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MINI-REVIEWS

New research trends in the processing and applications of iron-based nanoparticles as adsorbents in water remediation methods

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Abstract

The present comprehensive review is an account of recent advances in the syntheses of nanoparticles of iron-based materials via conventional and green routes and their adoptability as adsorbents in the purification of water. The green synthesized nanoparticles are proving to be more biocompatible with enhanced sorption properties than conventionally synthesized nanoparticles. The potential areas of research in the syntheses and application aspects are summarized. The identification of compounds in flora that serve as reducing, capping or stabilizing agents, production of uniform-sized nanoparticles using plat materials as 'biotemplates' and developing sorption affinity between the surface of nanoiron-based particles and pollutants are some of the important areas discussed. The redox, complex formation, adsorption and ion-exchange tendencies of iron nanoparticles may be suitably 'tailor-made' to improve their binding affinity towards the pollutants so that the said nanoparticles or their composite materials (especially bi-/multimetallic/mixed oxides) may be used as adsorbents in water remediation methods. One of the major inherent disadvantages of nanosized iron particles using as adsorbents is the rate of percolation water through the sorbent bed is low, and there is a loss of pressure head. Investigations are to be focused in developing open columns wherein nanoparticles are embedded in the matrix of synthetic or natural inorganic or organic polymers or in beads. In such cases, the host matrix may influence the characteristics of the nanoparticles and they are to be investigated for the advantage of removal of pollutants from wastewater.

Keywords Review · Nano-Fe/Fe_2O_3 · Phyto-methods · Adsorbents · Pollutants · Water remediation

Introduction

On perusal of the literature, it is evident that increasing research interest is seen in developing zerovalent nanoparticles of iron (nZVI) as well as its oxides as adsorbents in water remediation methodologies. Iron oxide or its oxyhydroxides have many forms, viz. Fe_3O_4, α-Fe_2O_3, γ-Fe_2O_4 and FeOOH [1, 2]. All these manifestations of iron find wide utility in many industries in view of their small sizes, large surface areas, magnetic nature and high surface potentials [3]. Further, these particles are biodegradable and hence eco-friendly. j

The adoptability of these materials as adsorbents in water remedial methods is assuming impotence in view of their redox nature, adsorption abilities and complexing and/or precipitating tendencies towards various pollutants as is evident from the subsequent narration in this review and also a review presented by Lu et al. [4]. In fact, the surfaces of oxide forms of iron are endowed with strong adsorption forces of diverse nature i.e. electrostatic interactions, ion-exchange and ion-association tendencies, complex formations, etc., and these play an important role in developing affinity between the pollutants and surface of the adsorbent. Consequently, pollutants are effectively removed from wastewater. The oxidation tendencies of nanoparticles of Fe are also controlled by alloying it with another stable metal or by entrapping them in the matrix of some templates or polymers (synthetic or natural) [4]. These zerovalent nanoparticles are used as catalysts in the oxidation of oxidizable organic and inorganic impurities in wastewaters.

This research review is a comprehensive account of investigations made so far in this aspect of pollution control and identification of potential areas of research. New trends that can be explored further with respect to the synthesises by green methods and adoption of thus synthesized nanoiron

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or iron oxide particles in developing water remediation methods for the removal of pollutants of diverse nature are discussed.

Review of syntheses by conventional methods

Iron/iron oxide nanoparticles are synthesized by adopting various physical and chemical methods that are reviewed by Li et al. [3] and Stefaniuk et al. [5]. Zerovalent iron nanoparticles (nZVI) are prepared by reducing the ferrous or ferric salts with various reducing agents especially $NaBH_4$ [6.] and by using suitable capping agents such as organic surfactants and stabilizers. The purpose of capping agents is to prevent the aggregation of the iron particles and to control the growth of the particles so as to obtain desired size of the nanoparticles [6]. These surfactants or capping agents after having been 'onto' the surface, intensify the repulsion forces between the aggregating particles and, thereby, ensure the stability of the nanoiron or iron oxide particles. Various chelating agents (complexing agents) such as EDTA, NTA, DTPA, CDTA, HEDTA, TRTA and CTAB are investigated for their ability to function as capping or stabilizing agents in the synthesis of nZVI and found to be successful [7].

In another modification, nanozerovalent iron particles are prepared using the supports of resin [8], kaolinite [9] and zeolite [10]. Singh and Misra [11] reviewed comprehensively the role of polymers and surfactants in the stabilization of zerovalent iron nanoparticles.

Iron oxide nanoparticles are commonly synthesized by a number of chemical and physical methods and of which worth mentioning are: co-precipitation, solgel method, hydrothermal syntheses, thermal decompositions and microemulsion cum heat treatment [12–14]. Chemical reduction by Palladium [15] and further electrochemical synthesis [16] are also successfully used. Rahman et al. [17] comprehensively discussed the various methods of syntheses of nanoiron oxides.

