REVIEW

Iron-based nanoparticles in wastewater treatment: A review on synthesis methods, applications, and removal mechanisms

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Abstract Nanomaterial is an emerging material with potential technological impacts in various applications. It imposes great opportunities in various disciplines including wastewater remediation. Industrial wastewater is generated with anthropogenic activities and is the most environmental threat that needs remediation to overcome the environmental damages, thereby reducing human risks. Currently, several wastewater treatment techniques are applied and the utilization of nanomaterials for pollutant removal is an emerging technology. This is evident that the publication trends in the field of iron-based wastewater have been drastically increased. In this work, the overview of the preparation of iron-based nanoparticles, such as different polymorphs of iron-oxides, oxyhydroxides, iron hydroxide, and zero-valent iron nanoparticles are reviewed. In addition to the detailed discussion on the preparation of iron-based nanoparticles, their application on waste water treatment, removal mechanisms, advantages, and limitations are also assessed and discussed. Moreover, the iron-based nanoparticles' removal efficiency for specific pollutants and perspective in environmental remediation are also analyzed. Additionally, the advancements and future perspectives of iron-based nanoparticles are highlighted.

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Contents

1. Introduction

Nanotechnology is a recent discipline dealing with an innovation that is implemented at the nanoscale and has wide applications in the real world [1,2]. It deals with nanomaterials that have at least one dimension ranging from 1 to 100 nm [3,4]. Extensive studies in the nanotechnology discipline started in the 1980s and have endured being a modern-day wonder of scientific discovery [5]. Nanotechnology studies are broadly carried out in our day-to-day activity and are changing the entire society to a new era [6,7]. It has started walking into agriculture and food manufacturing since 2003 when the US division of farming disbursed the first guide on September 9, 2003 [3]. Nanotechnology gives an extensive range of possibilities for the improvement of systems, substances, or gadgets with new properties in various areas like agriculture, food, environment, medicine, [8,9], and many others. For instance, nanomaterials have promising applications in biomarkers, diagnostics, antimicrobial agents, and cell labeling for biological imaging, drug delivery systems, in nano drugs for the treatment of various diseases, and used in the disinfection of drinking water [10,11,12]. It is a promising tool for removing a wide range of contaminants including pharmaceuticals and antibiotic-resistant pathogens from wastewater and water for drinking water production and irrigation [13]. Furthermore, due to the cost-effective and environmentally friendly manner, nanotechnology has attracted tremendous attention in enhancing oil recovery (EOR) [5,14]. The use of nanotechnology in wastewater and water remediation is surpassing extensive

visionary limits [15,16]. Nanotechnology is studied as an affordable, promising alternative, and effective for the removal of water, and wastewater contaminants, such as inorganics (toxic metals), organics, and microorganisms [17,18,19].

Different types of nanomaterials are reported by different researchers [20]. Metal-based nanoparticles, polymer nanoparticles, zeolites, carbon-based nanomaterials, self-assembled monolayer on mesoporous supports (SAMMS), biopolymers, and nanoscale metal oxide and chalcogenide semiconductor photocatalysts are some of the nanomaterials used nowadays [21,22,20]. Among these, metal oxide nanoparticles like titanium dioxide (TiO$_2$), zinc oxide (ZnO), iron oxide (Fe$_2$O$_3$/Fe$_3$O$_4$), and cerium oxide (CeO$_2$) show high reactivity and photolytic properties against wastewater and act as a great adsorbent for water purification because they have a massive surface area and their affinity towards diverse functionalized groups [23]. The advantage of these nanomaterials is due to their high adsorption capacity for several contaminants in water and wastewater [24,25]. These characteristics are because of having unique properties such as high reactivity, selectivity, large surface area, a high grade of functionalization [26,27]. Their ability to oxidize, precipitate, reduce, and adsorb the contaminants such as nitroaromatic compounds, inorganic anions, phosphates, radio elements, nitrates, phenols, organic dyes, and chlorinated and halogenated organic compounds, make them applicable for water and wastewater purification [28,29]. Among metal-based nanoparticles, iron-based nanoparticles received greater attention for treating contami-

nants from the wastewater due to cheaper cost and second most abundance metal on Earth [30,31].

Water is the most important and restrained aid on Earth, which has been contaminated due to the fast growth of industrialization combined with the increasing population, through the releasing of heavy metals, pathogens, insecticides, and many organic and inorganic constituents [23]. The contaminants pose several concerns to the environment and human health that strengthen the application challenges of conventional treatment technologies [32,33]. The chief sources of water and soil contamination are sewage water, industrial wastewater, and improper use of pesticides, fertilizers, and oil spills in the agricultural systems. Meanwhile, the quick growth of nanotechnology has added a lot of intrigue in the use of nanomaterial in enhanced systems for controlling and cleaning contaminants in the water, soil, and air segments [34,35].

Generally, conventional wastewater treatment methods contain physical, chemical, and/or biological routes and procedures to remove solids including colloids, soluble contaminants (metals, organics, etc.), organic matter, and nutrients. Coagulation-flocculation, precipitation, biodegradation, filtration (with gavels, sands, and others), and adsorption are the key conventional methods used in wastewater treatment [36,22]. Among these, the adsorption process is very cost-efficient, simple, widely used, and environmentally friendly [7,37]. Activated carbon is among the most studied and effective nanoporous sorbents due to its excellent sorption capacity. However, its usage has been limited because of its high cost, low selectivity, and regeneration problems which makes it unsustainable, and researchers divert their attention to iron-based nanomaterials [38].

The superiority of nanoparticles over conventional wastewater treatment methods is explored by many researchers. Some of the conventional methods are restricted in large-scale wastewater treatment applications [39] and are energy-intensive and uneconomical [40]. For instance, the above techniques are competent in treating particular contaminants. However, they are unequipped for eliminating other different toxins or impurities present in the wastewater [41]. For example, endocrine disruptor chemicals, although there is a need for optimization of treatment processes [28], organic matter, and chlorides, cannot be removed in conventional methods [42]. Furthermore, nanotechnology is a remarkable discipline in today's world, and have been studying the special properties of nanomaterials that can solve various difficulties that cannot be solved by conventional methods [41]. In the aspect of effluent treatment, techniques using the nanomaterials have shown a high degree of superiority over the use of conventional methods without employing additional systems [43]. Moreover, nanomaterials without secondary pollution characteristics are preferable, which makes nanotechnology a very hopeful discipline [42].

The prospective of iron-based nanoparticles to remove various contaminants has been revealed in both laboratory and on-site field tests. Today's mostly used iron nanoparticles in the use of wastewater treatment are based on adsorptive and photocatalytic mechanisms [28]. Disinfection and microbial control, and/or combined techniques/systems are other ways of wastewater treatment alternatives [44]. Iron-based nanoparticles can be produced in different forms such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), iron oxy-hydroxide (FeOOH), and metallic zerovalent iron. The

low cost, natural abundance, easy synthesis, and superparamagnetic properties of iron make them feasible and eco-friendly materials for industrial wastewater treatment [45]. They have a tremendous property to remove various contaminants in wastewater treatment when used as nano-adsorbent [12]. Iron oxide nanoparticles can be synthesized by several techniques, which all have their own merits and demerits. Co-precipitation, thermal decomposition, microemulsion, and sol–gel are the most commonly employed synthesis methods [46].

Many other nanomaterials including carbon-based nanoparticles have been extensively studied and reviewed for removing contaminants from wastewater. But, due to availability, less costly, and environmentally friendly behavior, iron-based nanoparticles, specifically magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), iron oxy-hydroxide (FeOOH), and metallic zerovalent iron are widely studied. This can be confirmed by observing the publication trend as shown in Fig. 1.

The publication trends with a general search query" Wastewater treatment by using Iron-based nanoparticles" was conducted at National Center for Biotechnology Information (https://pubmed.ncbi.nlm.nih.gov/). Journal article publication data was activated and found a total of 235 peer-reviewed papers. The publication date was customized from 2000/01/01 to 2020/12/30, but results were found from 2007 to 2020 with the predetermined search query. Moreover, the specific search query to the specific iron-based nanoparticles (i.e hematite, magnetite, goethite, zero-Valent iron oxides, and others) to the specific contaminant types (heavy metals, and azo-dyes) was retrieved. The retrieved journal articles that we found were both pure iron oxides and supported /composited with other organic and inorganic materials to enhance the removal efficiency of contaminants from wastewater. For example, the nanoparticles may be synthesized as chitosan and chitosan/nano-iron oxide, zeolite-supported nano zerovalent iron, and others. As can be seen from Fig. 1, the number of publications, especially from 2016 to 2020 end was found to drastically and consistently increase showing the field is recently attracting attentions in the wastewater treatments.

Nevertheless, iron-based nanoparticles need to be studied and reviewed widely due to the good properties stated above. This review appraises the essential characteristics, detailed synthesis methods, and removal capacities of iron-based nanoparticles for different contaminants in the wastewater. In addition, the limitations on iron-based nanoparticles for contaminant removal are highlighted. Emphasis is given to the different synthesis techniques and applications of iron-based nanoparticles
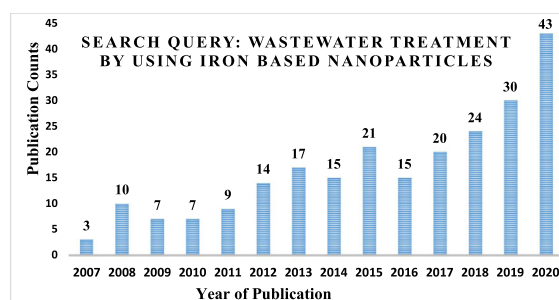
Fig. 1 Publication trends from the year 2007 to 2020 in the field of wastewater treatment by using Iron-based nanoparticles.

for the remediations of contaminants from wastewater. Moreover, potential removal mechanisms of iron-based nanoparticles for the effective remedy of contaminants are included. Finally, future directives and recommendations to the area are pointed out.

