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Green synthesis of iron nano-materials by plants and their use in removal of pollutants from wastewaters – a review

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ABSTRACT

Nano-materials are defined as structured components with dimensions ranging from approximately 1–100 nm. Because a smaller mass of material has increased specific surface area compared with conventional macroscale materials that can achieve the same objective, the consumption of raw materials is minimized significantly, with cost savings. Nano-sized iron in particular has many applications in the medical, biosensing, food, energy, and environmental fields because of its versatile properties and high level of catalytic activity. The green synthesis of nano-scale iron materials, especially from plants, has garnered substantial attention due to its ease of application, eco-friendly nature, and economy. Researchers and scientists worldwide have sought to assess the synthesis of iron nano-materials and the effectiveness of iron synthesized as such for the removal of environmental pollutants. These research efforts have involved numerous laboratory and field techniques. Green synthesis involves mostly the use of plants and the application of nano-sized iron materials for the removal of heavy metals, metal ions, dyes, chlorinated organic compounds, bacteria, and other pollutants such as nitrate, phosphate, chemical oxygen demand, and total organic carbon present in industrial wastewater, surface water, and groundwater. These themes will be explored in this paper.

Keywords: Iron nano-particles; Green synthesis; Plants; Pollutants removal

1. Introduction

The global population has grown significantly over the last few decades, and water demand has increased correspondingly. Reliance on surface water supplies alone seems to be insufficient because of their variability in quality to respond to this increasing demand. The uniform characteristics of ground water make it easy to use while continuous extraction of it can lead to negative long-term effects such as land subsidence. Treated wastewater is one of the promising alternatives especially in the areas where people suffer from lack of water. Treatment and reuse of wastewater would reduce the extensive amount of water extracted from the natural environment. Wastewater discharged from different industries is often contaminated with various waste constituents depending on the nature of the industry and must be treated according to the projected uses of the receiving waters. These constituents to be removed may be summarized as suspended solids, heavy metals, soluble organics, priority pollutants and cyanides, color, nitrogen, and phosphorus. Various treatment methods such as chemical precipitation, coagulation and flocculation, flotation, adsorption, ion exchange and membrane filtration, and biological methods can be employed to remove pollutants from wastewater. Conventional technologies have been refined and new technologies have been developed to meet increasingly more stringent water quality criteria. Effluent limitations on specific priority pollutants and toxicity to aquatic organisms have rendered many of the older conventional treatment facilities obsolete. The challenge today is to meet these new requirements in a way that is both environmentally acceptable and cost-effective. This has led to extensive research on advanced technologies that can provide the desired results.

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Nano-technology has become one of the most significant technologies of the 21st century. In the 2014 Strategic Plan of National Nanotechnology Initiative (NNI), nano-technology was defined as "The understanding and control of matter at dimensions between approximately 1 and 100 nm, where unique phenomena enable novel applications" [1].

Nano-sized materials can exhibit certain extraordinary, unique, and useful properties, which were not previously seen elsewhere, significantly changing physical, chemical, and biological properties due to their size and structure. The properties of the particles of solid matter in the visible scale differ slightly from what can be seen in a regular optical microscope. But when particles are created at nano-scale, the materials' properties change significantly from those at larger scales. Furthermore, properties of materials are size-dependent in this scale range. Thus, the properties of nano-sized particles such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle [2].

In the context of water and wastewater treatment, nano-technology has been shown to have great potential to improve treatment efficiency and to increase water supply by providing clean water. Nano-materials for environmental remediation have superiority in the fact that they offer high surface area to volume ratio. They also do not pose mass transfer limitations that are common to porous structures as all the surface area is outside the particle. Under the external magnetic field gradients, complete removal of the particles from their medium is possible. Nano-materials not only have the potential to improve the environment through applications of those materials to remove pollutants but also have the potential to design cleaner industrial processes and produce environmentally friendly products by using nano-technology.

There are many eco-friendly applications for nano-technology, such as materials that provide clean water from polluted water sources in both portable and large-scale applications. For example, antibiotics, arsenic, halogenated organic compounds, nitrate, and bacteria are some impurities detectable and removable from water by applying methods involving nano-materials [3–7].

In the last decade, a great deal of attention has been focused on the synthesis and application of nano-structured materials as adsorbents or catalysts to remove toxic and harmful substances from soil, water, and air. Various methods such as adsorption, nano-filtration, photocatalysis, and electrochemical oxidation involve the use of ceramic membranes, nano-wire membranes, carbon nano-tubes, TiO_2, metals and metal oxides, nano-structured boron-doped diamond to improve the water quality [8,9]. Nano-particles such as nano-sized zero-valent or other forms of irons have been used as adsorbents to provide pollutant removal/separation from water as well as catalysts for the destruction of contaminants present [10]. Nano-scale materials are classified into four classes as metal-based nano-particles, dendrimers, zeolites, and carbonaceous nano-materials [11].

Metal-based nano-particles include nano-sized metals such as silver, gold, palladium, and iron. Nano-silver forms are typically 10–200 nm in size. Silver nano-particle-coated polyurethane foam has been used as antimicrobial agent for *Escherichia coli* containing wastewater [12]. Palladium on gold nano-particles (Pd/Au NPs) have been shown to catalyze dechlorination of trichloroethene in water, at room temperature [13].

Zero-valent iron nano-particles include nano scale zero valent iron (nZVI), emulsified zero-valent iron, and bimetallic nano-scale particles (BNPs). BNPs include elemental iron and a metal catalyst such as gold, nickel, palladium, or platinum. Their size is generally between 50 and 100 nm. They are used in remediation of environment by reducing contaminants such as arsenic and heavy metal ions, nitrates, halogenated organics, phenols [14–17], and viruses and bacteria [18].

Metal oxide nano-particles include titanium dioxide (TiO_2), zinc oxide (ZnO), cerium oxide (CeO_2), and iron oxides. They are considered as a good adsorbent for water purification because of their large surface area. Adding various functionalized groups can increase their affinity. For example, effectiveness of ZnO nano-particles and silver (Ag) nano-particles as biocides against Gram-positive and Gram-negative bacteria was demonstrated by Motshekga et al. [19]. Silver-loaded nano-SiO_2 composite coated with chitosan has been found to have high biocidal activity against *E. coli* and *Staphylococcus aureus* [20]. Arsenic (III) has been removed using agglomerated Fe (III)–Al (III) oxide nano-particles [21]. Super paramagnetic iron oxide (Fe_3O_4) nano-particles with a surface functionalization of dimercaptosuccinic acid (DMSA) was found to be an effective adsorbent for toxic metals such as Hg, Ag, Pb, Cd, and Tl [22]. A Pd/Fe_3O_4 nano-catalyst has been used for selective dehalogenation in wastewater treatment process [23].

This review focuses on the green synthesis and use of zero-valent iron and iron oxides containing nano-materials.

2. Green synthesis of iron nano-materials

Common examples of iron nano-materials used for pollutants removal from water and wastewater include zero-valent iron, iron oxides, iron phosphate, and iron-based bimetallic particles. The conventional method for synthesizing nano-materials is one of the top-down or bottom-up methods.