All these methods need reducing, capping and stabilizing agents. In water-based methods, the procedure involved is to precipitate hydroxides of Fe (II/III) in reduction or oxidation environment and control the aggregation of species with suitable capping and stabilizing agents.

The main species formed in basic conditions is FeO(OH), and this species upon thermal treatment converts to different iron oxides. In α-Fe_2O_3, the oxide ions are in closed cubic structural arrangement while Fe^{3+} ions are randomly distributed in octahedral as well as tetrahedral interstices [2]. In the magnetic oxide, Fe_3O_4, oxide ions are in cubic close-packed arrangement while Fe^{2+} ions occupy octahedral interstices and Fe^{3+} ions occupy equally both the octahedral and tetrahedral interstices. The electrical conductance is attributed to the rapid oscillations of electrons between the two oxidation states of Fe ions [2]. This is the basic reason for all excellent physicochemical properties of the oxides of iron. Oxo-hydroxo iron species can be produced by controlled hydrolysis of ferrous and ferric salts as precursors, and each species has its own importance in one context or other in various industries.

The preparation of iron nanoparticles adopting the green methods is attracting researchers as the nanoparticles synthesized through these routes are proving to be stable, effective, biocompatible and eco-friendly than the conventionally synthesized particles. This may be attributed to the fact that the needed reducing agents, stabilizing agents and capping agents for the synthesis of nanoparticles are derived from the harmless flora materials.

Water/wastewater treatment with conventionally prepared iron/iron oxide nanoparticles

Iron-based nanoparticles are increasingly used for the removal of pollutants, both organic and inorganic, from water [9, 18–28]. In Table 1, the investigations in controlling various pollutants with iron-based adsorbents are summarized with respect to the pollutant, adsorbent, syntheses, mechanisms of extraction and adsorption capacity (in mg/g or %).

Lu et al. [4] reviewed comprehensively, the syntheses, importance and applicability of nanoparticles of zerovalent iron and various oxides of iron for the treatment of water/wastewater. The references presented in it are worth reviewing.

The iron-based nanoparticles are composed chemically either of sole metallic iron (nZVI), oxides of iron, FeO, Fe_2O_3 or Fe_3O_4 or metallic iron core encapsulated by thin iron oxide layers [26]. The nanometallic iron behaves as reductant, and further because of its size, it offers large areas (in contrast to metal iron) for the adsorption process to occur. At nanosize, the metallic iron is more prone for oxidation when it is in contact with water or moisture environment resulting in the transfer of electrons to the electron recipient (reducible pollutants) and release of Fe^{2+} ions. Thus, generated Fe^{2+} ions get oxidized to Fe^{3+} ions by the dissolved oxygen in waters especially in basic conditions resulting in the formation of ferric hydroxide; this is the basic principle of corrosion [29]. To prevent the oxidation, the nZVI particles are alloyed or doped with other metals atoms such as Ag [30] and Cu [31]. The alloyed metals prevent the rusting of iron either by the phenomenon of passivity or by sacrificial anodic process or by the noble character of alloyed metals [29, 32]. The iron nanoparticles can also be stabilized by incorporating them in some polymeric matrix. The nanoiron

Table 1 Iron-based nanoparticles as adsorbents in water remediation methods—a comparison