2. Synthesis method and application of iron-based nanoparticles

Different techniques such as physical, chemical, and biological methods, as shown in Fig. 2, have been implemented to synthe-

size Iron-based nanoparticles with suitable characteristics based on their surface chemistry. Up-to-date synthesis techniques, the nanoparticles characterization, and their use are reported in detail [47]. The nanoparticle synthesis methods can be top-down and bottom-up approaches. The physical processes are included in the top-down approach whereas chemical and biological processes are categorized under the bottom-up approach [19,40,48]. In top-down preparation methods, a destructive approach is applied by starting from the larger molecule, which is then decomposed into smaller

Table 1 Preparation considerations of some chemical preparation techniques of Iron oxide-based nano material [47,31,60].

Methods	Main activities occurred	Major Influencing factors	Advantage	Disadvantage
Co-precipitation	The reaction of iron salt, in an aqueous solution to a base in the presence of a mild oxidant. It involves the concurrent events of nucleation, growth coarsening, and/or agglomeration processes.	type of salt used, Fe^{2+} to Fe^{3+} ratio, pH, ionic strength, Temperature, agitation	Simple and effective.	Inappropriate for the synthesis of high untainted, precise stoichiometric phase, the pH value has to remain high during the synthesis and purification process.
Sol-gel	Revolves around hydroxylation and condensation of molecular precursors in solution followed by "sol" drying or "gelling" either by solvent removal or by chemical reaction.	pH, nature, and concentration of salt precursor, kinetics, temperature, agitation, and properties of the gel.	Aspect ratio, precisely controlled in size, and internal structure.	High permeability, weak bonding, low wear resistance.
Hydrothermal	Hydrothermal reactions are performed in a reactor or autoclave in an aqueous media at higher temperatures and pressure above the solvent boiling point.	residence time, the concentration of salt precursor, and hydrothermal temperature.	size and shapes are easily controllable.	High pressure and reaction temperature.
Micro-emulsion	Water droplets immersed in oil, which are stabilized by surface molecules followed by surfactant removal and washing of the colloidal.	type of salt used, surfactant type, pH.	diversity of NPs due to surfactant, nature, physiological conditions.	adverse effects of residual surfactants on the properties and difficulty in scale-up procedures.
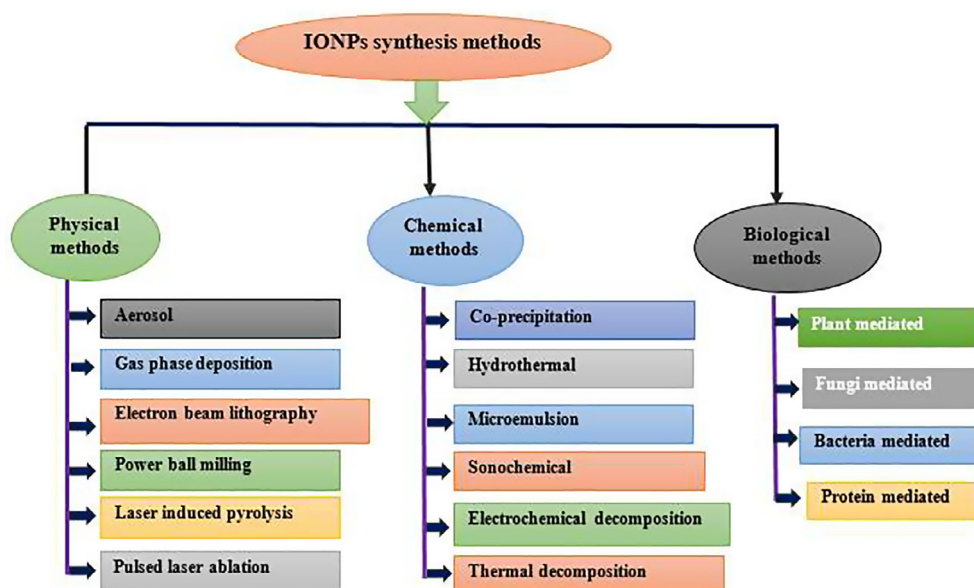
Fig. 2 The general synthesis methods of different iron-based nanoparticles modified from [47,56,57].

units, and then these units are transformed into appropriate nanoparticles [49]. Decomposition techniques including grinding, milling, and physical vapor deposition are examples of this method. Conversely, in the bottom-up approach, the opposite route is followed to synthesize suitable nanoparticles. Here nanoparticles are made from somewhat simpler matters or substances, hence this method is also named as a building up approach. Sol-gel, green synthesis, spinning, and biochemical synthesis, sedimentation and reduction techniques are examples of the bottom-up approach [4].

The most common synthesis methods of iron-based nanoparticles are co-precipitation, thermal decomposition, solvothermal synthesis, sol–gel and polyol methods, microemulsion, sonochemical method, microwave-assisted synthesis, electrochemical synthesis, biosynthesis and bioinspired synthesis, and other methods [50]. These and other common synthesis techniques are categorized into three classes and summarized in Fig. 2. Co-precipitation is the most universal method for producing iron oxide nanomaterials [51]. For typical co-precipitation synthesis methods, the pH of a Fe (II) or Fe (III) ion solution is increased through the addition of a base [47,52]. The phase and size of the particles depend on the concentration of cations, the presence of counter ions, and the pH of the solution [47]. Chemical co-precipitation has been engaged as a cheap and suitable method for producing Fe_3O_4 nanoparticles to be used as magnetic drug carriers [53].

The synthesis technique must be wisely nominated to ensure the control of shape, size, size distribution, and crystal behavior of the particles because of the magnetic properties dependency of iron oxide nanoparticles on composition and morphology [46]. The pollutant removal efficiency of synthesized nano-adsorbent depends on the specific surface area, shape, catalytic capability, surface charge, and the number of vacant/active sites for pollutants adsorption [48,23].

The size, shape, and composition of iron NPs synthesized through chemical methods depend on the type of salt used (as a precursor material), Fe(II) and Fe(II) ratio, pH, and ionic strength. Some other factors also influence the size of the NPs such as mixing rate, temperature, the inlet of nitrogen gas, agitation, and reactants ratio [47,54]. For example, The main species formed in basic conditions is FeO(OH), and this species upon thermal treatment may convert to different iron oxides [55]. Each method of preparation has its own influencing factor, advantages, and disadvantages. The major influencing factors and merits and demerits of some chemical methods are summarized in table 1.

In particular, several phases of iron oxy-hydroxide nanocrystallines were simply prepared from amorphous hydrous ferric or ferrous-oxide in thermal solution with a certain ethanol–water ratio and oleic acid by the phase-controlled transformation. Based on this method, goethite(α-FeOOH) nanorods in diameter of 3–4 nm, hematite(α-Fe_2O_3) nanocubes sized 20–30 nm, and magnetite (Fe_3O_4) nanoparticles in diameter of 6–7 nm were found [58]. Furthermore, the preparation of some iron oxy-hydroxides was studied during the hydrolysis of ferric nitrate with hydrazine monohydrate. Maghemite (γ-Fe_2O_3) was formed as the main product in the hydrolysis of a 0.05 M concentrated ferric nitrate solution and that of a lower concentration (0.005 M) resulted in α-FeOOH as the major product and at midway concentrations, γ-FeOOH or a

mixture of γ-FeOOH and α-FeOOH was resulted [59]. Preparation techniques for some specific iron-based nanoparticles are discussed in the following section.

2.1. Preparation of FeOOH

The FeOOH has around five polymorphs and the preparation methods, and discussions for each nanoparticle were conducted in the following section.

2.1.1. Preparation of goethite (α-FeOOH)

Goethite is one of the common polymorphs of iron oxyhydroxide and can be prepared using the chemical precipitation method. This method involves the reaction between a solution of iron precursor salt (nitrates, sulfates, etc.) and a basic solution (KOH, NaOH, etc.). For example, Rahimi et al. (2015) reported the preparations of goethite using Fe $(NO_3)_3·9H_2O$ in deionized water and by drop-wise addition of KOH solution under vigorous stirring followed by sonication for 30 min at room temperature and then placed in the oven for 70 min at 100 °C and centrifuged later [61]. The resultant solid was washed with refined water and acetone (CH_3-$COCH_3$) independently and allowed to dry at room temperature [61]. Guo et al. (2020) used a similar procedure as above to prepare α-FeOOH nanoparticle samples in an alkaline medium although they used different initial dosage values and operating equipment such as 70 °C reaction temperature instead of 100 °C and the product is freeze-dried instead of room temperature [62].

Solvothermal synthesis involves the use of any solvent under pressure (typically atmospheric and higher pressure) and temperature (commonly above solvent boiling point). If water is used as the solvent, the method is called the hydrothermal synthesis method. Zamiri et al. (2014) reported the synthesis of goethite (a-FeOOH) nanorods by the hydrothermal process with the aid of coordinating ligand, thiourea. In their preparation method, the proper amount of iron(III) chloride and thiourea ($SC(NH_2)_2$) was mixed with deionized (DI) water and maintained at 130 °C for 8 h in the autoclave, then the sample was cooled down gradually to room temperature. The dark precipitate was resulted and collected after filtration. The filtrate was washed and dried in an oven at 70 °C for 5 h [63]. In addition to the nanorods, they obtained fine needles with a diameter of (8.9–23.9 average) nm after doing the detailed characterization. In another finding, Rădiţoiu et al. (2012) reported the preparation of goethite (a-FeOOH) with controlled morphology by hydrothermal reaction at a temperature range of 145–155 °C from Fe(II) ions and an oxidant with the aid of a cationic surfactant [64]. In their process, cetyltrimethylammonium bromide (CTAB) was added and the clear solution was transferred into a Teflon lined stainless steel autoclave. Finally, they confirmed that the formation of a-FeOOH by X-ray diffraction (XRD), Mossbauer spectroscopy, FT-IR analysis, and visible diffuse reflectance spectroscopy.