In the top-down method, nano-sized materials are generated from breaking down of bulk materials, whereas in the bottom-up method, atoms and molecules assemble to form nano-sized structures. Based on these approaches, chemical, physical, and biological pathways have been utilized. As the other nano-scale materials, nZVI can be produced via top-down and bottom-up approaches. Bottom-up approaches involve bringing together iron atoms to form Fe^0 clusters at the nano-meter scale. This is achieved mainly by chemical reduction of ferrous or ferric salts. Top-down approaches break down bulk iron materials into nano-meter-scale particles through mechanical means. A drawback of the top-down methods is that they generally require specific and costly equipment, while the drawbacks of the bottom-up approaches are the safety issues due to the toxicity of reducing agents such as sodium borohydride used in the process, as shown in Reactions (1) and (2) [24], and the tendency to agglomeration.

$$2Fe^0_{(S)} + 4H_{(aq)} + O_{2(g)} = 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \quad (1)$$

$$Fe^0_{(S)} + 2H_2O_{(l)} = Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \quad (2)$$

Although these methods may successfully produce pure, well-defined metal nano-particles, the cost of production is relatively high both materially and environmentally.

In the conventional synthesis, the reducing agents such as sodium borohydride, capping agents, templates, and organic solvents such as toluene or chloroform used are considered hazardous, posing significant environmental and biological risks [25]. In any green synthesis of nano-particles, at least three green chemistry principles, (i) use of a green solvent such as water; (ii) use of an environmentally benign reducing agent; and (iii) use of an eco-friendly stabilizer should be applied. Using plant extracts having majority of antioxidant constituents which act as green reducing, capping, and stabilizing agents make all these principles applicable.

2.1. Synthesis of nZVI using plants

Plant extracts can act as reducing agents in replacement of toxic reductants such as borohydride, which is mostly used for nano-material synthesis. Particularly, plant extracts obtained from several plants are capable of reducing a variety of iron salts to generate nZVI and other nano-iron forms. Plant extracts can also have capping/stabilizing/templating properties to prevent agglomeration and chemical alteration.

Kozma et al. [26] recently presented a comparative evaluation of green and semi-green synthesis methods. In green synthesis, coffee (C), green tea (GT), and Virginia creeper (*Parthenocissus tricuspidata*, VC) leave extracts have been utilized. The semi-green methods were based on sodium dithionite and sodium borohydride. nZVI synthesis was carried out using untreated tap water at room temperature. The average particle diameter was found to be 124.2 ± 31.8 nm for C-Fe and 119.6 ± 25.8 nm for GT-Fe. nZVI performance was evaluated according to the time-dependent oxidation/reduction potential measurements and also by the reductive dehalogenation of volatile chlorinated organics in actual groundwater samples.

Elavarasi and Gomathi Priya [27] have reported the synthesis of iron nano-particles by biological (*Azadirachta indica* leaf extract) and chemical (sodium borohydride) methods and compared the activity of the resultant particles for the degradation of methyl orange (MO) dye. For the biosynthesis of iron nano-particles, a homogenous suspension of powdered *A. indica* leaves was prepared and mixed with a solution of 0.1 M $FeSO_4.7H_2O$ in the 1:1 ratio, and incubated overnight at 25°C. The high resolution scanning electron microscopy (HR-SEM) images of biologically synthesized iron nano-particles (BFeNPs) indicated that the BFeNPs were mostly spherical and uniform in size with an average diameter of about 28 nm .

Iron nano-particles were synthesized through a biosynthetic route at room temperature using eucalyptus leaf extracts (EL-FeNPs) by Wang et al. [28]. They proved the successful synthesis of the spheroidal iron nano-particles by scanning electron microscopy (SEM) and X-ray energy-dispersive spectrometer (EDS). They also showed that some polyphenols were bound to the surfaces of EL-FeNPs as a capping/stabilizing agent using X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FTIR). The particles were observed to have the diameters ranging from 20 to 80 nm. Reactivity of EL-FeNPs was evaluated for the treatment of swine wastewater and results indicated that 71.7% of total N, 30.4% of total P, and 84.5% of chemical oxygen demand (COD) were removed.

It was proposed in another study that iron nano-particles (FeNPs) synthesized by green tea (GT-Fe) and eucalyptus leaf (EL-Fe) extracts could be used for the efficient removal of nitrate. SEM and EDS confirmed the successful synthesis of spheroidal iron nano-particles with a diameter ranging from 20 to 80 nm for both EL-FeNPs and GT-FeNPs [29].

In another work, utilization of several tree leaves to produce extracts that are capable of reducing iron (III) in aqueous solution to form nZVIs has been evaluated. The extracts were classified according to their antioxidant capacity; oak, pomegranate, and green tea leaves produced the richest extracts, and transmission electron microscopy (TEM) analysis proved that nZVIs with the sizes of 10–20 nm could be produced using these tree leaf extracts [30].

One group of researchers synthesized nZVI from the leaf extract of *Coffea arabica* (coffee) under atmospheric conditions. The obtained iron nano-particles were found to be mainly in zero-valent oxidation state. A systematic characterization of nZVI has been performed using UV, XRD, and SEM studies. The diameter of iron nano-particles was found to be within the range of 50–100 nm [31].

Kuang et al. [32] synthesized iron nano-particles (FeNPs) using green, oolong, and black tea extracts as catalysts for the Fenton-like oxidation of monochlorobenzene (MCB). They showed that FeNPs synthesized using green tea extracts (GT-FeNPs) demonstrated the best MCB degradation and the basic nano-particles sizes ranged approximately between 20 and 40 nm whereas some ranged from 80 to 120 nm.

In another report, the synthesis of nZVI using green tea leaf extracts was performed by heating green tea (Alwald brand) to its boiling point, followed by filtration and, subsequently, the addition of iron (II) chloride solution to the extract at pH 6. TEM images in addition to an EDX spectrum of GT-FeNPs showed that the GT-FeNPs tend to form irregular clusters demonstrating some dispersion, with particle size ranging between 40 and 60 nm. Synthesized iron particles were used in a Fenton-like catalytic reaction for decolorization of aqueous solutions of methylene blue (MB) and MO dyes [33].

Hoag et al. [34] described a green single-step synthesis of iron NPs (Fe^0) using tea (*Camellia sinensis*) polyphenols. The rapid reaction between polyphenols and ferric nitrate was carried out at room temperature without the addition of surfactant or polymer as capping or reducing agents. The iron particles were found to be spherical in nature with size ranging from 5 to 15 nm. The NPs obtained were employed to study catalyzed hydrogen peroxide reactions for the bromothymol blue degradation.

Several other benign environmental methods using bacteria, fungi, yeast [35,36], vitamins [37,38], biodegradable polymers [39], and microwave heating [40–42] have been developed to generate various nano-structures. The utilization of natural or organic acids is also an alternative way for iron nano-particle preparation. Amino acids have been used to synthesize iron nano-particles by Siskova et al. [43]. Meeks et al. [44] successfully used ascorbic acid for the synthesis of iron-based nano-particles. Tannic acid and gallic acid as reducing agents to prepare iron oxide nano-particles have also been used by Herrera-Becerra et al. [45].