S. no	Synthesis and adsorption mechanism	Adsorbent	Adsorbent capacity (mg/g)/ % of removal	Pollutants	References
1	Chemical reduction cum adsorption	nZVI	609.4 mg/g	Azo dye, C.I. Acid Black 24 (AB24)	[18]
2	Reduction cum adsorption	nZVI	–	De-chlorination	[19]
3	Liquid-phase reduction cum adsorption	nZVI	–	Ba^{2+} ions	[21]
4	Reduction cum adsorption	nZVI	63%	4-chloro-3-methyl phenol	[27]
5	Reduction cum adsorption	nZVI	–	Cr(VI) and Pb(II)	[33]
6	Reduction cum adsorption	Zerovalent iron	3.5 mg/g	As(III)	[35]
7	Reduction cum adsorption	nZVI	100% As(V)	Arsenic(V)	[36]
8	Reduction cum adsorption	nZVI	90%	Hexavalent chromium, Cr(VI)	[45]
9	Reduction cum adsorption	Nano-Fe/Cu	98%	Nitrates	[46]
10	Co-precipitation–hydrolysis cum adsorption	Fe_3O_4/TiO_2	94% 93%	Removal of As(V) and As(III)	[49]
11	Reduction cum Adsorption	nZVI	Partial	Removal of Se(IV)	[50]
12	Reduction cum adsorption	Green-nZVI	Partial	Degradation of bromothymol blue	[52]
13	Reduction cum adsorption	Fe/Pd	Partial	Degradation of chlorinated organics	[55]
14	Bioelectrochemical denitrification	nZVI	Partial	Bioelectrochemical denitrification	[62]
15	Reduction cum adsorption	Green synthesized iron nanoparticles	21.59 mg/g	Removal of As(V)	[81]
16	Liquid-phase reduction cum adsorption	Polyethylene glycol-stabilized nanozerovalent iron supported by biochar	125.22 mg/g	Removal of Cr(VI)	[82]
17	Co-precipitation–hydrolysis cum adsorption	Coating Fe_3O_4 Magnetic nanoparticles with humic acid	46.3 mg/g	Cu(II)	[83]
			50.4 mg/g	Cd(II)	
			92.4 mg/g	Pb(II)	
			97.7 mg/g	Hg(II)	
18	Co-Precipitation–hydrolysis cum adsorption	Amino-functionalized magnetic nanoparticles	25.77 mg/g or 98%	Removal of Cu(II) ions from aqueous	[84]
19	Reduction–formation of beads–cum adsorption	Sodium alginate-dispersed nanozerovalent iron	96.4%	Removal of hexavalent chromium	[85]
20	Reduction cum adsorption	Nanozerovalent iron	98%	DDT removal	[86]
21	Reduction method cum adsorption	Nanoscale zerovalent iron	Pb^{2+} removal (> 95%)	Removal of lead for aqueous	[87]
22	Solgel–hydrolysis–precipitation cum adsorption	Magnetic Oxide (Fe_3O_4)	23.8 mg/g or 82%	As(III)	[88]
23	Microwave irradiation Method cum adsorption	γ-Fe_2O_3	94.33 mg/g	Cd(II)	[89]
			86.20 mg/g	Ni(II)	
			60.60 mg/g	Co(II)	
24	Chemical Oxidative polymerization cum adsorption	Fe_3O_4 doped SiO_2	83.23 mg/g	Pb(II)	[90]
			119.06 mg/g	Cr(VI)	
25	Reduction assisted by biochar cum adsorption	Magnetic nanoscale zerovalent iron-assisted biochar (nZVI2-BC)	98.8%,	Cd^{2+}	[91]
			99.9%,	Ni^{2+}	
			98.8%	Zn^{2+}	
26	Microwave irradiation method cum adsorption	γ-Fe2O3	111.11 mg/g	Cu(II)	[92]
			84.95 mg/g	Zn(II)	
			71.42 mg/g	Pb(II)	
27	Co-precipitation- hydrolysis cum adsorption	Polymer-coated magnetic iron oxide	62.75%	Cr(VI)	[93]

Table 1 (continued)

S. no	Synthesis and adsorption mechanism	Adsorbent	Adsorbent capacity (mg/g)/ % of removal	Pollutants	References
28	Chemical Co-precipitation cum adsorption	γ-Fe2O3	67.02 mg/g	As (III)	[94]
			95.37 mg/g	As (IV	
29	Co-precipitation cum adsorption method	Modified magnetic iron oxide nanoparticles	0.6 mg/g or 96.2%	Hg(II)	[95]
30	Chemical Co-precipitation cum adsorption	γ-Fe_2O_3	22.0 mg/g	Cr(VI)	[96]
31	Solvent thermal cum adsorption	α-Fe_2O_3	95 mg/g	As(III)	[97]
			47 mg/g	As(IV)	
32	Chemical Co-precipitation cum adsorption	Haematite (α Fe_2O3)	84.46 mg/g	Cu(II)	[98]
33	Co-precipitation method cum adsorption	Magnetite nanoparticles	0.149 mg/g	Mn(II)	[99]
			0.177 mg/g	Zn(II)	
			0.184 mg/g	Cu(II)	
			0.189 mg/g	Pb(II)	
34	Reduction method	zerovalent iron nanoparticles	97%	Removal [Cr(VI)] from aqueous solution	[100]
35	Co-precipitation method	Fe_3O_4@SiO_2	73.31 mg/g	Removal of Cu(II) ions from aqueous solution	[101]

or ferrous ions reduce the reducible pollutants while ferric iron oxidizes the oxidizable impurities by virtue of the redox potentials of the systems: Fe^{2+}/Fe (-0.45 V) and Fe^{3+}/Fe^{2+} (0.77 V) coupled with the large surface areas.

The interactions of nanoparticles of the oxides or hydroxides towards pollutants are due to adsorption (physical or chemical), ion-exchange and/or complex formation. The physicochemical adsorption is resulted due to the residual valences or imperfections in the iron oxide matrix. Redox tendencies of the Fe^{2+} and Fe^{3+} ions may also contribute for the adsorption process. Further, if the nanoparticles contain core iron enveloped with the oxides of iron, as has been described by Yan et al. [26], the mechanism of interaction is multiple in nature: reduction, ion exchange, precipitation, co-precipitation or sorption, depending upon the nature of ingredients and experimental conditions. These aspects are presented in Fig. 1.

The iron-based nanoparticles synthesized by chemical methods using sodium borohydride as the reductant with various capping agents are investigated for their utility in controlling various pollutants. Investigations are made to remove Cr(VI) and Pb(II) [33], Ni(II) [34] and As(III, V) [35, 36] from contaminated water.