2.1.2. Preparation of feroxyhyte (δ-FeOOH)

According to the method described by Nishida et al. (2016), δ-FeOOH nanoparticles were prepared by using the oxidation of precipitates obtained from the modified hydrazine reduction reaction of ferric chloride ($FeCl_2$) and hydrazine (N_2H_4) in

the presence of sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$) and gelatin in an alkaline condition. Initially, they started by dissolving $FeCl_2 \cdot 2H_2O$ (ferric chloride), $Na_2C_4H_4O_6 \cdot 2H_2O$ (sodium tartrate), and gelatin in water followed by pH adjustment, mixing, the addition of $N_2H_4 \cdot H_2O$ (hydrazine) solution, washing, and drying [65]. The obtained δ-FeOOH nanoparticles were subsequently characterized using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD), Mossbauer spectroscopy, and superconducting quantum interference device (SQUID).

Da Silva et al. (2017) reported the establishment of a simple co-precipitation method to prepare feroxyhyte (δ-FeOOH). It was synthesized by blending concentrated NaOH solution with a solution containing $Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$ After the formation of green rust precipitated materials, H_2O_2 was immediately added with vigorous stirring [66]. Based on their experiment, the precipitate turned from green rust to reddish-brown within a few seconds, indicating that the formation of δ-FeOOH nanoparticles.

2.1.3. Preparation of lepidocrocite (γ-FeOOH)

Lepidocrocite (γ-FeOOH) nanoparticles can be prepared using the procedure described by Sheydaei and Khataee (2015) [67]. Initially, ferric sulfate was dissolved in double-distilled water at 35 °C. Then, a CO_2-free airstream was bubbled continuously into the ferric sulfate solution, and a 3-butyl amine solution was dropping to the iron solution to adjust its pH. During the preparation, the solution color was reformed to dark greenish blue and finally to orange. The resulted orange suspension was allowed to reach room temperature and the filtration was done. Finally, the filtered particle was γ-FeOOH nanoparticles and washed and then desiccated in an air oven at 70 °C for a day [67]. Moreover, X-ray diffraction, transmittance electron microscope, scanning electron microscope, and nitrogen adsorption/desorption analysis approved that the synthesized γ-FeOOH nanoparticles were of an average width of 60–70 nm.

Lepidocrocite can be also prepared through the reaction of ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$), and sodium nitrate ($NaNO_3$) via a method described by Rahimi et al. (2015) [61]. Initially, an appropriate amount of $FeCl_2 \cdot 4H_2O$, $C_6H_{12}N_4$, and $NaNO_3$ was dissolved in distilled water. The $FeCl_2 \cdot 4H_2O$ and $C_6H_{12}N_4$ solutions were mixed immediately, under continuous stirring until a blue-green precipitate ($Fe(OH)_2$) was formed which was then titrated with $NaNO_2$ solution at 30 °C. One hour sonication was done for the resulted brick red color suspension at 55 °C. The obtained precipitate was washed and then dried at ambient temperature [61]. The prepared lepidocrocite was characterized and approved using DLS, FTIR, and SEM techniques to determine the size distribution and average particle size of nanoparticles.

2.2. Preparation of maghemite (γ-Fe$_2$O$_3$)

Analytical grade (AR) ferric ammonium citrate (Fe content 20.5–22.5%), 30% H_2O_2, and Methyl orange are common raw materials for the synthesis of mesoporous magnetic Fe_2O_3 nano-samples by thermal decomposition of ferric ammonium citrate in air. Wang et al. (2017) reported the fol-

lowing procedure uses for γ-Fe$_2$O$_3$ synthesis via pyrolysis method without any templates or surfactants [68]. First, a certain amount of ferric ammonium citrate was crushed to less than 100 mesh sieve and put into a muffle furnace, heated to a temperature of 300 °C at a heating rate of 10 °C/min and kept for 5 h under air atmosphere, then cooled down to room temperature [68]. The resulted product was characterized by XRD, N_2 adsorption–desorption, SEM, TEM, and VSM, and the synthesized γ-Fe$_2$O$_3$ product was confirmed. Besides this finding, further increments of temperature such as at 400 °C, a mixture of hematite and maghemite nanoparticle appeared, and at 550 °C pure hematite nanoparticle was obtained.

Ianoş et al. (2018) followed similar steps using iron nitrate (Fe (NO_3)$_3 \cdot 9H_2O$), triethylenetetramine ($C_6H_{18}N_4$), and warm distilled water as a starting material at 60 °C followed by stirring the mixture and heating at its maximum temperature of approximately 450 °C for 30 min [69]. The obtained nanomaterials were hand-grounded, washed with distilled water, and allowed to dry for 12 h at 60 °C. The formation of maghemite nanoparticles was confirmed by XRD, SEM, and FT-IR analysis.

Zhang et al. (2020) also reported the preparation of γ-Fe$_2$O$_3$-ZnO-biochar nanocomposites in trimethylene glycol using a thermal decomposition method with N_2 gas protection to avoid a high-temperature treatment process [70]. Triethylene glycol and biochar were put into a three-neck flask (100 mL), which was wrapped and sonicated for 10 min to ensure effective mixing. After that, Fe(III) 2,4-pentanedionate, and Zn(II) acetylacetonate were instantly added into the mixture under vigorous stirring. The mixture was heated to 120 °C, then degassing, and purging with N_2 gas was conducted three times. The collected nanocomposite was washed and dried in a vacuum [70]. This preparation witnessed the need for modification of maghemite nanoparticles for effective contaminant removal; in this case, the removal performance of Rhodamine B (RhB) dye was evaluated.

Preparation of maghemite (γ-Fe$_2$O$_3$) nanoparticle by chemical precipitation method, involves ferric chloride ($FeCl_3$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), hydrochloric acid (HCl), ammonium hydroxide (NH_4OH), deionized water, and ethanol (CH_3CH_2OH) [71]. First, $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ were dissolved in de-ionized water to form a solution with either $FeCl_3$ or $FeCl_2 \cdot 4H_2O$ and the dissolution was magnetically agitated. After obtaining the homogenous solution, the $NH_3 \cdot H_2O$ solution was added drop-wise to the solution and allowed to settle for 10 min until the final pH becomes 8.3. The obtained solution was allowed to cool to room temperature. The brown precipitate was collected through filtration and then washed. Lastly, the obtained precipitate was dried at room temperature [71,72]. The obtained maghemite (γ-Fe$_2$O$_3$) nanoparticle had recorded their mean particle size of 9 nm.

2.3. Preparation of hematite (α-Fe$_2$O$_3$)

Abdelrahman et al. (2019) reported the preparation of hematite (a-Fe$_2$O$_3$) nanoparticles with different crystallite sizes range from 40 to 59 nm by insecticide cans obtained from Egypt via the combustion method [73]. The organic fuels used for combustion were urea, glycine, L-alanine, and L-valine.

Moreover, the hematite can be prepared with the stepwise oxidative transformation of magnetite and/or goethite. For example, the hematite was produced from the wasted iron-based sludge (containing iron oxyhydroxide) at 500 ^{0}C that has been confirmed by the phase of crystalline [74].

The hematite nanoparticles can also be prepared by the precipitation method proposed by Dehbi et al. (2020) [75]. Ferric nitrate nonahydrate (Fe(NO$_3$)$_3$9 H$_2$O) and NH$_4$OH were used as the starting materials. The concentrated ammonium hydroxide (NH$_4$OH) is added dropwise to an aqueous solution of the iron (III) nitrate nonahydrate as shown in step-wise reaction (1) and reaction. In this step, the crystal tends toward a state of greater stability by increasing its size. The growth stops when the balance is reached. The resultant precipitate was collected after centrifugation and washed with DI water several times after filtration. Lastly, the precipitate was dried overnight in a vacuum oven. This synthesis method allows forming an intermediate product (Reaction (3)), which is then calcined under air at 500 °C for 3 h to obtain the hematite (Reaction (4)). The following reactions were suggested to synthesize hematite nanoparticles from ferric nitrate nonahydrate and ammonium hydroxide.

$$\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 3\text{NO}_3^- \qquad \text{(Reaction 1)}$$

$$\begin{aligned}\text{Fe}^{3+} &+ 3\text{NO}_3^- + 3\text{NH}_4\text{OH} \\ &\rightarrow \text{Fe(OH)}_3 + 3\text{NH}_4\text{NO}_3 \qquad \text{(Reaction 2)}\end{aligned}$$

$$\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \qquad \text{(Reaction 3)}$$

$$2\text{FeOOH} \rightarrow \alpha\_\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \qquad \text{(Reaction 4)}$$
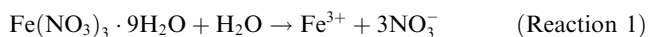
Raw materials such as; Poly (vinylpyrrolidone) (PVP), deionized water, FeCl$_3$·6H$_2$O, NaAc, ethanol, and various equipment and materials were used to synthesize hematite nanoparticles by the hydrothermal method [76]. Factors affecting the possible formation mechanism of α-Fe$_2$O$_3$ including the concentration of the precursor, precipitation agent, stabilizing agent, and reaction time were systematically investigated in their work. Lin et al. (2014) also reported using the hydrothermal process to synthesize octadecahedral α-Fe$_2$O$_3$ nanoparticles [77]. After the reaction, the precipitate was collected and washed with ethanol and deionized water. The final α-Fe$_2$O$_3$ powder was obtained after drying the precipitate in a vacuum oven overnight. Ma et al. (2010) followed a similar procedure to prepare α-Fe$_2$O$_3$ by hydrothermal method except doing some changes (reagents, solvent amounts, and materials). For example, the reaction time of 24 hr was allowed to heat the sample, and FeCl$_3$·6H$_2$O was first directly dissolved in 15 mL of ammonia-water followed by stirring [78]. The remaining procedures were similar to the procedure described by Lin et al. (2014). Moreover, Tadic et al. (2014) also reported the synthesis of α-Fe$_2$O$_3$ by hydrothermal method with the above similar procedures described [79]. Here NaOH, ethanol, oleic acid, and Fe sulfate heptahydrate Fe$_2$(SO$_4$)$_3$·7H$_2$O were utilized for the preparation. And the solution was mixed by electromagnetic stirring for 6 h. The characterization of the crystal structure of the sample was done by X-ray diffractometer radiation and the size, morphology, and microstructure were analyzed by TEM (transmission electron microscopy). Magnetic measurements were performed on a commercial Quantum Design MPMS-XL-5 SQUID-based magnetometer.