Capping agents affect the crucial growth mechanism of nano-particles. Varying quantity of capping agent can also adjust the size and morphology of nano-particles [46]. Therefore, the synthesis of nano-materials with capping agents produces stable nano-particles that are less susceptible to agglomeration and chemical alteration reactions. Synthesis of nano-materials using chemical capping agents has been previously studied. However, many of the common chemical capping agents such as triethanolamine (TEA), oleic acid, thioglycerol [47], ethylenediaminetetraacetic acid (EDTA), and tetraethylammonium bromide [48] are known to accumulate in the environment as persistent pollutants which may have ecological risks. During the green synthesis of nano-materials, environmental-friendly capping agents such as tea polyphenols and sorghum bran extract [34,49] have been applied for synthesis instead of chemical capping agents. Additionally, they simultaneously act as reducing and stabilizing agents.

During green synthesis, ionic liquid-based green solvents can be used as both template and co-solvent. In one study, ionic liquid-based green synthesis was utilized to control the size of iron nano-particles using neoteric solvents. In this work, the structures and the crystalline phases of α-Fe_2O_3, α-Fe, and β-FeOOH nano-rods were confirmed by TEM images and XRD patterns [50].

Templates or surfactants are frequently required for nano-particle synthesis in order to control the growth of nano-particles and prevent agglomeration. Green templates obtained from plant extracts have been used in a number of studies, by adding to the solution with a certain amount of iron salts and stirring the solution for a certain period of time to complete the reaction.

Polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A), which is a nontoxic and biodegradable surfactant, has been used in the synthesis of nZVI [51]. It has been demonstrated from the experiments that PV3A could serve as an effective dispersant for nZVI reducing nZVI particle size from 105 to 15 nm, and the ζ-potential from +20 to −80 mV at neutral pH.

Many other reports on the green and biogenic synthesis of zero-valent iron nano-particles using plants and other environmentally friendly reducing agents are available in the literature [52–59].

2.2. Synthesis of nano-iron oxides using plants

Ferrites and the other iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite, and magnetite can be synthesized using green pathways.

Punica granatum leaf extract was utilized to synthesize Fe^0/Fe_3O_4 nano-particles by Rao et al. [54]. These nano-particles were coated on two strains of yeast cells *Yarrowia lipolytica*, which is inherently biosorbent. The sizes of Fe^0/Fe_3O_4 nano-structures were determined to be 100–200 nm in diameter and prone to aggregation. The bio-nano-composite was evaluated for its capacity to remove hexavalent chromium.

Iron oxide nano-particles using extracts of Omani mango leaves were successfully synthesized by Al-Ruqeishi et al. [60]. The polycrystalline nano-rods (IONRs) with 15 ± 2 nm in average length and 3.0 ± 0.2 nm in average diameter produced were utilized for heavy oil viscosity treatment. It was concluded from the results that as-produced nano-rod was a promising agent for heavy oil cracking process.

Iron (III) oxide nano-particles were synthesized by the reduction of hepta-hydrous iron sulphate using the leaf extract of garlic vine [61]. The crystalline phase of trivalent iron embedded in the primitive lattice of hexagonal β-Fe_2O_3 was obtained from the experiments. UV–Vis analysis and FTIR measurements, in accordance with XRD result, showed the formation of iron(III) oxide nano-crystals with iron predominantly occupying the octahedral sites.

Synthesis of nano-magnetites as high-quality nano-crystals by using Mustard oil was also reported. IR spectra, XRD, and high resolution transmission electron microscopy (HRTEM) confirmed the formation of nano-magnetites from mustard oil having size of 20–100 nm [62].

Thakur and Karak [63] demonstrated a technique to prepare iron oxide/reduced graphene oxide nano-hybrid (IO/RGO) at room temperature by using banana peel ash aqueous extract as the base source and *Colocasia esculenta* leaves aqueous extract as the reducing agent. Typical particle size was found to be in the range of 10–25 nm. Iron oxide/reduced graphene oxide nano-hybrids were used to remove tetrabromobisphenol A (TBBPA), lead, and cadmium.

The iron oxide nano-particles have been synthesized by adding *Eucalyptus globulus* leaf extract into the aqueous solution of ferric chloride. The synthesized nano-particles were characterized by UV, XRD, TEM, SEM, and FTIR. TEM and SEM images showed the nano-structures of as-prepared iron oxide nano-particles having the size of about 100 nm [64].

Fe_3O_4 nano-particles were prepared by using *Caricaya papaya* leaves extract at room temperature. The synthesized nano-particles were characterized by using UV–Vis, FTIR, XRD, and SEM with EDS techniques. From the XRD, the average particle size of magnetite nano-particles was observed to be 33 nm [65].

Synthesis of iron oxide nano-particles using leaf extract of *Ocimum sanctum* was also investigated [66]. FTIR spectrum indicated the Fe–O stretching of Fe_2O_3 nano-particles. The XRD spectrum confirmed crystalline Fe_2O_3. The average particle size of the synthesized iron oxide nano-particles was estimated to be 47 nm using the Scherrer equation. TEM image of iron oxide nano-particles showed that the nano-particles size was below 20 nm.

Plantain peel extract and $FeCl_3.6H_2O$ solution for synthesizing magnetite nano-particles were used by Venkateswarlu et al. [67]. In this study, iron salt solution was hydrolyzed to form ferric hydroxide, which was subsequently reduced by polyphenols and carbohydrates in the extract of plantain peels to Fe_3O_4 nano-particles having the size of about 50 nm. According to the results obtained for Brunauer Emmett and Teller surface area and pore volume, the structure of nano-particles was assigned to be microporous with the pore size of 1.8 nm. These Fe_3O_4 microporous magnetic nano-particles (MNPs) were considered to have potential application in separation of toxic metals and dyes from environment.

In another report, the synthesis of palladium and iron NPs, using aqueous extract of *Terminalia chebula* fruit was demonstrated [68]. Reduction potential of aqueous extract of polyphenol-rich *Terminalia chebula* was determined to be 0.63 V vs. standard calomel electrode by cyclic voltammetry.

It was considered that this value makes the extract a good green reducing agent for reducing palladium and iron salts to palladium and iron NPs, respectively. TEM micrograph of iron NPs showed a chain-like morphology with particle size less than 80 nm. UV–Vis, elemental analysis showed formation of iron oxide NPs. No other elements observed in the EDS spectrum proved the formation of pure iron NPs in the form of oxides.

In another work, magnetite nano-particles have been successfully synthesized in pistachio leaf extract at ambient temperature. The synthesized magnetite nano-particles were characterized by FTIR, SEM, and XRD. XRD analysis showed that the synthesized magnetite nano-particles were highly crystalline and well mono-dispersed with 4.8 nm of average diameter. Nano-particles' size was proven to be controlled in the range 5–12 nm by the amount of pistachio leaf extract in one-pot reaction at ambient temperature [69].

Iron oxide (Fe_3O_4) nano-particles were synthesized by reduction of ferric chloride solution with *Tridax procumbens* leaf extract [70]. It was suggested that water-soluble carbohydrates which have aldehyde groups as a reducing agent might cause the formation of Fe_3O_4 nano-particles. It was identified that Fe_3O_4 nano-particles were irregular sphere shapes with rough surfaces with the sizes ranging 80–100 nm. Fe_3O_4 nano-particles against *Pseudomonas aeruginosa* was shown to be an effective bactericide.