Sequestration studies on toxic metal ions like Zn(II), Pb(II) Cd(II), Ni(II), Cu(II) and Ag(I) are investigated using zerovalent iron nanoparticles and found that the removal mechanism is reduction or complex formation or adsorption or their combination depending upon the reduction potentials and extraction conditions [34]. Li et al. [3] reviewed the preparations and applications of these nanoparticles.

Efecan et al. [24] investigated the adsorption nature of zerovalent iron towards the Ni^{2+} and compared it with other cationic pollutants, viz. Cu^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+} from the view point of standard reduction potentials. Uzum C. et al. [37] investigated the sorption of Co^{2+} ions from waters using nanosized zerovalent iron (nZVI) as adsorbent and found that the extent of Co^{2+} uptake increased with the increasing pH. Further, the fixation of Co^{2+} ions onto the surface is found to be through the interaction of Co^{2+} ions with the oxo-[hydroxyl groups on the iron nanoparticle surface in addition to spontaneous precipitate formation at high loadings.

The presence of oxo- hydroxyl groups on the surface of zerovalent iron is due to the conversion of some surface iron atoms to hydroxides or hydrated oxides when the surface is in contact with waters (Fig. 1). The tendency of formation of such hydroxides or oxides layers is more with the increase in pH [37].

Elebi et al. [21] studied the adsorption behaviour of Ba^{2+} onto the nanoparticles of iron chemically synthesized. The binding of Ba^{2+} ions to the surface of the adsorbent may be due to the formation of oxo-hydroxyl groups of iron on the surface that are inherently possesses complexing or cation-exchange ability towards the said ion [21]. Shu et al. [18] investigated the decolouration of azo dye, Acid Black, using chemically synthesized zerovalent iron (nZVI), and the extractions are found to be effective in the pH range 4–9.

Nanoparticles of iron are also used in the purification of ground-polluted waters. Wei et al. [25] demonstrated the use of nZVI, synthesized chemically, for the effective

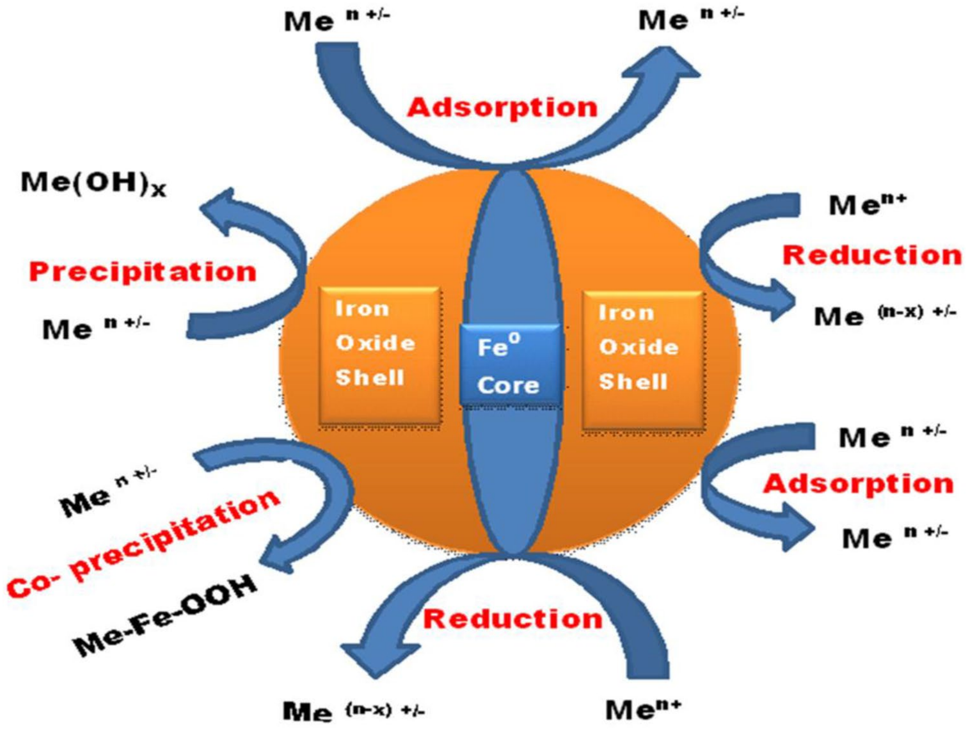

Fig. 1 Mechanisms of removal of pollutants (Me) from water by iron/iron oxide nanoparticles

remediation of ground waters contaminated with chlorinated organic compounds. The effect of trichloroethylene (TCE) concentration and commonly dissolved groundwater solutes, viz. NO_3^-, Cl^-, HCO_3^-, SO_4^{2-} and HPO_4^{2-}, on the rates of nZVI-promoted TCE de-chlorination and H_2 evolution, are investigated in batch methods by Liu [20].

It is found that anions have marginal effect on hydrogen evolution, but TCE reduction is interfered in the order $Cl^- < SO_4^{2-} < HCO_3^- < HPO_4^{2-}$. It is interesting to note that this order is same as the efficiency of these ions to form complexes with iron oxide and this reflects the existence of oxide/hydroxide layers on the surface of nanoiron particles.

