parameters used to determine the conditions of the plant extract include different varieties of phytochemicals, amount of the phytochemical, temperature, pH and quantity of metal are used to regulate the rate of nanoparticle formation along with their yield and stability [101]. In contrast to bacteria and fungi, phytochemicals found in extracts derived from plant have a huge capability to minimise metal ions in less period of time, requiring longer incubation time [102]. Extracts of plant are thus thought to be a benign and excellent source of nanoparticle synthesis of metal along with metal oxide. In addition, extract derived from plant plays a twin role in the synthesis process of nanoparticles by acting as both reducing and stabilising agents to support the manufacture of nanoparticles [103]. The composition of the extract derived from the plant also plays a key role in synthesizing the green nanoparticles (Fig. 2), for instance various plants contain different concentration levels of phytochemicals [104, 105]. Terpenoids, flavonoids, carbohydrates, aldehydes, ketones, amides and carboxylic acids used to bio reduce nanoparticles are the main phytochemical compounds present in plants [106]. Flavonoids, which have the ability to increase metal ion reduction, contain different functional groups. Due to tautomeric transformations in flavonoids in which enol-form is converted to keto-form, the reactive hydrogen atom is released. The reduction of metal ions into metal nanoparticles realises this process. In Ocimumbasilicum (sweet basil) extracts, for example, enol-to-keto-transformation is the main element in the synthesis of biogenic silver nanoparticles [107].

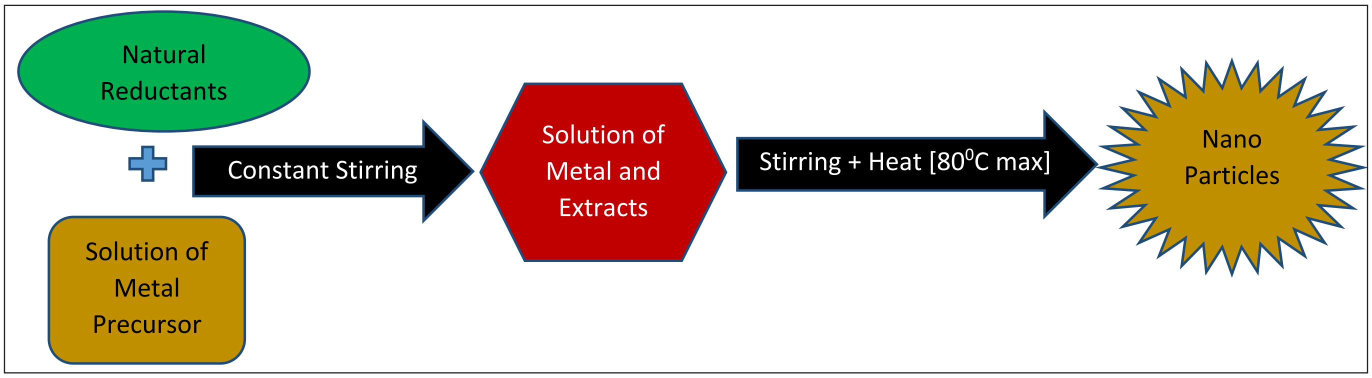

Fig. 2: Nanoparticles Synthesis from Plant Extract [58]

Plant sugars like glucose and fructose, which are found in plant extracts, may also play a role in the formation of metallic nanoparticles. Glucose-mediated gold and silver nanoparticles, on the other hand, can take on a variety of shapes and sizes, whereas fructose-mediated gold and silver nanoparticles are naturally monodisperse [108]. Analysis of FTIR for green synthesized nanoparticles with extracts from plant proved that emerging nanoparticles were recurrently found to be connected with proteins [109]. Likewise, amino acids have several means for reducing the metal ions [110]. Clem [110] reported that amino acids such as arginine, cysteine, methionine and lysine are capable to attach with ions of silver. Tan *et al*. [111] the progress in peptide synthesis of metal nanoparticles has been slow due to the lack of peptide design rules. It is difficult to establish sequence-reactivity relationships from peptides isolated from biological sources (e.g., biomineralizing organisms studied all 20 natural α-amino acids and proved that they can efficiently reduce Au0 metal ions. Extracts from plant are composed of proteins and carbohydrates biomolecules, which serve as a capping and reducing agent thereby improving the formation of metallic nanoparticles [112]. Furthermore, the functionalize amino groups (–NH_2) in proteins which are found in the plant extracts are proved to be active in the reduction process of metal ions [113]. For instance, the functional groups–C–O–C–, –C–

O, –C=C–, and –C=O–] found in phytochemicals like alkaloids, flavones, anthracenes and phenols can facilitate in the generating of metallic nanoparticles. Jiale *et al*. [114] reported the peaks absorption of FTIR spectra at (1) 1042 and 1077, (2) 1606 and 1622, and (3) 1700–1800 cm^{-1} which infer the stretching of (1) –C–O– C– or –C–O–, (2) –C=C– and (3) –C=O, respectively. Based on the analysis of FTIR, they established the fact that functional groups like –C–O–C–, –C–O–, –C=C–, and –C=O, are the capping ligands of the nanoparticles [115] 2.0 mg l-1 IBA and 0.5 mg l-1 BAP was found to be more suitable for the induction of callus and multiple shoots in papaya. The extract of callus obtained by grinding showed ability of synthesis of silver nanoparticles when treated with silver nitrate (1 mM. Stabilization and retardation of further growth during the synthesis of nanoparticle in order to prevent agglomeration is the major function of the capping ligands. Kesharwani *et al*. [26] reported the fabrication of reduced silver metal via wrapping photographic films with an emulsion of silver bromide. The silver bromide was sensitised after being exposed to light; the exposed film was then put in a solution of hydroquinone, which was then oxidised to quinone by the method of sensitised silver ion. The silver ion was reduced and remained in the emulsion as silver metal.