Hydrothermal method used to synthesize nano-materials is a green method and involves the preparation of the plant extract and dissolution of the desired molarity of the metal salt in it. The mixture is allowed to react in an autoclave under atmospheric pressure at different temperatures for a certain period.

An example for the use of hydrothermal method for the synthesis of magnetite (Fe_3O_4) nano-particles using ferric acetyl acetonate [$Fe(C_5H_8O_2)_3$] and *Aloe vera* plant extract has been reported by Phumying et al. [71]. The influences of different reaction temperatures and times on the structure and magnetic properties of the synthesized Fe_3O_4 nano-particles were investigated in this study. The synthesized nano-particles were found to be crystalline and have particle sizes of about 6–30 nm, as revealed by TEM. The results of XRD, HRTEM, and selected area electron diffraction indicated that the synthesized Fe_3O_4 nano-particles have the inverse cubic spinel structure without the presence of any other phase impurities.

A hydrothermal method was also used for the preparation of meso-porous α-Fe_2O_3 nano-particles using the extract of green tea (*Camellia sinensis*) leaves. This one-step method carried out dissolving $Fe(NO_3)_3{\cdot}9H_2O$ in green tea extract and heating it for certain time period at ambient pressure in an autoclave was proposed to be scaled up for large-scale synthesis. The nano-particles were reported to be highly pure and well crystallized with an average particle size of 60 nm. α-Fe_2O_3 was demonstrated to show two times higher activity than commercial α-Fe_2O_3 in terms of hydroxyl radical formation and enhanced performance in a photoelectrochemical cell [72].

In another work, production of iron oxide nano-particles by reducing iron ions was achieved using a homogeneous suspension of powdered milled alfalfa prepared in an ultrasonic bath [73]. A solution of $FeNH_4(SO_4)_2{\cdot}12H_2O$ was prepared in deionized water and both solutions were mixed homogeneously in the ultrasonic bath for 20 min. Optimum pH to obtain nano-particles of size less than 10 nm was determined to be 10. The generation of cubic-based clusters of wuestite ($Fe_{0.902}O$) and magnetite (Fe_3O_4) was demonstrated with the aid of a microscopic analysis. Optimal size distribution around 3.1 nm with a standard deviation of 2.1 nm was confirmed by TEM characterization of the nano-particles at controlled pH conditions during the synthesis.

Cellulosic materials [74], plant biomass [75], and tea waste [76] were also investigated to produce nano-iron oxides. A variety of iron oxide NPs has also been synthesized in an eco-friendly manner by using microorganisms under ambient conditions [77–79].

Turmeric (*Curcuma longa* L.) leaves were used to synthesize iron oxide nano-particles by calcination (Fe-NPCal) and microwave-assisted method (Fe-NPMw) for comparison with their efficiency in terms of orthophosphate (PO_4), COD, and *E. coli* removal from domestic wastewater [80]. The average particle sizes of the nano-particles synthesized by calcination method were estimated to be in the range of 66–148 nm, whereas those synthesized by microwave method were observed to be in size range of 17.9–28.7 nm.

Another example for the microwave-assisted synthesis of nano-composite using pine wood shavings and a spacer (saturated NaCl) was reported by Ramasahayam et al. [81].

Biosynthesis of FeS nano-particles from contaminant degradation [82] and biosynthesis of iron phosphate nano-powders with the yeast cells as a biologic template [83] were also investigated.

3. Removal of environmental pollutants from wastewaters by iron nano-materials synthesized using plants

In recent years, a great deal of attention has been focused onto the applicability of nano-structured materials as adsorbents or catalysts in order to remove toxic and harmful substances from wastewater since the materials of such kind possess extraordinary properties such as enhanced surface area to volume ratio and magnetism, and special catalytic properties comparing the bulk materials. The high surface area and surface reactivity compared with larger scale enable the nano-particles to remediate more material at a higher rate and with a lower generation of hazardous by-products.

Several technological developments are employed on a daily basis but nano-technology has proved to be one of the advanced pathways for water and wastewater treatment. It is also evaluated as economically feasible and environmentally applicable treatment technology for efficiently treating water and wastewater meeting the ever-increasing water quality standards.

Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment. The surface area or active sites, the lack of selectivity, and the adsorption kinetics usually limit efficiency of conventional adsorbents. Nano-adsorbents offer significant improvement with their extremely high specific surface area and associated sorption sites, short inter particle diffusion distance, and tunable pore size and surface chemistry. Nano-metal oxides such as iron oxide, titanium dioxide, and alumina are effective adsorbents for heavy metals and radionuclides because of these unique properties. It has shown that as the particle size of nano-magnetite decreased from 300 to 11 nm, its arsenic adsorption capacity increased more than 100 times [84]. Metal oxide nano-adsorbents can be easily regenerated by adjusting solution pH. Furthermore, metal-based nano-adsorbents can be produced at relatively low cost by applying green synthesis methods. The high adsorption capacity, low cost, clean production, easy separation, and regeneration make metal-based nano-adsorbents technologically, environmentally, and economically advantageous.

nZVI is also an effective adsorbent for removing various organic and inorganic contaminants from water and wastewater.

In catalysis, chemical reactions are accelerated by introducing a solid phase that contains enough amounts of the right kind of site for chemical reactants to adsorb, react, and desorb. Because optimization of the catalyst requires increasing the numbers of sites to expand surface area, the catalytic particle size must be decreased. Therefore, active catalysts can be prepared with nano-meter-sized particles on supports with nano-meter-sized pores or structural features.

Different nano-materials have been reported for removal of heavy metals, metal ions, inorganic solutes, complex organic compounds, natural organic matter, nitrate, phosphate, pathogenic microorganisms, and other pollutants present in surface water, ground water, and/or industrial wastewater.

Pollutants removed by iron nano-materials synthesized using plants have been selected for the purpose of this review.

3.1. Removal of heavy metals

Several studies have revealed that nano-particles have better efficiency in removing metallic pollutants from aqueous solutions. Metal-based nano-materials have been explored to remove a variety of heavy metals such as arsenic, lead, mercury, copper, cadmium, chromium, nickel and have shown great potential to outcompete activated carbon. Iron oxide nano-particles and zero-valent iron nano-particles mostly synthesized by conventional methods have been reported for the removal of metallic pollutants such as Cd, Zn, Se, As, Cr Ag, and Pb from aqueous solutions and industrial effluents [85].

Heavy metals removed by using zero-valent iron and iron oxide nano-materials synthesized especially from plant extracts will be contained in this section.

nZVI synthesized using oak, mulberry, and cherry leaf extracts (OL-nZVI, ML-nZVI, and CH-nZVI) proved to be promising agents for As(III) and Cr(VI) removal from aqueous solutions [86]. Characterization results of produced nZVI materials confirmed the formation of zero-valent iron particles within the size of 10–30 nm. It has been shown that the adsorption kinetics followed the pseudo-second-order rate equation described by the Freundlich isotherm model. The adsorbents had high affinity for both As(III) and Cr(VI) over a pH range from 4.0 to 8.0. It was concluded from the results that nZVI produced by leaf extracts were relevant for preparing environment friendly, non-poisonous, and low-cost adsorbent to remove As(III) and Cr(VI) from aqueous solutions.