Yan et al. [26] investigated nanoscale zerovalent iron (nZVI) particles with respect to their core–shell structure and its interactions with three pollutants, namely Hg(II), Zn (II) and H_2S. Surface morphological studies using X-ray energy-dispersive spectroscopy (XEDS) and scanning transmission electron microscope (STEM) revealed the layer-wise structure for the nanoparticles with metallic iron core covered with thin oxide layers (Fig. 1). The results indicate the multiple reactive pathways owing to the dual nature of nanoparticles. It is observed that the removal of Hg(II) is due to chemical reduction by core iron atoms to Hg while that of Zn^{2+} is attributed to the sorption nature of surface-coated iron oxide/hydroxide. The removal of H_2S is due to the formation of precipitates FeS or FeS_2. Wang et al. [38] studied the dechlorination of 2,4-dichlorophenol using Pd/Fe nanoparticles modified with poly(methylmethacrylate) (PMMA), polyacrylic acid (PAA) and cetyltrimethylammonium bromide (CTAB). The results indicate that with these modified Pd-Fe nanoparticles, the degradation of 2, 4-dichlorophenol is enhanced markedly.

Reduction in nitrate using nZVI [39–42], copper-coated nZVI [43] and nanobimetallic Fe/Ni [44] are investigated. Di Palma et al. [45] evaluated the reduction in Cr(VI) in soils also using nZVI. Muradov et al. [46] investigated the catalytic reduction in nitrate in waters by using nanoparticles of zerovalent iron as well as nano-Fe doped with different concentrations of Cu. Nitrates are successfully reduced to ammonia and nitrogen. The presence of Cu enhances the reduction ability of nZVI.

Arancibia-Miranda et al. [47] investigated the sorption nature of adsorbents prepared by impregnating nZVI in the zeolite and montmorillonite towards Pb^{2+} and found to be effective. This is attributed to the synergistic effect caused by nanoparticles on clays and vice versa in enhancing the sorption nature of the mixed adsorbents.

The removal of As(III) and As(V) from waters is investigated by Daryoush Afzali et al. [48] using 'Fe_2O_3 nanoparticles-coated sand' as adsorbent. 100% removal of As (III, V) is observed at optimum pH: 7, and the adsorption capacity is: 0.284 mg g^{-1}. Fatama Beduk et al. [49] successfully investigated the mixed oxide nanomaterials of iron and Ti as adsorbent for the removal of As(III) and As(V) from polluted water. Removal of Se (IV) using nZVI as adsorbent from water is studied by Ling et al. [50]. Zhang [51] and Stefaniuk et al. [5] reviewed the syntheses and environmental applications of nZVI.

In these investigations, chemical or physicochemical methods are used for the preparation of nanoparticles. They involve various toxic chemicals as reducing, capping and stabilizing agents. Some traces of these hazardous substances are adsorbed ‘onto’ the surface of the nanoparticles of iron/iron oxide causing ill effects, and moreover, these processes are costly.

So, the green methods of synthesis of nanoparticles using plant extracts containing compounds having functional groups such as –COOH, –HCHO, –OH, C=O, amino, esters and amide groups, which functions as reducing, capping and stabilizing agents are attracting the researchers as is evident from the following narration.

Plant-meditated nanoiron/iron oxide particles in water purification

Chemical methods of synthesis of iron/iron oxide nanoparticles are not eco-friendly because the residues of the chemicals remain on the surface of particles. So, the researchers are trying to prepare plant-meditated nanoparticles in view of the fact that the plant extracts are non-toxic and biodegradable. The biodegradable nature has merits because even when the nanoparticles are let into environment after their applications, they do not cause environmental problems. Such studies are increasingly found in the recent literature.

These green methods of preparation of nanoparticles are single-step processes, and the needed reducing agents or dispersive substances or capping agents such as polyphenols, sugars, flovonoids etc., are derived from the flora materials.

Hence, the biomaterials are being investigated for the constituents that meet the requirement of reducing, dispersive and capping agents so as to form the stable nanoparticles [52]. Thus, synthesized nanomaterials are found to have enhanced adsorption properties. They are being increasingly investigated as adsorbents in water remediation methods. This concept of preparing nanoparticles using the extracts from plants that serves as capping, stabilizing or reducing agents can be illustrated as shown in Fig. 2.

Nadagouda et al. [53] studied the in vitro biocompatibility of nZVI using tea polyphenols while Hoag et al. [54] studied the degradation of bromothymol blue dye using thus prepared nanoparticles. Njagi [55] synthesized the iron nanoparticles using Sorghum bran extracts. Shahwana et al. [56] prepared the nanoparticles using extracts of green tea leaves. These extracts have polyphenols that act as reducing agents as well as capping agents. Nanoparticles obtained by using these extracts are used as catalysts for disintegrating and removing of methylene blue and methyl orange [56]. It is observed that with these green synthesized nanoparticles, % removal of the dyes is more than that of nanoparticles synthesized by conventional chemical reduction with sodium borohydride.