2.4. Preparation of magnetite (Fe$_3$O$_4$)

Magnetite nanoparticle is very known nano-adsorbent. Its foremost physiochemical properties, cheap strategy, and easy recovery within the sight of outside attractive fields make it a commonly prepared material for water treatment [80]. Radwan et al. (2019) employed the co-precipitation technique to prepare Fe$_3$O$_4$ nanoparticles by using. FeCl$_3$ .6H$_2$ O and FeCl$_2$·4H$_2$O salts as a starting material. The possible reaction in this process is shown as follows:

$$2Fe^{3+} + Fe^{2+} + 4OH^- \rightarrow Fe_3O_4 + 4H^+$$

Initially, a mixture containing both FeCl$_3$ and FeCl$_2$ was added to distilled water. Then this mixture of FeCl$_2$·4H$_2$O and FeCl$_3$·6H$_2$O mixed into one solution, and a 1.5 M NaOH was added to the solution dropwise with vigorous stirring and mechanical agitation at a rate of 0.5 mL per second. After that, a dark-black precipitate resulted immediately. The solution was decanted and then the obtained Fe$_3$O$_4$ sample was washed with distilled water several times and then washed with acetone and drying operation was done in a furnace for five hours at 80 °C [81]. After drying, the sample size was reduced to the smallest possible particle size and appropriate characterization confirmed the formation of magnetite nanoparticles.

Wu et al. (2011) also proposed the preparation of Fe$_3$O$_4$ nanoparticles with a diagram via the co-precipitation method as summarized by Fig. 3 using ferrous sulfate hexahydrate as a starting material. First Fe(OH)$_3$ precipitate was rinsed with deionized water several times and then Fe(OH)$_3$ precipitate dissolved with hydrochloric acid to obtain FeCl$_3$ solution. The Fe^{3+} and Fe^{2+} molar ratio in the FeCl$_3$ solution was adjusted to 1.5:1 by adding a measured amount of FeSO$_4$·7H$_2$O Sodium hydroxide (NaOH) was added under ultrasonic agitation and the black precipitate was produced consequently [82], with the principle reaction as follow: $2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$
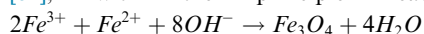
The resulting Fe$_3$O$_4$ precipitate was heated at 65 °C for a half-hour in an ultrasonic water bath. The prepared Fe$_3$O$_4$ samples were rinsed repeatedly with water (deionized) and ethanol to purify the particle. The particles were then dried at 74 °C in a vacuum. Finally, product characterization was done with XRD, field-emission scanning electron microscope (FE-SEM), and vibrating sample magnetometer (VSM) [82,84]. As a result, 15 nm in diameter-sized Fe$_3$O$_4$ particle was obtained that revealed super-paramagnetic performance, and C$_{12}$H$_{25}$OSO$_3$Na was added as a surface-active mediator, supporting to obtain Fe$_3$O$_4$ nanoparticles with uniform size and shape distribution [83]. Moreover, the co-precipitation method was used to synthesize Fe$_3$O$_4$ and gelatin composite similarly [85]. The major factor that determines the size and shape of synthesized Fe$_3$O$_4$ nanoparticles through the co-precipitation method depends on the type of salt used and the Fe(II) and Fe(III) ratio. Some other factors also influence such as pH, and ionic strength, mixing rate, temperature, the inlet of nitrogen gas, and agitation.
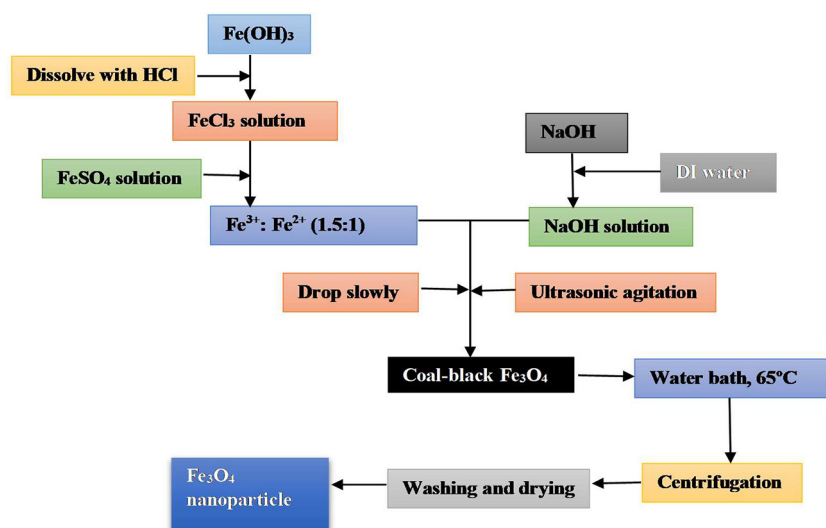
Fig. 3 Preparation scheme of magnetite (Fe₃O₄) nanoparticle via co-precipitation method. Redrawn with modification from [83]..

Chang and Shih (2018) introduced a procedure to synthesis magnetite, hematite, and maghemite with a similar route and they stated the conditions that happened in the transformation from one phase to another phase as shown in Fig. 4. Reagent grade ferrous chloride tetrahydrate (98%), propylene oxide (99%), and absolute ethanol were used as raw materials.

The synthesis procedure followed different steps with the treatment conditions described. First, $FeCl_2 \cdot H_2O$ was mixed with ethanol in a round-bottomed flask that produced an ethanolic solution. Thereafter, the propylene oxide was poured into this ethanoic solution, which was then heated to 78 °C (the boiling point of the solution) on an electric jacket under vigorous stirring by agitating mechanically until the color changed from clear to dark brown. The nucleation of Fe_3O_4 in the solution was observed because of a gray opaque sol formation after

the solution heated for half-hour. The Fe_3O_4 nanoparticle was purified with centrifugation at the predetermined revolution per minute and subjected to vacuum drying. The Hematite (α-Fe_2O_3) nanoparticle can be oxidatively transformed with a drying of the paste-like wet gel of Fe_3O_4 (evaporation of Fe_3O_4 solution) at 150 °C in an atmosphere controlled oven. Maghemite (γ-Fe_2O_3) nanoparticles were produced by the drying of the sol at 100 °C and further heat-treatment of the obtained xerogel at 150 °C in the air [86,87].

2.5. Preparation of Iron(III) oxide-hydroxide (Fe(OH)₃)

Zelmanov and Semiat (2013) used a sol–gel method to prepare Iron(III) oxide-hydroxide (Fe(OH)₃) nanoparticle adsorbents from an aqueous solution of ferric salt [FeCl₃·6H₂O, Fe
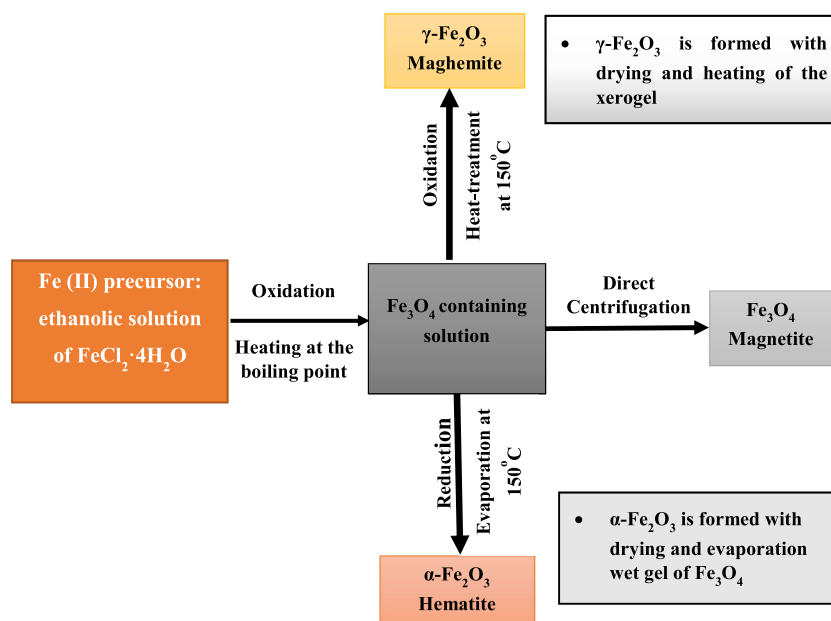
Fig. 4 Processing steps of Fe_3O_4, α-Fe_2O_3, and γ-Fe_2O_3 nanoparticle preparation with the same starting material. Redrawn with modification from [86].

(NO$_3$)$_3$·9H$_2$O], followed by adjusting the pH to 8 value [88]. Synthesized nanoparticles were rinsed with distilled water to obtain pure and neutral products. Subsequently, the wet precipitate was gel-dried or freeze-dried by vacuum. In their study, iron oxide-hydroxide nanoparticle sol was obtained by hydrolysis and pH changes. The preliminary material used for preparing Fe(OH)$_3$ nanoparticles were analytical grade iron chloride hexahydrate (FeCl$_3$·6H$_2$O). A 10% sol iron nano-sorbent was prepared via hydrolysis with an initial pH of 0.8. The possible reaction that shows the preparation is:

$$FeCl_3.6H_2O(in\ water) \rightarrow nano\ Fe(OH)_3 + H_2O + 3H^+ + 3Cl^-$$
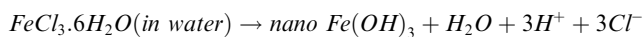
The main product of the above reaction is Fe(OH)$_3$ nanoparticle, with the hydrolysis of the iron salt resulted in an acidic pH in the solution. Characterization techniques were employed for the confirmation of nanoparticle formation.

2.6. Plant-mediated preparations of iron-based nanoparticles

Plant-mediated preparation of iron nanoparticles has perceived progressive attention due to its cost-effective and eco-friendly nature [89,90]. The biosynthesis technique of iron nanoparticles is based on the metabolites produced during bioprocesses, such as carbohydrates, glycosides, alkaloids, flavonoids, saponins, phenols, proteins, quinine, steroids, and tannin. These metabolites are used as reducers in the route of nanoparticle preparation hence, substituting hazardous chemicals known with other synthesis techniques, chemical, and physical methods [91]. Furthermore, the biosynthesis method of nanoparticles has helped to a great extent to reduce some limitations, such as high energy and space requirement as well as high cost and hazard associated with various known physio-chemical methods [92].