Mystrioti et al. [57] investigated the applicability of iron nano-particles synthesized by green tea for the removal of hexavalent chromium in column tests. Polyphenol coated nZVI particles have been synthesized mixing green tea extract with $FeCl_3$ solution. GT-nZVI suspension was introduced in columns containing a calcareous soil material. The Cr(VI) reducing effectiveness of soil columns containing the nZVI particles was evaluated by introducing a solution containing 5 mg/L of Cr(VI) with two different flow rates. They suggested that the reductive precipitation of Cr followed a pseudo-first-order kinetic law. It was proved from the leaching test that precipitated chromium was not soluble.

A method has been used to synthesize zero-valent iron nano-particles taking *Emblica officinalis* leaf extract as reducing and stabilizing agent at ambient temperature and using $FeCl_3$ solution as a source of iron to be reduced. These ZVI nano-particles at 20 mL/L concentration was observed to exhibit significant potential to remediate Pb^{2+} present in aqueous solution at different concentrations within 24 h of application and the efficiency was found to be positively correlated with the duration of application and concentration of ZVI nano-particles. It has been evaluated this ability as a significant potential of ZVI particles for the remediation of lead and other heavy metals from industrial waste effluents [58].

Fe^0/Fe_3O_4 nano-particles synthesized by using *Punica granatum* leaf extract were utilized after coated on two strains (NCIM 3589 and NCIM 3590) of yeast cells *Y. lipolytica*, to remove hexavalent chromium [54]. Magnetically modified yeast cells were found to have three times more adsorption capacity than that of unmodified yeast cells. At initial chromium concentration of 1,000 mg/L and under optimum conditions, modified NCIM 3589 was observed to show better adsorption capacity (186.32 mg/g) than modified NCIM 3590 (137.31 mg/g).

The effectiveness of a biocomposite of iron nano-particles with the cellulose to remove hexavalent chromium from industrial wastewater was demonstrated [87]. The iron nano-particles were synthesized on the orange peel pith. The nano-particles were characterized for size, composition, oxidation state, and distribution before and after the Cr(VI) exposure. The nano-particles were obtained to be mostly 20 nm × 80 nm tubular shapes, but some octahedral crystals of 20–40 nm were also observed. It has been concluded that the biocomposite with the nano-particles exhibited twice the Cr (VI) removal of the unmodified orange peel pith and also possessed over twice the adsorption capacity of 5.37 mg/g vs. 1.90 mg/g.

Nickel removal has been reported using green synthesized magnetic iron nano-particles coated by olive oil [88]. It was observed from the SEM image that the resulting nano-particles were spherical with size of 37.8–77.6 nm. Analyte concentration, pH, type of disperse solvent, absorption time, ionic strength effect, type of desorption solvent, and desorption time were examined for optimization. Nano-composite was found to act as an extractor phase. It has been reported that nano-composite coupled with UV–Vis spectroscopy has been used for extraction of Ni(II) from a number of real samples.

Ehrampoush et al. [89] synthesized iron oxide nano-particles using tangerine peel extract and used it as adsorbent for cadmium ions removal from contaminated solution. The maximum removal of cadmium ions (90%) occurred at pH 4 and adsorbent dose of 0.4 g/100 mL. Adsorption of cadmium ions by iron oxide nano-particles was obtained to follow Freundlich adsorption model and pseudo-second-order equation. It has been concluded that these nano-particles could be a good adsorbent for the removal of cadmium from wastewater.

In one of the recent studies, Fe_3O_4 nano-particles were prepared by hydrolyzed precipitation, assisted by sonication, using a waste material (pineapple peel pulp extract) [90]. A new ligand (DEAMTPP) was attached to the surface of Fe_3O_4 nano-particles for the removal of Cd(II). A removal efficiency as high as 96.1% was achieved with a maximum adsorption capacity of 49.1 mg/g by using DEAMTPP-capped Fe_3O_4 nano-composite. It has been concluded that the ferromagnetic property of the suspended MNPs made separation easy from large-volume samples using an external magnetic field.

Venkateswarlu et al. [91] described a method to remove Pb(II) by using DMSA anchored Fe_3O_4 magnetic nano-rods (MNRs) which were synthesized utilizing *Punica granatum* rind extract. It was shown from the TEM images of Fe_3O_4 and DMSA@Fe_3O_4 MNRs that particles had an average diameter of 40 nm and length above 200 nm. The adsorption isotherm data was found to fit well with Langmuir isotherm and Freundlich model, the monolayer adsorption capacity was found to be 46.18 mg/g at 301 K. The experimental kinetic data showed the pseudo-second-order model. They concluded from the results that the biogenic synthesized DMSA@Fe_3O_4 MNRs acted as significant adsorbent for removal of Pb(II) from aqueous environment.

Arsenic [As(III) and As(V)] sequestration has been focused in recent years due to the widespread occurrence of arsenic in groundwater and more stringent regulations for arsenic concentration in drinking water supplies.

It was demonstrated in a report that mixing ferric nitrate with liquor of commercially available tea resulted in nZVI having an average size of 59.08 ± 7.81 nm [92]. nZVI particles loaded on montmorillonite K10 (MMT K10) were found to be able to remove As(III) from water up to the extent of 99% within 30 min at both high and low pH (2.75 and 11.1). It was also observed that MMT K10 alone provided only smaller than 10% removal. Removal mechanisms for As(III) from water were proposed to be adsorption at low pH and precipitation at higher pH. It has been concluded that complete stabilization of the nZVI particles was not provided by the tea polyphenols and that the use of a supporting stabilizer might provide better results.

Iron oxide/reduced graphene oxide nano-hybrid (IO/RGO) synthesized at room temperature by using banana peel ash aqueous extract and *Colocasia esculenta* leaves aqueous extract was observed to remove both organic and inorganic pollutants within a short time [63]. 10 ppm of TBBPA was removed in 30 min and lead and cadmium were removed in 10 min at optimum experimental conditions. The adsorption kinetics was determined to follow pseudo-second-order and isotherm was revealed to fit the Langmuir model. From the thermodynamics parameters calculated from the temperature-dependent isotherms, the adsorptions of TBBPA, Cd^{2+}, and Pb^{2+} by the nano-hybrid were indicated to be endothermic and spontaneous. It was concluded from the results that the nano-hybrid had efficient pollutants removal capacity with excellent reusability.

3.2. Removal of dyes

Iron nano-particles synthesized using biological (*Azadirachta indica* leaf extract) and chemical (sodium borohydride) methods were compared for the degradation activity of MO dye [27]. According to the kinetic studies and FTIR analysis, it was concluded that BFeNPs demonstrated more effective capability for the degradation of the dye both in terms of extent and speed of dye removal compared with CFeNPs. It was suggested from these results that BFeNPs-catalyzed hydrogen peroxide has potential in the treatment of industrial effluents containing dyes.