Iron-based nanoparticles are synthesized by Smuleac et al. [57] using green tea extracts containing naturally present compounds that serve as complexing as well as reducing agents besides capping nature. Thus, prepared nanoparticles are successfully used for degradation of chlorinated organics, trichloroethylene (TCE), in polluted water samples [57]. Senthil and Ramesh [58] synthesized nano-Fe_3O_4 by treating $FeCl_3$ solution with the leaves extract of *Tridax procumbens* plant and explored its antibacterial activity.

Using leaves extract of *Caricaya papaya*, Latha and Gowri [59] synthesized nano-Fe_3O_4; Venkateswarlu et al. [60] used *plantain peel extract* for synthesizing the nano-Fe_3O_4 of size 50 nm with 11.31 m^2/g BET surface area. However, their sorption abilities for water/wastewater remedial methods for toxic pollutants are not investigated.

Kuang et al. [61] used green tea, black tea and oolong tea extracts for iron nanoparticles preparation and studied the heterogeneous Fenton-like oxidation of monochlorobenzene. Iron nanoparticles prepared from the extracts of green tea and/or eucalyptus leaves are used in the removal of nitrate from waters [62], control of eutrophication [63] and degradation of malachite [64].

Abdul-Raheim et al. [65] synthesized a special adsorbent by doping nano-Fe_3O_4 into potato starch–acrylic acid polymer and its adsorption nature with respect to heavy metal ions, namely Cu^{2+}, Pb^{2+} and Ni^{2+}, was studied and found that at optimum pH:5.5 and temp. 35 °C, the adsorption capacity was of the order $Ni^{2+}>Cu^{2+}>Pb^{2+}$ with 100, 70 and 100 $mgg^{-1}$of the adsorbent.

Cao et al. [66] investigated the removal of phosphate using iron oxide nanoparticles synthesized with the extracts of eucalyptus leaves as reductant and CTAB as the capping agent. Adsorptive removal of chromium (VI) was investigated using zerovalent iron particles prepared from *Eucalyptus globulus leaves* [67] and by using iron oxide nanoparticles prepared from *pomegranate leaf extract* [68].

Banana peel ash is used in the preparation of nanoparticles of oxides of iron which is found to remove effectively the organic and inorganic pollutants in water/wastewaters [69]. *Tridax procumbens* leaves [70] and *deciduous Omani mango tree leaves* [71] extracts are used to synthesize nanoparticles based on iron or its oxide. However, their sorption nature towards pollutants is not investigated. Maid et al. [71] have graphically presented the method of preparation of nanoparticles of Iron oxide, and this work is highly appreciable.

Ehrampoush et al. [72] investigated the synthesis of nanoiron oxide using the extracts of *tangerine peels* and adopting the co-precipitation method. It is observed that the size of nanoparticles is markedly affected by the extract concentrations. By enhancing the concentration from 2 to 6%, the size of the nanoparticles is decreased