The green preparation of iron-based nanoparticles has been attained using eco-friendly plant extract. It was analyzed that the leaf extract of *Camellia sinensis* can reduce iron ions into iron nanoparticles at room temperature [93] and it was synthesized with particle size 10–30 nm by a green approach using tannic acid as a reducing and capping agent. Furthermore, the prepared nanomaterials were also assessed for their antifungal activity [12]. Plant-mediated preparation of iron nanoparticles has substantial advantages over the traditional physical and chemical preparation techniques although it has significant limitations, especially controlling the shape, uniformity, and monodispersity. These difficulties can be eliminated by optimization studies and controlled reactions [94,90,95].

Different researchers had been synthesized verities of iron-based nanoparticles using specific materials. For example, *Ficus carica* known as common fig dried fruit extract was adopted to produce iron oxide nanomaterials [96] but the specific type of iron-based nanoparticles was not yet mentioned. Additionally, iron-based nanoparticles (IONPs) were synthesized via this method using marine algae species, *Enteromorpha spp.* extract as a biological reductant agent. Consequently, the synthesized IONPs were utilized as an adsorbent for Cu(II) removal from aqueous solutions. To examine the optimum adsorption conditions batch experiments were done and the equilibrium, kinetics, and mass transfer modeling were also estimated. The maximum monolayer coverage capacity of IONPs for Cu(II) adsorption of 188.68 mg/g at an optimum temperature value of 35 °C was obtained [24]. Both, Fe$_3$O$_4$

and γ-Fe$_2$O$_3$ nanoparticles were produced using iron salts and NaOH as precipitation agents, and Aloe Vera as a stabilizing agent. The produced nanoparticles showed that the prepared iron oxide nanoparticles have a narrow size distribution near100 nm. After applying it to the wastewater sample, approximately 70% of mercury removal was established by atomic absorption spectroscopy measurements [97]. Shuai et al. (2019) studied the structural effects of hematite (α-Fe$_2$O$_3$), 2-line ferrihydrite (HFO), and goethite (α-FeOOH) on diethyl phthalate ester (DEP) degradation. Their result showed that in the presence of goethite, faster degradation of DEP was achieved under 365 nm light irradiation than in the dark. The kinetic rate of DEP degradation showed ferrihydrite(HFO) greater than goethite, and goethite equal to hematite in the dark light, and HFO greater than hematite and goethite, and also hematite greater than goethite under 365 nm light irradiation [98].

Nnadozie and Ajibade (2020) prepared a magnetite nanoparticle using an extract from the root of *Chromolaena odorata* by the facile and green biosynthetic method. The particle size within the range of 5.6–16.8 nm was obtained. Basification of the plant root extract inhibited the co-precipitation of other cations in solution; encouraging the formation of water-dispersible hydrophilic nanoparticles [99].

A novel iron nanoparticle was effectively prepared by a simplistic and green approach using the *Mediterranean cypress (Cupressus sempervirens)* aqueous extract. The synthesized nanomaterial also showed great potential for dye removal from waste aqueous solution in a time-dependent manner [100]. Decolorization efficiency of 95% was achieved for methyl orange removal with a contact time of 6 h. In other research, Iron-based nanoparticles were prepared using green tea leaves extracts. Mainly iron oxide and iron oxyhydroxide were obtained after characterization using XRD, TEM, SEM, XPS, and FTIR techniques. The fabricated nanoparticles were then used for methyl orange (MO) and methylene blue (MB) dyes removal. The results showed that the kinetic data of methylene blue removal followed a second-order rate, while those of methyl orange removal followed a first-order rate [101]. Moreover, about 90% of color and 89% of COD were removed when the textile dye effluent was treated with 0.5 g of nanoparticles. The removal might have been attained by the adsorption followed by the flocculation process. Magnetic iron-based nanoparticles might be recovered from the treated sample using an external magnetic force and can be reused for other treatment purposes [102].

The exploitation of iron-based nanoparticles in various fields has been reported. Some of the fields are wastewater treatment [103,56], anti-bacterial drugs [104], numerous marketable and home applications, which include medicines, energy-based investigation, and environmental studies [4,105], and Table 2 summarized the synthesis methods and application areas of various IONPs.

2.7. The need for modification of iron-based nanoparticles

Some of the iron-based nanoparticles have an extensive magnetic property and can be modified or functionalized with various functional groups so that researchers came up with the modification of iron-based nanomaterials by incorporation of supporting materials like Graphene [118] and different func-

Table 2 Synthesis methods of different iron-based nanoparticles with their corresponding potential uses.

Types of Nanoparticles	Method of preparation	Size (nm)	Uses	Reference
FeOOH	simple hydrolysis method	40–50	a biomedical field for magnetic resonance imaging (MRI)	[106]
L-Cystine functionalized δ-FeOOH	precipitation of an Fe^{2+} solution	14	Hg(II) removal	[107]
α-FeOOH	electrochemical method	5–10	photo-Fenton-like degradation of 2-chlorophenol (2-CP)	[108]
Fe_3O_4	co-precipitation	5.6–16.8	Cation reduction in the solution	[99]
		50	dye removal (reactive Red F3B))	[102]
		130	arsenic removal	[109]
	Using leaf extract of Azadirachta indica	25	heavy metals removal and also as potent contrasting agents in X-ray imaging	[110]
chitosan-coated Fe_3O_4	co-precipitation		wastewater treatment (Cu ion removal)	[81]
γ-Fe_2O_3	co-precipitation	4–17	removal of Cr(VI)	[111]
		11.5	BTEX (benzene, toluene, ethylbenzene, and xylene) removal from produced water	[112]
	pyrolysis method	3.1	photocatalytic activities for dye removal	[68]
α-Fe_2O_3	Sol-Gel	11.55	reduction of Cadmium (II)	[113]
	modified sol–gel	13	removal of toxic heavy metal ion, Cr^{6+} from water	[114]
	pyrolysis method	2.7	photocatalytic activities for dye removal	[68]
	combustion method using Egyptian insecticide cans	40–59	methylene blue (MB) and Crystal violet (CV) removal	[73]
	green synthesis using pomegranate (Punica granatum) seeds extract	25–55	degradation of dyes (reactive blue)	[115]
$Fe(OH)_3$	injection method		Removal of dyes and heavy metal ions.	[116]
$Fe(OH)_3$@Cellulose Hollow Nanofibers	electrospinning	143	Water Purifications	[117]

tional groups [23] used as capping or stabilizing agents [55] such as; phosphonic acids, carboxylic acid, dopamine, cysteine, trimethoxy silane, and amine [56]. Typically, magnetic nanomaterials are coated with organic layers (polymers or surfactants such as polyethylene glycol and dextran) or inorganic elements (gold, platinum, cobalt oxide, aluminum oxide silica, activated carbon, and others) to make them stable against aggregation, oxidation, and corrosion [48], and to increase the adsorption capacity [119]. For example, iron-coated sand (Fe-sand) can remove between 1.10 and 1.34 mg/g Se(IV) and between 1.026 and 1.10 mg/g Se(VI), which was more effective than uncoated Fe nanoparticles [120]. Moreover, the surface modification of iron oxide, oxy-hydroxide, and hydroxide nanoparticles helps to develop biocompatibility, colloidal stability in complex biological environments, and in vivo performance when the modification is done with polymers [46]. The modification of these nanoparticles(nanoadsorbents) shows high attraction to take-away different pollutants such as Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), and As(III) at once from wastewater [20]. Typically, synthesized goethite nanorods and magnetite nanoparticles proved the removal of As (III), with 5.8 and 54 times higher than the micron-sized relatives respectively after modification [58].

Factors such as the pH of the nanoparticles, the temperature of adsorption, adsorbent dose, and incubation time affect the adsorption of different heavy metals on iron-based

nanoparticles [20]. So, effective analysis of these factors should be done before and after modification. Fe_3O_4 combined with other materials can create a good adsorption capacity [121], for example, when Fe_3O_4 is combined with Polyaniline it creates Polyaniline/Fe_3O_4 Nanocomposite, and have a chromium removal capacity of 51.2% [122]. Generally, surface modification or addition of functional groups of iron-based nanoparticles has helped in the synthesis of easily reusable magnetic nanoparticles, nano-sorbents, and nanocatalysts [90].

3. Applications of iron-based nanoparticles in wastewater treatment

Iron-based nanoparticles (IONPs) have shown tremendous applications in multidisciplinary areas. For example, it is used as a catalyst material, as an adsorbent in water and wastewater treatment, as a pigment in the manufacturing industry. Moreover, they are essential raw materials for coatings, gas sensors, ion exchangers, magnetic recording devices, magnetic data storage devices, magnetic resonance imaging, bio-separation, and medicinal applications [123]. At present, the research has been dedicated to the sustainable remediation methodology for waste reclamation and environmental remediation [30,124,23]. Recently, the synthesis and utilization of iron-based nanomaterials having new properties and functions have been widely studied, due to their size in nano-range, high

surface area to volume ratios, and superparamagnetism[56,47]. IONPs have exclusive physicochemical properties, which make them unique among nanoparticles. Hence, many experiments have been done to develop superficial synthesis methods for these particles and to make them biocompatible and nano-adsorbents [125]. Due to the growing need for various field applications, aspects related to its environmental stability, mobility, long-term fate, and toxicological impact have received tremendous attention [126].