Hoag et al. [34] has described a green single-step synthesis of iron NPs (Fe^0) using tea (*Camellia sinensis*) polyphenols. NPs obtained were used to evaluate catalyzed hydrogen peroxide reactions for the bromothymol blue degradation. The focus of this study was to compare the nano-scale zero-valent iron with Fe-ethylenediaminetetraacetate (Fe-EDTA) and Fe-(S,S)-ethylenediamine-N,N′-disuccinic acid (Fe-EDDS) as catalysts for free-radical production from H_2O_2. They obtained from the results that the highest rate of bromothymol blue degradation occurred with GT-nZVI-catalyzed H_2O_2 with increasing concentrations of GT-nZVI. Catalysis with Fe-EDTA and Fe-EDDS proved to be less effective. They concluded that GT-nZVI-catalyzed hydrogen peroxide has potential as an effective method for treatment of toxic organic contaminants found in the environment.

nZVI synthesized using green tea leaf extracts was utilized in a Fenton-like catalytic reaction for decolorization of aqueous solutions of MB and MO dyes [33]. The fast removal of the dyes was considered to indicate MB followed second-order kinetics, whereas MO was closer to first-order kinetics. Almost complete removal of both dyes from water was achieved over a wide range of concentration, 10–200 mg/L. Removal of dyes with iron nano-particles produced by borohydride reduction was found to be less effective as a Fenton-like catalyst, both in terms of kinetics and percentage removal.

Njagi et al. [49] investigated biosynthesis of iron and silver nano-particles at room temperature using aqueous sorghum bran extracts as both the reducing and capping agent. The HRTEM results revealed that the amorphous iron nano-particles synthesized were spherical with sizes ranging from 40 to 50 nm. The reactivity of iron nano-particles was tested by the H_2O_2-catalyzed degradation of bromothymol blue via free-radical pathways. Bromothymol blue was shown to be degraded rapidly in the presence of iron nano-particles and H_2O_2, indicating the iron nano-particles acted as catalysts for free radical production from H_2O_2.The catalyst effect of H_2O_2 increased with increasing concentrations of iron nano-particles, leading to increase in the rate of degradation of bromothymol blue. It was suggested that iron nano-particles synthesized using aqueous sorghum extracts were potentially useful for degradation of organic pollutants.

In another report, the synthesis and characterization of green iron–polyphenol (Fe–P) NPs using Australian native plant extracts from *Eucalyptus tereticornis*, *Melaleuca nesophila*, and *Rosmarinus officinalis* has been demonstrated [56]. The synthesized nano-particles were then utilized as a Fenton-like catalyst for decolorization of acid black 194 in solution. The batch experiments showed that 100% of acid black was decolorized, and over 87% total organic carbon (TOC) was removed. In addition, kinetics of removal of acid black 194 fitted well to the pseudo-first-order model. Comparison with the conventional Fenton reaction was made and the Fenton-like reaction with Fe-PNPs was shown to take place more sustained within 200 min.

Noruzi and Mousivand [93] recently reported synthesis of nZVI by using *Thuja orientalis* extract and their ability to degrade MB and antibacterial properties. The average size of particles was found to be 92 nm being in the range from 50 to 740 nm. Complete degradation of MB as a model pollutant was performed using nZVI synthesized. nZVI showed also a strong antibacterial effect on *Bacillus subtilis* and *Erwinia amylovora* bacteria. It was concluded that this method could compete with chemical synthesis methods, and the synthesized nano-particles could be applied to the degradation of pollutants and bacteria.

It has been reported by Abbassi et al. [94] that green synthesized clay-supported nano-iron particles were used for color removal of Malachite Green dye. The removal process was optimized using a response surface methodology. Phyto-toxicity results on *Vigna radiata* by using the treated and untreated dye solution demonstrated the decrease in toxicity after treatment with CnIPs. Regeneration of CnIPs was also performed for evaluating the reuse potential of the CnIPs in repeated cycles.

3.3. Removal of halogenated organic compounds

Halogenated organic compounds (HOCs) have been used in a wide variety of applications and their presence in water as contaminant is a serious problem because of their toxicity, persistence, and accumulation in plants and animal tissues. Degradation of HOCs by nano-sized iron particles represents a promising technology for environmental remediation. Nano-sized iron particles are known to be able to cleave carbon–halogen bonds of HOCs in water.

A comparative evaluation of green and semi-green synthesis methods for removing volatile chlorinated organic compounds from groundwater samples obtained from a real remediation target site was recently presented by Kozma et al. [26]. Coffee (C), green tea (GT), and Virginia creeper (*Parthenocissus tricuspidata,* VC) leave extracts were utilized for green synthesis while sodium dithionite and sodium borohydride were used for semi-green method. The average particle diameter was found to be 124.2 ± 31.8 nm for C-Fe, 119.6 ± 25.8 nm for GT-Fe and 47.5 ± 8.8 for VC. Particles in the other five ZVI samples were found to be averaged below 100 nm in diameter. All reactions were carried out at ambient conditions in untreated tap water. nZVI performance was assessed on the basis of oxidation/reduction potential measurements and also by the reductive dehalogenation of volatile chlorinated organics in groundwater samples. It was demonstrated from the results that semi-green methods yielded iron nano-particles with smaller average diameter and better reducing abilities than green ones.

It was reported in another work that membranes containing reactive nano-particles (Fe and Fe/Pd) immobilized in a polymer film (polyacrylic acid, PAA-coated polyvinylidene fluoride, PVDF membrane) were prepared with nano-particles synthesized using green tea extract [95]. As-prepared membrane supported NPs were reported to be used successfully for the degradation of trichloroethylene (TCE) in a model solution. The rate of TCE degradation was found to increase linearly with the amount of Fe immobilized on the membrane with the surface normalized rate constant (k_{SA}) of 0.005 L/m^2 h. The addition of a second catalytic metal, Pd, to form bimetallic Fe/Pd increased the k_{SA} value to 0.008 L/m^2 h. Fe and Fe/Pd nano-particles were also synthesized in membranes using sodium borohydride as a reducing agent for comparison. Although the initial k_{SA} values for this case (for Fe) were one order of magnitude higher than that of the NPs synthesized by tea extract, the rapid oxidation was shown to reduce their reactivity to less than 20% within four cycles. For the green tea extract NPs, the initial reactivity in the membrane was observed to be preserved even after 3 months of repeated use.

Iron oxide/reduced graphene oxide nano-hybrid (IO/RGO) synthesized at room temperature by using banana peel ash aqueous extract and *Colocasia esculenta* leaves aqueous extract was used to remove TBBPA [63]. The adsorption kinetics was determined to follow pseudo-second-order and isotherm was revealed to fit the Langmuir model. From the thermodynamics parameters, the adsorptions of TBBPA by the nano-hybrid were indicated to be endothermic and spontaneous. It was concluded from the results that the nano-hybrid has efficient pollutants removal capacity with excellent reusability.

FeNPs synthesized using tea extracts (green tea, black tea, and oolong tea) were utilized for the degradation of MCB via Fenton-like oxidation by Kuang et al. [32]. The XRD pattern of GT-FeNPs was shown to correspond to zero-valent iron (α-Fe), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and iron hydroxide. The specific surface area of GT-FeNPs was found to be 5.82 m^2/g with the average particle size of 20–50 nm. Degradation of MCB of 69%, 53%, and 39% were observed by FeNPs synthesized using extracts of green tea, oolong tea, and black tea, respectively. The best degradation was observed by GT-FeNPs. It was suggested that this enhanced performance was due to higher caffeine/polyphenols contents of green tea extract. In addition, batch experiments showed that the oxidation of MCB and the removal of COD using GT-FeNPs were 81% and 31%, respectively, at optimal conditions. It was concluded from the results that GT-FeNPs were successful in removing MCB from wastewaters via Fenton-like oxidative mechanism.