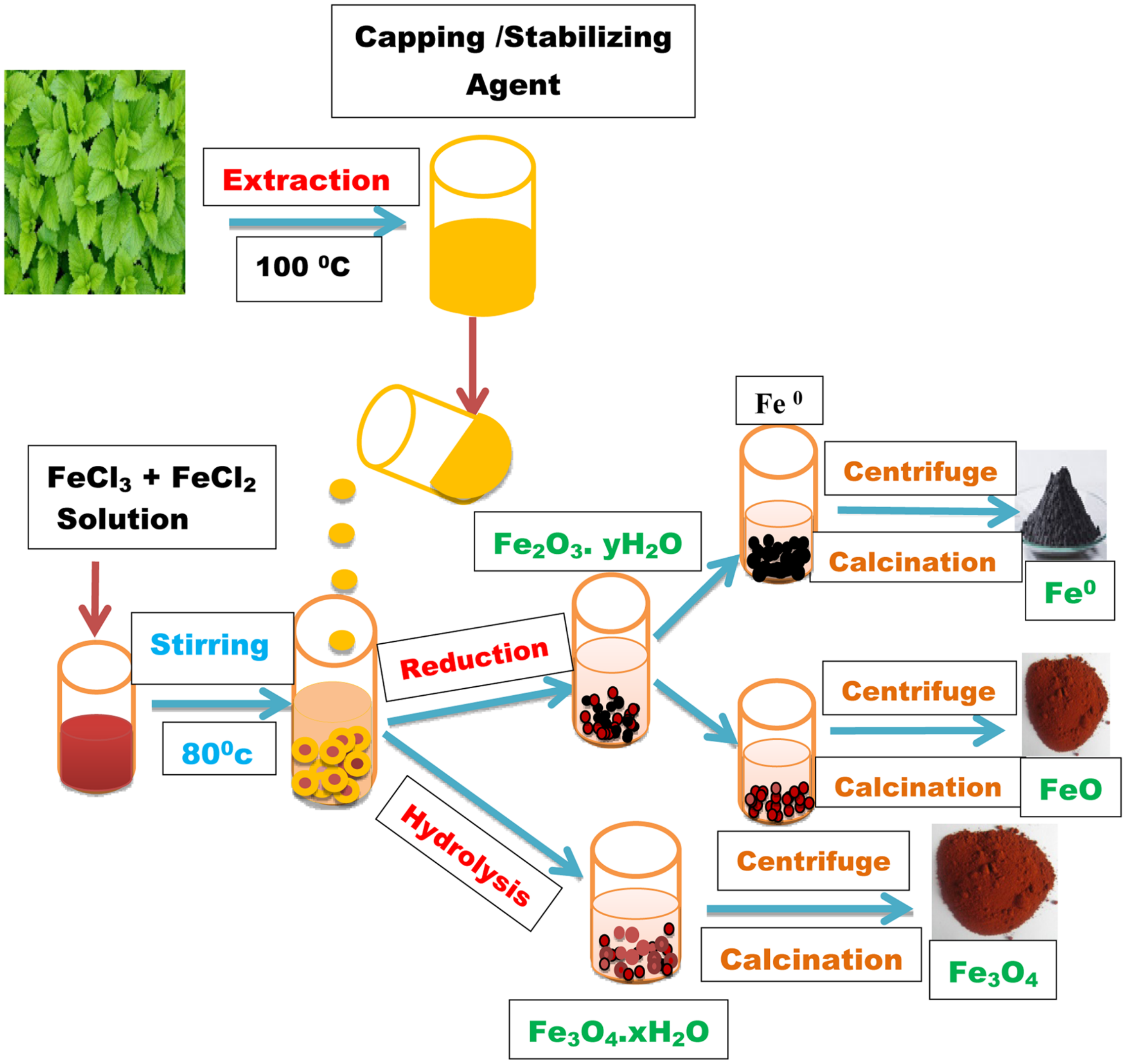

Fig. 2 Phyto-mediated (green) synthesis of iron or iron-based nanoparticles

from 200 nm to 50 nm. Thus, prepared nanoparticles are studied for their adsorption nature towards Cd^{2+} and found that at pH: 4, about 90% removal of Cd^{2+} (20 mg/L) is possible with the sorbent concentration: 4.0 gm/l.

Raiza Rasheed and Meera [73] prepared ‘sand-coated with iron oxide nanoparticles’ using polysaccharide templates. Vélez et al. [74] synthesized nanoparticles of Fe_3O_4 and γ-Fe_2O_3 using iron salts and NaOH as precursors and aloe vera as capping and stabilizing agent and studied their sorption nature towards Hg^{2+} and found 70% removal; Yew et al. [75] developed a green method of synthesizing nano-Fe_3O_4 of size 14.7 nm using the extract of *Kappaphycus alvarezii* as reducing and stabilizing agent. They have emphatically demonstrated the possible interactions between the surface of the nanoparticles and the *bio-molecules* present in the extract of seaweed *K. Alvarezii* [75].

Lu et al. [4] reviewed the investigations on the use of different nanomaterials, viz. Ag, Fe and Zn; metal oxides: TiO_2, ZnO and iron oxides; CNTs; and nanocomposites, as adsorbents in the removal of various pollutants from water and wastewater. Xin et al. [76] synthesized nanozerovalent iron particles using *Guanyin tea extract* as reducing and stabilizing agents and investigated its catalytic activity in the degradation of Bromothymol blue. Imtiyaz Hussain and Singh [77] reviewed the importance of green methods of synthesis adopting plant extracts and microbes with reference to some inorganic ions including Fe_3O_4.

Conclusions and research prospectives

Iron is a multivalent element and its oxidation states are +2 and +3 and reduction potentials for the redox systems are: $Fe^{3+/}Fe^{2+} = +0.77$ V and $Fe^{2+}/Fe = -0.45$ V. So the zerovalent iron nanoparticles or iron oxide nanoparticles (FeO, Fe_2O_3, Fe_3O_4) when hydrated undergo either reduction or oxidation. The oxidizable or reducible impurities in water, whether they are of organic or inorganic nature, get removed depending upon the potentials, and further, if the products of the redox process involve phase separation (gases or solids), the effect of removal is enhanced.

The metallic iron at nanosized dimensions, being endowed with large surface area and many active centres, is more facile for oxidization. Its standard reduction potential for Fe/Fe^{2+} is -0.45. So, Fe/Fe^{2+} behaves as good reluctant for pollutants possessing more reduction potentials. As for example, metallic Fe can displace pollutive Cu^{2+} ions from wastewater and precipitate it as metallic Cu on the surface of metal iron [32]. Efecan et al. [24] explored the difference in reduction potentials and successfully removed metal ions: Cu^{2+} (+0.34 V) and Ni^{2+} (-0.26 V) which have more reduction potential than the Fe^{2+}/Fe system.