Contaminants present in water and wastewater can be generally categorized into three classes: pathogenic microorganisms, toxic organics, and inorganics [44]. The wastewater generated from different sources contains many strong pollutants. For example, The non-biodegradable dye from the textile, paint, and leather industries is the most pollutant of the environment [127,128,102]. Heavy metals are allowed to flow with wastewater from various industries. They can be toxic or carcinogenic and can cause severe problems for humans and aquatic ecosystems [129]. Hence there is a need for effective treatment of such contaminants. Industrial wastewater treatment and industrial water pollution control are currently on the track of huge comprehension and deep scientific vision [130]. To overcome the environmental threats different nano-materials are employed nowadays. Among them iron-based nanoparticles with several forms are mentioned, typically, iron oxides (magnetite, hematite, and maghemite), iron ox-hydroxides such as goethite (α-FeOOH), akaganeite (β-FeOOH), and lepidocrocite (γ-FeOOH) are being assessed for their usage in wastewater treatment for the removal of toxic metal ions [123]. Nanoscale zerovalent iron (nZVI) is also one of the broadly applied nanomaterial in groundwater hazardous waste treatment [126,56,131].

3.1. Types of iron-based nanoparticles

Iron oxides are a combined term for oxides, hydroxides and oxy-hydroxides made up of Fe(II) and/or Fe(III) cations and O^{2-} and/or OH^- anions. Currently, sixteen pure phases of iron oxides are acknowledged as shown in Fig. 5. These are Fe

$(OH)_3$, $Fe(OH)_2$, $Fe_5HO_8 \cdot 4H_2O$, Fe_3O_4, FeO, five polymorphs of FeOOH, and four of Fe_2O_3 [132,133]. Magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (a-Fe_2O_3) are the most known oxide forms of Iron [23,59]. Researches on the ZVI oxidation or aging have so far acknowledged several products, including goethite (α-FeOOH), akaganeite (β- FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), green rusts I/II (a group of bluish-green Fe(II)–Fe (III) hydroxyl salts), siderite ($FeCO_3$), and iron sulfide, etc. [126]. In addition to the above oxyhydroxide forms feroxyhyte (δ-FeOOH), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$ approx.), or $5Fe_2O_3$-$\cdot 9H_2O$, better recast as $FeOOH \cdot 0.4H_2O$, and high-pressure FeOOH is another oxide/hydroxide forms of iron oxides [133].

Iron oxide nano adsorbents such as hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) have been widely utilized by researchers for removal of various pollutants such as As(V), Cr(VI), $Cr_2O_7^{2-}$, MnO_4^-, Cu(II), Pb(II), and Hg(II) from environmental or industrial effluents [134]. The most common iron-based nano adsorbents in wastewater remediation will be reviewed in the following sections.

3.1.1. Zero-valent iron (ZVI) nanoparticle

Zero-valent iron (ZVI) nanoparticle is one of the most commonly employed metallic reducing agents for the treatment of toxic pollutants from wastewater [135,136] and for remediation of contaminated land and groundwater [137]. On-going studies indicated that nanoscale zero-valent iron (nZVI) is powerful for enriching several metal ions from the wastewater while fulfilling waste-treatment requirements [30]. ZVI nanoparticles are prepared under laboratory conditions and tested for their effectiveness for the removal of hexavalent chromium (Cr(VI)) from aqueous solutions and compared with the commercial-grade ZVI nanoparticles. The results confirmed that the synthesized ZVI nanoparticles reduced greater than 99% of Cr(VI) at the dosage rate of 0.2% (w/v), while commercial ZVI nanoparticles resulted in 59.6% removal of Cr(VI) at the same dosage [138]. In other research, batch-based experiment studies were conducted to analyze the quantitative removal of Co(II), Cr(VI), Cu(II), and Ni
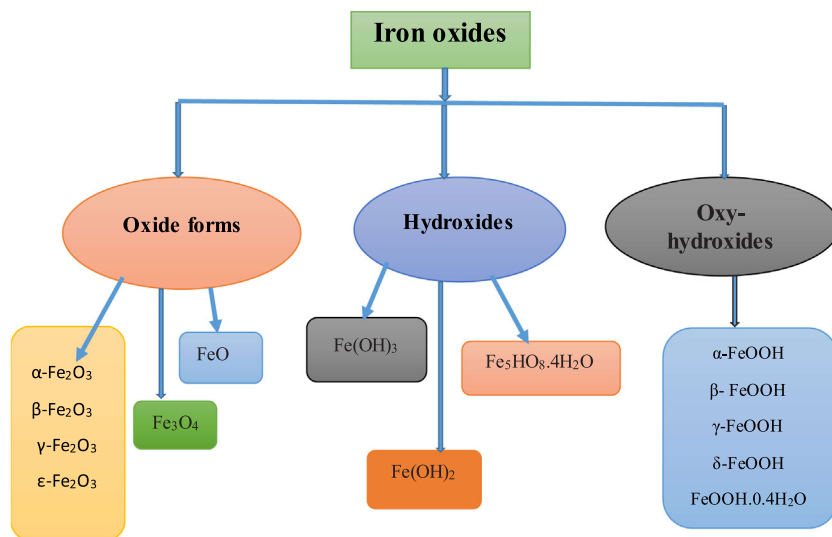

Fig. 5 The basic forms of iron-based nanoparticles: oxides, hydroxides, and ox-hydroxides.

Table 3 Some of the pollutants removed by zero-valent iron nanoparticle and their removal mechanisms with some parameters capacity.

Iron nanoparticle type	Removed pollutant	Opt. pH	Removal Mechanisms	Kinetic models	Contact time (min)	Removal capacity		Reference
						(%)	mg/g	
ZeroValent Iron	Dye (textile)		Adsorption			90	–	[102]
	dye(reactive red198)	4	Adsorption		40	91	–	[128]
	As(V)		Adsorption			99		[146]
	Cr(VI)	3	Reduction	2/3-order		47		[140]
	NO_3^-	6.5–8.0		Zero-order		66.9–85.2	–	[147]
		2–4			180	95		[145]
	[PO4]-P	4.5	Adsorption		30	> 95		[148]
	Cu(II)	> 7	Chemical reduction			99.8		
	Zn(II)	> 7	Adsorption			92.4		
Zerovalent-graphene (GO)	Cd(II)		co-precipitation and reduction		50		425.72	[149]

(II) after 30-minute treatment with a fixed amount of ZVI nanoparticle in acid conditions. In this report, the process of adsorption was highly dependent on pH, which enables the nanoparticles to remove effectively these metals in an aqueous solution. The maximum removal efficiency of more than 95%) for Cu(II) and Cr(VI) was obtained around pH ranges of 2–2.5 approximately with a contact time of 30 min [139]. Mitra et al. (2011) also studied the reduction of chromium ion (Cr(VI)) in waste aqueous solution by zero-valent iron in the form of a thin plate over a pH range of 3–5.5. The rate of removal of Cr(VI) drops sharply at a longer time indicating passivation of the surface. As indicated in table 2, the reduction reaction follows 2/3-order kinetics for the Cr(VI) concentration, and the passivation reaction is linear in the Cr(VI) concentration [140]. Furthermore, the ZVI nanoparticle can achieve fast and simultaneous elimination of various heavy metal ions.

Batch experiments showed that ZVI nanoparticles can perform simultaneous removal of various heavy metals and arsenic. More than 99.5% of Arsenic, Copper, and many other toxic ions were attained with more than 12 months of operation [141]. In general, the zero-valent iron nanoparticle is the best nanomaterial for treating wastewater containing heavy metals and reported a systematic approach using it for wastewater treatment.

Li et al. (2014) performed a preliminary test for treating smelting wastewater by zerovalent iron (ZVI) nanoparticles. Their procedure comprised of two consecutive treatment units; each had a ZVI nanoparticle reactor, a clarifier, and a ZVI nanoparticle recirculation pump. Then, ZVI nanoparticle was added and mixed with the waste sample in the reactor, allowed to settle in the clarifier, and reverted by the recirculation pump. The removal efficiency of arsenic was more than

Table 4 Some basic pollutants removed by iron hydroxide nanoparticles and their process phenomenon.

Iron hydroxide nanoparticle	Removed pollutant	Opt pH	Mechanism	Isotherm model	Kinetic model	Con. Time	Removal capacity		Reference
							(%)	mg/g	
$Fe(OH)_3$	As (III) and As (V)	4–9	Adsorption	Dubinnin-Radushkevich		240			[152]
	Congo Red (CR	6.6	Adsorption		pseudo- 2nd order			308	[116]
	Cr(VI)		Adsorption	Langmuir				52.94	
	Pb(II)		Adsorption	Langmuir				75.64	
clinoptilolite-supported iron hydroxide $(Fe(OH)_3/Cp)$	PO_4^{3-}	2			pseudo-2nd order	480	93		[153]
	NO_3^-	2			pseudo-1st order		81		
$Fe(OH)_3$@Cellulose	Congo Red	6	Adsorption	Langmuir isotherm	pseudo-2nd order			689.65	[154]

99.9% and the average removal capacity was recorded as 239 mg/g. The removal capacity of ZVI nanoparticles was obtained to be 226 and 245 mg/g of Fe for Cu(II) and As(V) ions respectively. All metal ions, such as Cu, Zn, and Ni, were reduced to less than 0.1 mg/l simultaneously [142].

Zero-valent iron nanoparticle was also examined in deactivating the particular bacteria namely; gram-positive *Bacillus subtilis* var. *niger* and gram-negative *Pseudomonas Fluorescens*, and the fungus namely; *Aspergillus Versicolor*. Initially, the ZVI nanoparticle was prepared using $Fe(NO_3)_3 \cdot 9H_2O$ and $NaBH_4$ with a fairly uniform size of about 20–30 nm [143].

The degradation of crystal violet (CV) dye in waste aqueous solution was studied using kaolin-supported zero-valent iron nanomaterial (K-ZVI). It was obtained that K-ZVI with an equal ratio of kaolin and zero-valent iron nanoparticles was most successful in removing crystal violet. Batch experiments confirmed more than 97.29% crystal violet was reduced using K-ZVI, where the solution sample contained 100 mg/l crystal violet at a pH of 6.5 [144].

Zero-valent iron nanoparticle has also been used for the removal of nitrate in the water. Ahmadi et al. (2011) aimed at subjecting the reduction of nitrate by iron nanoparticles produced via a physical method. The average diameter of 25 nm ZVI nanopowder that is characterized by the large specific surface area (40–60 m^2g^{-1}) reduced about 95% of nitrate within a period of 3 h in the controlled pH between 2 and 4 as shown in Table 3 [145].