3.4. Removal of bacteria

Senthil and Ramesh [70] recently reported the synthesis of iron oxide nano-particles (Fe_3O_4) by reduction of ferric chloride solution with *Tridax procumbens* leaf extract and the antibacterial activity of nano-particles against *P. aeruginosa* as a model for Gram-negative bacteria. Bacteriological tests were performed in potato dextrose agar medium on solid agar plates and in liquid systems supplemented with different concentrations of nano-sized Fe_3O_4 particles. The growth of bacteria was observed to be inhibited gradually as the concentration of nano-particles increase. It was concluded from the results that green synthesized Fe_3O_4 nano-particles could be a promising antimicrobial agent against *P. aeruginosa*.

Iron oxide nano-particles synthesized using turmeric (*Curcuma longa* L.) leaves by calcination (Fe-NPCal) and microwave-assisted method (Fe-NPMw) were compared with their efficiency in terms of orthophosphate (PO_4), COD, and *E. coli* removal from domestic wastewater [80]. Fe-NPCal exhibited superior antimicrobial activity than Fe-NPMw and completely inhibited *E. coli*.

Noruzi and Mousivand [93] demonstrated the use of zero-valent iron nano-particles synthesized by *Thuja orientalis* extract for complete degradation of MB. Zero-valent iron nano-particles showed also a strong antibacterial effect on *B. subtilis* and *E. amylovora* bacteria. It was concluded that this method could compete with chemical synthesis methods, and the synthesized nano-particles could be applied to the degradation of pollutants and bacteria.

In another study, magnetite iron oxide nano-particles were synthesized from aqueous ferrous chloride, ferric chloride, and sodium hydroxide using Al-Abbas's Hund fruit extracts [96]. The average size of Fe_3O_4 particles obtained from nano-composite was found to be about 45 nm. It was revealed from the SEM images that iron oxide nano-particles seemed to be spherical in morphology. As-synthesized iron oxide nano-particles were intended to treat the Al-'alqami River water. The removal efficiency of bacteria was observed to be 80% after 12 h of treatment whereas treatment for 24 h killed all the bacteria in water.

In another recent study, green synthesis of silver, ferrous, ferric, magnesium, manganese, lead, and copper nano-particles was demonstrated using ethanol extract of unbaked beans of *Coffea arabica* [97]. Antibacterial activity of these nano-particles against *S. aureus*, *E. coli, Shigella dysenteriae, Klebsiella pneumoniae* and *B. subtilis* was also investigated using agar well diffusion method. Antibacterial activity was evaluated determining the inhibition zone for all the bacteria. Out of these nano-particles, silver, copper, and ferrous nano-particles were observed to exhibit better activity against microorganisms tested.

Biosynthesis of copper, zero-valent iron (ZVI), and silver nano-particles using leaf extract of *Dodonaea viscosa* has been investigated by Kiruba Daniel et al. [53]. No additional surfactants/polymers were suggested for use as a capping or reducing agent for syntheses. The synthesized nano-particles were confirmed to have spherical morphology and the average size of 29, 27, and 16 nm for Cu, ZVI, and Ag, respectively. The very low concentrations of as-synthesized nano-particles (CuNPs – 10 μg, ZVINPs – 12 μg, and AgNPs – 15 μg) in aqueous form was observed to show better antimicrobial activity compared with the concentrations of nano-particles of 100 μg used in previous studies. Biosynthesized Cu, ZVI, and Ag nano-particles were tested against human pathogens viz. Gram-negative *E. coli, K. pneumonia, Pseudomonas fluorescens* and Gram-positive *S. aureus* and *B. subtilis*, and concluded to show good antimicrobial activity.

3.5. Removal of the other pollutants

In a recent study, orthophosphate (PO_4) and COD besides *E. coli* removal from domestic wastewater was investigated by iron oxide nano-particles synthesized using turmeric (*Curcuma longa* L.) leaves [80]. It was demonstrated from the experiments that PO_4 and COD removal efficiency was 82% and 83%, respectively.

The reactivity of iron nano-particles synthesized using eucalyptus leaf extracts (EL-FeNPs) was evaluated for the treatment of swine wastewater and results indicated that 71.7% of total N and 84.5% of COD were removed [28].

Iron nano-particles (FeNPs) synthesized by green tea (GT-Fe) and eucalyptus leaves (EL-Fe) extracts have been proposed to be used for the removal of nitrate by Wang et al. [29]. Nano-particles synthesized were confirmed to have quasi-spherical shape with a diameter ranging from 20 to 80 nm. Nitrate removal of 59.7% and 41.4% by GT-Fe and EL-Fe nano-particles was achieved fitting the pseudo-second-order kinetic model.

In another report, Fe-P NPs synthesized using *Eucalyptus tereticornis, Melaleuca nesophila, and Rosmarinus officinalis* plants extracts were utilized as a Fenton-like catalyst for decolorization of acid black 194. Over 87% TOC was removed while 100% of acid black was decolorized [56].

Iron oxide nano-particles synthesized using leaves extracts of Omani mango were utilized for heavy oil viscosity treatment by Al-Ruqeishi et al. [60]. The IONRs were observed to have 15 ± 2 nm in average length and 3.0 ± 0.2 nm in average diameter. It was shown that the nano-rods were a good candidate for heavy oil cracking process. It was concluded from the results that oil viscosity reduced by 10%, 38%, and 49% when an amount of 0.2, 0.4, and 0.6 g/L IONRs was added to 1 L of heavy oil at 30°C.

Researches related with applications involved nano-iron particles synthesized using plants extracts are summarized in Table 1 showing the plants used for synthesis, nano-particles produced, their sizes, target pollutants, removal mechanisms, and performances.

4. Outlook

Safe water has become a competitive resource in many parts of the world due to increasing population, climate change, and related results. Because nano-materials have unique characteristics such as large surface areas, size, shape, and dimensions, they are considered particularly effective for water/wastewater treatment applications such as adsorption, destruction, and membrane separation.

This review of the literature has shown that water/wastewater treatment using nano-materials is a promising field for current and future research and applications. On the other hand green NP production using plant extracts is an emerging and innovative area of nano-technology. Therefore, the use of plants for NP production is a sustainable, eco-friendly, and inexpensive route. Toxic chemicals are not required, resulting in contaminant-free production and synthesis that can easily be performed at a large scale. The waste products of plant extracts are non-toxic and easily disposable. Furthermore, NPs synthesized by plants are more stable and effective than those produced by conventional methods. Considerable effort has been invested in obtaining secondary metabolites from the extracts of plants that may act as reducing, stabilizing, and capping agents in the synthesis of nano-materials, as seen from this review. Capping and stabilizing agents present in plants are proven to act as growth terminators and inhibit agglomeration processes, thus enhancing the stability and persistence of NPs. The reports on the application of green synthesized nano-iron materials for the removal of heavy metals, metal ions, dyes, chlorinated organic compounds, bacteria, and other pollutants such as nitrate, phosphate, COD, and TOC present in industrial wastewater, surface water, and groundwater found in the literature is summarized here. Great majority of investigations encountered in the literature have been carried out in research laboratories on a small scale. It will be necessary to explore the potential and applications of NPs by producing them on a large scale to satisfy the future demands.