Further, the metallic iron nanoparticles catalyse certain reactions and these reactions may be conducive for the successful removal of pollutants. As, for example, Shahwana et al. [56] successfully degraded cationic and anionic dyes in polluted waters using zerovalent iron nanoparticles as catalyst, Wei et al. [25] reported the catalytic degradation of vinyl chloride in polluted ground water. Thus, the zerovalent iron can be further investigated for water purification processes by exploring its catalytic and reduction nature.

The nanoiron oxide particles possess besides redox natures, the ion-exchange abilities and also complex forming tendencies [78]. The redox nature is due to the redox system: Fe^{2+}/Fe^{3+} and ion-exchange nature is due to the functional groups such as –OH, =O groups or active centers possessing charges. The complex forming tendencies are due to Fe^{2+} or Fe^{3+} ions or –OH groups present on the surface [1]. These multiple tendencies towards different pollutants (organic as well as inorganic) in water/wastewaters for the successful extractions of the pollutants are to be explored.

It is interesting to note that the nanoparticles derived by using plant extracts have changed surface morphologies than the conventionally prepared nanoparticles and it is attributed to the adsorption of some biocompactable compounds present in the natural extracts [79].

Investigation made by Kar and Ray [80] is interesting. In this investigation, the uniform microscopic pores naturally existing in petals of Hibiscus rosa sinensis plant are used as 'template' in obtaining uniform nano-Ni particles. This concept may the extended to the iron-based nanoparticles, thereby bringing into lime light the hidden advantages bestowed on us by the nature. These novel concepts are to be investigated in conjunction with water treatment methods.

The surface characteristics of nanomaterials based on these types of inorganic materials can be 'tailor-made' to our specific needs and requirements in adsorptive removal of pollutants from waters. The nanoform of zerovalent iron when in contact with water and dissolved oxygen get oxidized to oxyhydroxide of iron. This conversion is similar to that of corrosion which is an unwanted phenomenon in metallurgy. But this product of oxidation has the capacity to bind impurities via complex formation, ion-exchange and physical/electrostatic interactions besides the redox potential energies. Further, the oxides of iron serve as a flocculent for removing organic colloidal suspensions and also traps the adsorbable metal ions and thereby scavenge the pollutants present in the contaminated water. Thus, the 'disadvantage' in metallurgy is an 'advantage' in water remedial methods when surface forces are properly evoked.

Furthermore, the preparation of zerovalent iron or iron oxide nanoparticles adopting green syntheses is a vast area of research. Many investigations may be pursued in developing cost-effective, eco-friendly and effective methods in obtaining stable nanoparticles of iron. The green synthesized particles are found to possess additional or enhanced physicochemical properties beside biocompatibility than conventionally prepared nanoparticles by chemicals or physical methods or both. The green synthesized nanoparticles of iron-based materials have to be explored for their utility in controlling pollutants.

Thus, the investigations are to be made in the following aspects:

1. Green procedures are to be developed for the syntheses of iron-based nanoparticles by identifying the naturally existing compounds in the rich flora in our environment, which serve as capping, reducing and complexing agents in stabilizing the nanoparticles. In this aspect, the plant species possessing natural surfactants may be investigated. This aspect of research is wide open in view of diversity of plant species.
2. Using plant materials as biotemplates, uniform-sized iron/iron oxide nanoparticles of desired shapes and sizes can be developed. Further, the green methods of syntheses are to be improved from laboratory scale to large scale to meet the day-to-day increasing demand
3. Doping foreign metal ions in the matrix of the nanoparticles of iron/iron oxide alter the surface morphologies and characteristics, and hence, by judiciously 'tailor

making' the dopant concentrations, the selectivity of the nanoiron/iron oxide adsorbent towards a particular pollutant may be enhanced. Innovative researches can be pursued by employing the nanosized mixed oxides or bi- or multimetallic substances for the treatment of waters or wastewaters [43, 44].

4. One of the major disadvantages of these plant-mediated syntheses is that the chemical composition of the extracts may change even in the same species of the plant from season to season, place to place and one growth stage to another, thereby limiting their applications and this results in hampering the growth of these phyto-green methods. But this disadvantage can be overcome by identifying and isolating the compounds present in the bioextracts and then using them for water remediation purpose. Investigations have to be undertaken in this direction.
5. Iron-based nanoparticles synthesized by green methodologies are to be probed as adsorbents for successful removal of different pollutants by evoking redox, complex formation and ion-exchange tendencies towards the pollutants. In view of diverse nature of pollutants in different environments, 'Pandora's box' of investigations will be resulted.
6. An inherent disadvantage of nanosized iron particles using as adsorbent is that water flow in continuous columns through the bed of nanosized particles needs pressure head. Hence, methodologies are to be developed with open columns wherein the nanoparticles are embedded in the matrix of synthetic or natural inorganic or organic polymers or in beads. The host matrix may also alter the structural characteristics of the nanoparticles, and they have to be exploited for the advantage of the removal of pollutants from wastewaters [47].

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author, Prof. Dr. K. Ravindhranath, states that there are no conflicts of interests.

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