Generally, the potential use of zero-valent iron (ZVI) nanoparticles for the treatment of toxic metal ions, organic dyes, and phosphates, and nitrates from wastewater mainly by adsorption mechanisms, photocatalytic degradation, and reduction-precipitation (if the nanoparticles contain core iron enveloped with the oxides of iron) depending upon the reduction potentials and extraction conditions [55].

3.1.2. Iron hydroxide ($Fe(OH)_3$) nanoparticle

Excellent adsorption stability, recyclability, and Fenton-like catalytic properties of $Fe(OH)_3$ nanomaterial made it successful in water treatment technologies. A green yet low-cost injection method was employed to synthesize three-dimensional flowerlike $Fe(OH)_3$ nanomaterial to take away organic dyes and toxic metal ions [116]. The adsorption kinetics of Congo Red (CR) on $Fe(OH)_3$ microspheres conformed to the pseudo-second-order model. Cr(VI) and Pb(II) adsorption behaviors on $Fe(OH)_3$ microspheres fitted the Langmuir isotherm model. As shown in Table 4, the adsorption capacities of the prepared $Fe(OH)_3$ microsphere were 308, 52.94, and 75.64 mg/g for CR, Cr(VI), and Pb(II) respectively. In parallel, $Fe(OH)_3$ nanoparticles can selectively remove neutral dyes from wastewater with much higher capacities than those of conventional a-FeOOH and a-Fe_2O_3 nanoparticles when used as adsorbents, indicating a great potential for utilizing in wastewater treatment [150]. Its motivating behavior for wastewater treatment is due to insufficient bioavailability from such particles when compared with ferrous salts [151].

Zhang et al. (2019) [155] studied the removal of arsenic from wastewater by the oxidation of $FeSO_4$ with $CaCO_3$ in air and the mechanisms of removal were suggested. Oxidation of Fe(II) into $Fe(OH)_3$ was done with the assistance of $CaCO_3$. The hydrolyzed OH^- obtained from $CaCO_3$ changed the conversion route of Fe(II) ion to $Fe(OH)_3$ nanoparticle. Freshly generated $Fe(OH)_3$ showed high activity (99.93% removal) for the removal of arsenic, with a molar ratio of 2 of Fe/As [155].

Table 5 The basic pollutants removed by iron oxy-hydroxide nanoparticles with their process phenomenon.

Iron ox-hydroxide	Removed pollutant	Opt.pH	Mechanisms	Isotherm model	Cont.time	Removal capacity (%)	mg/g	Reference
FeOOH	As(V)		Adsorption	—	–	–	8.67–9.43	[158]
	As(III)	9	Adsorption	——	—	–	5.21–5.65	[158]
	Cr(VI)	< 3	Photoreduction	———	—	70	–	[157]
	F⁻	4	Adsorption	Langmuir and Freundlich/2nd order	–	90	–	[15]
α-FeOOH	Pb(II)		Adsorption	Langmuir/ pseudo 2nd order	45		15.11	[159]
	Cd(II)	7	Adsorption	Langmuir/ pseudo-2nd order			167	[160]
feroxyhyte (δ-FeOOH)	PO_4^{3-}	acidic	Adsorption & precipitation	Freundlich /pseudo-2nd order		94.1	–	[161]
	Rhodamine B (RhB) dye	6.6–8.4	Photocatalytic oxidation	–	60	59	—	[66]
L-Cystine functionalized δ-FeOOH (Cys- δ-FeOOH)	Hg(II)	7	Adsorption	Pseudo 2nd order	–	–	217	[107]
Co_3O_4/δ-FeOOH	Lomefloxacin (LMO)	6.08	Degradation	–	–	> 82	–	[162]

Clinoptilolite-supported iron hydroxide nanoparticles (Fe (OH)₃/Cp NPs) can effectively be used for simultaneous removal of NO_3^- and PO_4^{3-} from water resources. Remediation was investigated in a range of initial concentrations of NO_3^- (0–25 mg/L) and PO_4^{3-} (0–25 mg/L) at pH range of 2–8, nanoparticles concentration (1 and 0.5 g/L). As indicated in Table 4, 93% of pollutant removal was achieved for PO_4^{3-} in 5 to 1 ratio of iron to clinoptilolite and 81% for NO_3^- in a 1 to 2 ratio of iron to clinoptilolite at the pH of 2 [153]. Kinetic data for NO_3^- and PO_4^{3-} were well followed in the pseudo-first-order model and pseudo-second-order model, respectively.

3.1.3. Iron ox-hydroxide (FeOOH) nanoparticles

Iron oxy-hydroxide nanoparticles are the most commonly used nanomaterial for wastewater treatment. Iron oxy-hydroxide nanoparticles have been supposed to be a potential adsorbent to take away fluoride (F⁻) ions from water [156]. In this finding, the maximum adsorption capacity of the sorbent was 16.70 mg/g for fluoride at room temperature. Equilibrium sorption data show a better fit to Freundlich isotherm than Langmuir followed by Temkin, Dubinin-Radushkevich models, respectively. The mechanism of fluoride removal using iron oxide-hydroxide nanoparticles conform that both for the ion-exchange and physisorption phenomenon. As enumerated in Table 5, Sujana and Mohanty found 90% removal of fluoride ions by using FeOOH nanoparticles at an optimum pH of 4 [15].

Fang et al. (2018) produced a FeOOH nanorod array by using a facile hydrothermal method. The synthesized nanoparticle had photoreduction efficiency of 70% to Cr(VI) for transforming to less toxic Cr(III) after 4 h illumination and pH of less than 3 as seen from Table 5, which indicates the FeOOH nanorods array has an active interface in the photoreduction of Cr(VI) in water [157].

Within the green synthesis technique, FeOOH was integrated with the biodegradable root powder (RP) of long-root *Eichhornia crassipes* for the improvement of the adsorption performances for aqueous arsenic contaminants. After modification with FeOOH, the adsorption rates and capacities of the root powder were improved to remove arsenate (As (V)) and arsenite (As(III)), and the adsorption capacities reached up to 8.67–9.43 mg/g for As(V) and 5.21–5.65 mg/g for As(V) respectively at optimum pH of 9.0 and contact time of 50 min [158].

All the above researchers didn't report the type of polymorphs of FeOOH, but the following findings presented some types of FeOOH utilized for wastewater management. As shown in Table 5, Iron ox-hydroxide (FeOOH) nanoparticles consist of ferrihydrite, goethite, akaganeite, lepidocrocite, and feroxyhyte.

Several works informed the promising use of goethite (α-FeOOH) for water treatment. goethite nanoparticle, which is one of the commonly used polymorphs of Iron oxide-hydroxide, is an environmentally friendly material and is used in various technological applications as adsorbents [163,164]. Its performance on the elimination of Cd(II) ions from aqueous waste solutions was investigated. Goethite nanocrystalline powders were also produced by high-energy ball milling techniques followed by tests for toxic metals removal from aqueous solutions. Furthermore, batch experiments were performed to determine the sorption equilibrium, kinetics,

and thermodynamic parameters of toxic heavy metal ions by pulverized goethite. The adsorption graph touched a maximum value rapidly within 6 min and the adsorption parameters conformed to both isotherms (Langmuir and Freundlich) and a pseudo-second-order kinetic model was achieved. The adsorption capacity of Goethite on Cd(II) ion was evaluated to be 167 mg/g at 55 °C at a pH of 7 as sown in Table 4 [160]. Mohamed et al. (2017) synthesized Goethite (α-FeOOH) nanomaterial by precipitation route using Fe (NO₃)₃ and KOH to be utilized as a nano-adsorbent for removing the heavy toxic metals from wastewater. The removal of the lead (II) using the produced goethite nanomaterial was studied as a function of the adsorbent amount and contact time of 168 h, and pH with a lead concentration of 100–500 mg/L. Adsorption kinetics was followed by the pseudo-second-order kinetic equation. A high correlation coefficient was obtained for the Langmuir model [159]. The uniform urchin-like α-FeOOH hollow spheres nanomaterial has been prepared via a facile [165] and green synthesis route. The obtained urchin-like α-FeOOH nanoparticle was effective for dyes and heavy metal toxic ions removal in wastewater [163].

When goethite is combined with other materials, high removal efficiency can be achieved. Graphene oxide-supported ultrathin α-FeOOH nanorod was prepared by a simple hydrothermal method with a diameter of 6 nm and an average length of 75 nm, which are far thinner than GO-free a-FeOOH nanorods [166]. Also, goethite nanoparticles could be attached to graphene oxide (α-FeOOH + Ac/GO) and Akaganeite anchored onto graphene oxide (β-FeOOH/GO) were prepared by hydrolysis method, and their fluoride removal capability was compared. BET data showed a larger specific surface area and smaller pore size of synthesized α-FeOOH + Ac/GO than β-FeOOH/GO. α-FeOOH + Ac/GO shown an adsorption capacity of 19.82 mg/g with a broader pH range from 2.75 to 10.8, which was superior to that of β-FeOOH/GO and also other iron oxide particles [167]. The high toxicity of Arsenic has caused worldwide attention. To overcome this pollution the goethite impregnated graphene oxide (GO)-carbon nanotubes (CNTs) aerogel (a-FeOOH@GCA) was prepared by a simple self-assembly method of GO-CNTs induced by in-situ Fe(II) reduction. α-FeOOH@GCA exhibited excellent adsorption capacities of 56.43 mg/g for As(V) ion comparing with that of 25.71 mg/g of As(V) ion than that of α-FeOOH, respectively [168].

Water-soluble akaganeite (β-FeOOH) Nano spindles with small size were synthesized in the water phase without other organic reaction agents, using a simple hydrolysis method of inorganic salts aided water bath treatment with different incubation time. The longitudinal length and transverse diameters were about 40–50 nm and 10 nm, respectively. The FeOOH nano-spindles had low cytotoxicity in the environment [106]. Carbon nanotubes (CNTs) and akaganeite (β-FeOOH) hybrid nanoparticles with a diameter of 3 nm were prepared by an ultrasonic-assisted hydrolysis method using the precursor FeCl₃ and CNTs. It can be used as good adsorbents for the removal of Congo red from the wastewater system [169]. Bundle-like β-FeOOH nanostructures were successfully prepared by a simple hydrolysis process with the assistance of urea and its potential for wastewater treatment was studied [170]. Besides, PEG-coated *B*-FeOOH nanoparticles were synthesized through the electrostatic complex formation of IONPs

Table 6 Pollutants removed by Magnetite (Fe_3O_4) nanoparticle together with their process optimization.