Table 1
Summary of the literature findings

Nano-iron produced	Plants used for synthesis	Size, nm (surface area, m^2g^{-1})	Target pollutant	Performance	Mechanism/ isotherm model	Refs
nZVI	Oak, pomegranate Green tea leaves	10–20	–	–	–	[30]
nZVI	*Coffea arabica* leaf (Coffee)	50–100	–	–	–	[31]
nZVI	*Syzygium aromaticum*	100	–	–	–	[52]
β-Fe_2O_3	Garlic vine leaf *(Mansoa alliacea)*	18.22	–	–	–	[61]
Fe_3O_4	Mustard oil	20–100	–	–	–	[62]
β-Fe_2O_3	*Eucalyptus globulus* leaf	100	–	–	–	[64]
Fe_3O_4	*Caricaya papaya*	33	–	–	–	[65]
Fe_2O_3	*Ocimum sanctum*	<20	–	–	–	[66]
Fe_3O_4	Plantain peel	<50 (11.31)	–	–	–	[67]
FeO	*Terminalia chebula* fruit	<80	–	–	–	[68]
Fe_3O_4	Pistachio leaf	4.8	–	–	–	[69]
Fe_3O_4	*Aloe vera*	6–30	–	–	–	[71]
$Fe_{0.902}O$ Fe_3O_4	Alfalfa	<10	–	–	–	[73]
Fe_3O_4	Soya bean sprouts	8	–	–	–	[75]
nZVI	Coffee (C) Green tea (GT) Virginia creeper (VC) (*Parthenocissus tricuspidata*) leaves	C-Fe: 124.2 ± 31.8 GT-Fe: 119.6 ± 25.8 VC-Fe: 47.5 ± 8.8	Volatile chlorinated organics	Complete degradation of PCE (perchloroethene) and TCE (trichloroethene) Appreciable degradation of DCE (1,2-dichloro ethene) and VCE (chloro ethene)	Reductive dehalogenation	[26]
nZVI Fe_3O_4	*Azadirachta indica* leaf	28	Methyl orange	76%	Degradation with FeNPs-catalyzed H_2O_2	[27]
nZVI	Green tea leaves	40–60	Methylene blue Methyl orange	Efficient removal	Fenton-like catalytic reaction	[33]
nZVI	Tea (*Camellia sinensis*)	5–15	Bromothymol blue	Efficient removal	Degradation with FeNPs-catalyzed H_2O_2	[34]
nZVI	Sorghum bran extracts	40–50	Bromothymol blue	Efficient removal	Degradation with FeNPs-catalyzed H_2O_2	[49]
nZVI	*Dodonaea viscosa* leaf	20–40 (Average 27)	*Escherichia coli, Klebsiella pneumoniae, Pseudomonas fluorescens, Staphylococcus aureus, Bacillus subtilis*	Good	Reductive destruction	[53]
nZVI	*Emblica officinalis* leaf	22.6	Pb^{2+}	99.9%	Adsorption, reduction, oxidation/ reoxidation, and precipitation	[58]

(Continued)

Table 1 *(Continued)*

Nano-iron produced	Plants used for synthesis	Size, nm (surface area, m^2g^{-1})	Target pollutant	Performance	Mechanism/ isotherm model	Refs
nZVI	Oak, mulberry, and cherry leaves	10–30	As(III) Cr(VI)	374.4 mg g^{-1} 446.4 mg g^{-1}	Adsorption/ Freundlich	[86]
nZVI	Tea liquor	48–70	As(III)	Average 95.75%	Adsorption at low pH Precipitation at higher pH	[92]
nZVI	*Thuja orientalis* leaves	Average 92 (50–740)	Methylene blue *B. subtilis*, *E. amylovora* bacteria	Complete degradation Strong anti-bacterial effect	Reductive destruction	[93]
nZVI	Green tea leaves	50–60	Malachite Green dye	95.16%	Adsorption/ chemical destruction	[94]
nZVI	Green tea	30 (25)	TCE	65%–70%	Reductive dehalogenation	[95]
nZVI	*Coffea arabica*		*S. aureus*, *E. coli*, *Shigella dysenteriae*, *K. pneumoniae*, *B. subtilis*	Excellent inhibitory effect	Reductive destruction	[97]
Fe^0-iron oxide Polyphenols	Eucalyptus leaf	20–80	Total N Total P COD	71.7% 30.4% 84.5%	Adsorption/ co-precipitation/ reduction	[28]
Fe^0-iron oxide Polyphenols	Green tea (GT) Eucalyptus leaf (EL)	20–80	Nitrate	GT-Fe 59.7% EL-Fe 41.4%	Adsorption/ co-precipitation/ reduction	[29]
nZVI γ-Fe_2O_3 Fe_3O_4	Green tea (GT) Black tea (BT) Oolong tea (OT)	20–40 (5.82)	Monochlorobenzene (MCB) COD	GT 69% OT 53% BT 39% GT 31%	Fenton-like oxidation reaction	[32]
Polyphenol capping iron	*Eucalyptus tereticornis*, *Melaleuca nesophila*, *Rosmarinus officinalis*	50–80	Acid black 194 TOC	100% 87%	Fenton-like catalytic reaction	[56]
α-Fe_2O_3 γ-Fe_2O_3 (maghemite)	Omani mango tree leaves	15 × 3	Oil viscosity	49%	Cracking	[60]
Fe_3O_4	Banana (*Musa acuminata*) peel ash and *Colocasia esculenta* leaf	10–15	Pb^{2+} Cd^{2+} Tetrabromobisphenol A	Complete removal according to pH	Adsorption/ Langmuir	[63]
Fe_3O_4	*Tridax procumbens* leaf	80–100	*Pseudomonas aeruginosa*	The growth of bacteria was inhibited gradually as the concentration of Fe_3O_4 nano-particles increase	Reductive destruction	[70]

(Continued)

Table 1 *(Continued)*

Nano-iron produced	Plants used for synthesis	Size, nm (surface area, m^2g^{-1})	Target pollutant	Performance	Mechanism/ isotherm model	Refs
Fe_3O_4	Turmeric (*Curcuma longa* L.) leaf	66–148 Calcination (Cal) 17.9–28.7 Micro-wave-assisted (Mw)	Orthophosphate (PO_4) Chemical oxygen demand (COD) *E. coli*	FeNPMw 82% FeNPCal 17% FeNPMw 83% FeNPCal 82% FeNPCal complete removal	Reductive destruction	[80]
Fe_3O_4	Olive oil	37.8–77.6	Ni	–	Extraction	[88]
Fe_3O_4	Tangerine peel	50	Cd^{2+}	90%	Adsorption/ Freundlich	[89]
DEAMTPP@ Fe_3O_4	Pineapple (*Ananas comosus*) peel pulp	10–16 (11.25)	Cd^{2+}	49.1%	Adsorption/ Langmuir	[90]
DMSA@ Fe_3O_4	*Punica granatum* rind	40 × 200 (10.88)	Pb^{2+}	46.18 mg g^{-1} 96.68%	Adsorption/ Freundlich Adsorption/ Langmuir	[91]
Fe_3O_4	Al-Abbas's (A.S.) Hund Fruit	45	*E. coli*	100%	Reductive destruction	[96]

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