A. Dye Degradation

The main groups of organic contaminants used in various applications are anionic and cationic dyes [116]. Organic dyes play a significant role in the paper, textile, plastic, printing, leather, pharmaceutical, and food industries due to their high demand. The textile industries account for nearly 60% of the dyes used in the coloration process for many fabrics [117]. Almost 15% of dyes are wasted during the cloth manufacturing process and released into waterbodies, where they become significant sources of contamination due to their recalcitrant nature [118]. The waste products from these manufacturing plants are widely regarded as the most pervasive sources of environmental pollution. They cause undesirable turbidity in the water, which reduces sunlight penetration, resulting in biological adverse effects and photochemical synthesis resistance in both marine and freshwater biota [119, 120]. As a result, one of the most difficult challenges in the field of nanoparticle synthesis is regulating effluents containing dyes [121].

The demand for safe and hygienic drinking water is rapidly increasing daily. In view of this fact, oxidizing toxic pollutants using metal oxide and metal semiconductor nanomaterials has become of significant importance in the contemporary research material fields [122, 123, 124]. In the synthesis of nanoparticles, materials of semiconductor have greater photocatalytic activity comparative to the bulky counterpart materials. Nanoparticles semiconductor from metal oxide such as TiO_2, WO_3, SnO_2, CuO and ZnO have been useful particularly for the synthetic dyes photocatalytic degradation [124, 125, 126]. The advantages of these nano photocatalysts for example TiO_2 and ZnO nanoparticles are attributed to their higher surface area to its volume ratio which increase the organic pollutants adsorption. Hence, due to the availability of larger reactive sites on the surface of nanoparticles, the surface energy tend to increase, thereby resulting to a raise in the removal of pollutant at less concentrations. Therefore, nanocatalyst of low quantity will be needed to purify contaminated water relatively to its bulk material [127]. Similar to nanomaterials of metal oxide and metal nanoparticles also exhibit improved photocatalytic degradation of several dyes pollutant; for instance, synthesized silvernanoparticles from leaf extract of *Z. armatum* were employed for the degradation of different dyes pollutant [120].

B. Heavy Metal Removal

Numerous heavy metals for instance Fe, Ni, Zn, Cd, Co, Cu, Cr, Cr, Mn, Hg and Pb are recognized contaminants in the soil, water and air. There are several sources of pollution of heavy metal these include vehicle emissions, mining waste, natural gas, dye industries, paper, coal, and plastic [128]. Several metals such as cadmium, copper, lead and mercury ions depict improved potential toxicity even at a very low concentration [129]. Hence, toxic metals identification in the aquatic and biological environs has become an indispensable requirement for the appropriate remediation processes [130]. Remediation of water based on the conventional systems using some instrumental techniques commonly result to an outstanding sensitivity in multi-element analysis. But, performing such analysing by set ups the experiments are consuming lots of time, very expensive, non- portable and skill-dependent. Metallic nanomaterials have been widely used for the detection of heavy metal ions in polluted water systems due to their tenable distance and size dependent optical properties [130]. The cost-effectiveness, high sensitivity at sub-ppm levels, and versatility of using metal nanoparticles as colorimetric sensors for heavy metal ions in research are all advantages. Karthiga and Anthony [131] reported the synthesis of AgNPs utilizing different extracts of plant which are utilized as colorimetric sensors for heavy metal ions this include chromium (Cr^{3+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), calcium (Ca^{2+}) and zinc (Zn^{2+}) in water. The as-synthesized Ag nanoparticles depict colorimetric sensing of mercury and zinc ions (Hg^{2+} and Zn^{2+}). Similarly, synthesized AgNPs utilizing mango dried and fresh leaves (ie. sun-dried, MD-AgNPs and fresh MF-AgNPs) showed selective sensing for lead and mercury ions (Pb^{2+} and Hg^{2+}). In addition, AgNPs fabricated utilizing green tea extract (GT-AgNPs) and pepper seed extract exhibited selective sensing properties for Pb^{2+}, $Zn^{2+}$and Hg^{2+} ions [131].

VII. Conclusions

Over the last decade, several researchers have concentrated on green mediated synthesis of metal and metal oxide nanoparticles. Bio-components such as bacteria, fungi, yeast, and plant extracts have all been used as important constituents in the fabrication or synthesis of nanomaterials. Plant extract, for example, has been shown to be efficient as a capping, reducing, and stabilising agent for the synthesis of precise nanomaterials with controlled shapes, structures, sizes, and other characteristics. Furthermore, synthesis of nanomaterials using plant extracts has the ability to reduce metal ions in a shorter period of time than bacteria and fungi, which take a longer incubation time. In conclusion, the fabrication of suitable sustainable and greener synthetic nanoparticles with precise morphology, structure, shape and size for the preferred activities is essential. Thus, the present review highlighted the fundamental procedures and mechanisms of plants mediated biosynthesis techniques, particularly on the metal and metal oxides synthesis using plant extracts. Similarly, the functions of some of the biological components, that's the essential phytochemicals such as alkaloids, aldehydes, terpenoids, amides and flavonoids which serve as solvent systems and reducing agent has been discussed. The toxicity and stability of the nanomaterials and their related surface structural techniques to achieved biocompatibility are also highlighted. Lastly, several applications of the biosynthesized nanomaterials for the water and wastewater purification in terms of photocatalytic degradation of dyes and removal of heavy metals ion were highlighted.

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