Iron nanoparticle	Removed pollutant	Opt pH	Mechanism	Isotherm/kinetic model	Cont time (min)	Removal capacity (%)	Removal capacity mg/g	Reference
Fe_3O_4	As(V)		Adsorption		300		8.25	[173]
	Cr(VI)	2	Adsorption	Langmuir/Pseudo 2nd order			34.87	[179]
	Pb(II)	5	Adsorption	Langmuir/Pseudo 2nd order			53.11	
	bacteria		Reduction	–	720	80%		
	reactive Red F3B	7.6	Reduction	–		90	–	[102]
	Reactive Black 5 (RB5)	< 4	Adsorption	Langmuir		90	18	[87]
	crystal violet	10	Adsorption	Langmuir	50	99.99	–	[180]
	Bromocresol green	3	Adsorption	Langmuir	50	99.9	–	[180]
	Scenedesmus sp. microalgae	7.38	adsorption	Langmuir	27	95		[181]
Tangerine peel.Fe_3O_4 nanocomposite	Pb(II)	4.5	Adsorption	Monolayer/rate-limiting	95	95		[182]
Polyacrylic acid stabilized Fe_3O_4	Cd(II)	6.5			1440(24 h)	100	–	[131]
Iron oxide coated activated sludge granules	Cd (II)	9	Adsorption	Langmuir-Freundlich/ pseudo 2nd order	120	91.6	9.25	[183]
Fe_3O_4–gelatin	direct yellow 12 (DY12)	2	Adsorption	Langmuir/pseudo 2nd order	600	98.884	1250	[85]

with poly (ethylene glycol)-poly (aspartic acid) block copolymer [PEG-P (Asp)] in distilled water and used as novel magnetic resonance contrast agents for in vivo cancer imaging [171].

L-Cystine functionalized feroxyhyte nanoparticles (Cys-δ-FeOOH) were prepared by an inexpensive and direct method with 14 nm crystal size for use as an adsorbent of Hg (II) in an aqueous solution. The maximum Hg (II) removal capacity of the δ-FeOOH and Cys-δ-FeOOH of 35 mg/g and 217 mg/g respectively were obtained at pH 7. The kinetics data were best fitted to the pseudo-second-order model [107]. Organic ligands particularly acetate significantly improve the crystalline structure of iron ox-hydroxide (FeOOH) and are studied in the fluoride adsorption performances, thus improved its fluoride adsorption performance and mechanism. It would be very important to know the interface behaviors of minerals mediated by natural organic ligands in water or soil matrices [167]. Li et al. (2019) prepared mesoporous feroxyhyte (δ-FeOOH) nanoparticles and utilized them for the removal of phosphate that is a serious global environmental issue. Results showed that δ-FeOOH/Fe(II) system had 94.1% removal performance for phosphate(PO_4^{3-}) with acidic pH. Adsorption and chemical precipitation were the mechanisms observed in the phosphate removal by the δ-FeOOH nanoparticle. Phosphate removal by δ-FeOOH nanoparticle followed the Freundlich isotherm and pseudo-second-order kinetic model [161].

3.1.4. Magnetite (Fe_3O_4) nanoparticle

Magnetite (Fe_3O_4) is a naturally occurring mineral [172] but can be also easily prepared in the laboratory from solutions containing ferric and ferrous ions. The iron nanoparticles are, highly pure and low carbon, nitrogen, oxygen, sulfur, phosphorus contents, and free of other harmful elements [173]. Hence, magnetite (Fe_3O_4) nanoparticles are mainly used as a magnetic material to create magnetic adsorbents because of their relatively simple, easily controllable sized synthesis by varying the synthesis conditions, and they have high magnetic characteristics in comparison with other iron oxides [121]. Iron oxide (Fe_3O_4) nanoparticle is a very hopeful material used in water treatment particularly for heavy metals and dyestuffs because of their ease of separation through an external magnetic field, high surface area, unique morphology as well as high stability. These nanomaterials can be used as an adsorbent, photocatalyst, and coagulating agent for water remediation based on their composite materials or surface functionalities [174,175,51]. The fabrication of water-dispersible hollow iron oxide (hematite and magnetite) nanocapsules from the nano-structural transformation of readily synthesized from β-FeOOH nanoparticles is stated [176]. Besides the above finding, magnetite nanoparticle was also prepared with an average size of 45 nm from aqueous ferrous chloride ($FeCl_2·4H_2O$), ferric chloride($FeCl_3·6H_2O$), and NaOH by a simple and environmentally friendly method using Hund Fruit extracts called *Al-Abbas's*, which was used as a stabilizer and reductant. 80% of bacteria reduction was achieved after twelve hours of treatment whereas 24 h of treatment led to killing all the bacteria in water by magnetite nanoparticle [177].

D et al. (2019) successfully produced magnetite nanoparticles by chemical method for reactive green 19A and direct

yellow 12 dyes removal from wastewater solution. In this study, both Fe_2O_3 and Fe_3O_4 nanoparticles were obtained after characterization, and their performance was compared for dye removal [178]. As indicated in Table 6, 99.99% of reactive green 19A was removed by Fe_2O_3 nanoparticles at pH of 9, the initial color concentration of 10 mg/l, and adsorbent dosage 400 mg at a contact time of 80 min. 99.9% efficiency was obtained for Direct yellow 12 removals by Fe_3O_4 nanoparticles and 99.47 at pH of 7, initial concentration of 10 mg/l, an Adsorbent dosage of 400 mg, and at a contact time of 80 min. In other research, Fe_3O_4 hollow nanosphere was studied to remove neutral red dye from the water phase; the sorption of neutral red can attain an equilibrium within 1 h at an initial concentration of 200 mg/l, and the maximum dye adsorption capacity was 105 mg/g [45].

For heavy metal removal, the magnetite nanoparticle with an average diameter of 10 nm was synthesized by the co-precipitation method. Olive oil and flaxseed oil have been employed as a covering material, due to their advantages to the environment. These nanoparticles were successfully tried to catch up with some toxic metal ions from waste streams such as Cr(VI), copper, cadmium, and nickel. The adsorption procedure was tested in acidic conditions at a pH of 2.5 the overall efficiency is above 90% [184]. Besides, the evaluation of Fe_3O_4 nanoparticle, stabilized with poly-acrylic acid on cadmium removal from the contaminated soils was investigated and the maximum of 100% removal rate of Cd(II) was obtained at 500 ppm nano-fluid concentration, pH of 6.5, and contact time of 24 hr [131]. Moreover, surface modification of Fe_3O_4 nano-adsorbent was performed by using silica, metformin, and amine (NH_2). Silica-coated Fe_3O_4 nanoparticles led to 92% copper removal due to a high affinity towards copper [185]. Furthermore, a super magnetic starch-functionalized magnetite nanoparticle with 6 to14 nm size, was synthesized by a co-precipitation method. The produced nano-adsorbent was used for the removal of Cr(VI) ions from the aqueous waste stream by the batch adsorption procedure. The adsorption capacity of nano-adsorbents was decreased as the pH of the Cr(VI) solution increased. Under optimum pH conditions, the maximum experimental adsorption capacity of starch-functionalized magnetite nanoparticles for Cr(VI) was 26.6 mg/g. While the adsorption was endothermic, the equilibrium adsorption data could be best fitted to the Freundlich adsorption isotherm model and the kinetics followed the pseudo-second-order. The starch-functionalized magnetite nanoparticles could be easily recovered and used repeatedly in chromium removal without altered properties [186].

3.1.5. Maghemite (γ-Fe_2O_3) nanoparticle

Maghemite (γ-Fe_2O_3) is a typical ferromagnetic mineral and thermally unstable substance. γ-Fe_2O_3 as well as magnetite (Fe_3O_4) are easily converted to magnetic material and show high magnetic behavior when introduced to an external magnetic field [187]. Although the adsorption capacity of iron-based nanomaterials is high enough, they are rarely used as magnetic adsorbents due to their affinity to aggregate resulted from high surface energy inherent to fine-particle structures and their non-selectivity [121]. Consequently, for using γ-Fe_2O_3 as an adsorbent, the addition of some functional groups is important during waste decontamination and removal.

Kalia et al. (2014) prepared maghemite nanoparticles functionalized with glycine via co-precipitation methods in an environmentally friendly manner for the highly efficient elimination of copper (Cu(II)) ions from wastewater [188]. Ismail et al. (2019) used magnetic Fe_2O_3-AgBr composite photo-catalysts as an effective catalyst for bacterial inactivation in drinking water with light-emitting diode lamp irradiation. Outcomes showed that Fe_2O_3-AgBr nano-composites inactivated both *S. aureus* and *E. coli* bacteria. Bacterial inactivation occurs under anaerobic conditions and suggested the generation of ROS by Fe_2O_3-AgBr by oxidation of H_2O_2 generation from the conduction band of Fe_2O_3 and the direct oxidation of H^+ of AgBr [10]. In other research, maghemite (γ-Fe_2O_3) nanoparticle was prepared using the co-precipitation method functionalized with starch, which was superparamagnetic and hence utilized as adsorbents for the Cr(VI) removal from the waste stream. In this study, Cr(VI) adsorption on the super starch combined maghemite adsorbents surface

Table 7 Removal mechanism, efficiency, and capacity of Maghemite nanoparticles for different contaminants.

Iron nanoparticle	Removed pollutant	Opt. pH	Mechanism	isotherms model	Kinetic model	Con. time	Removal capacity (%)	mg/g	Reference
γ-Fe_2O_3	Cr(VI)	2	Adsorption	Freundlich	pseudo-2nd order		–	24.76	[111]
	Cd(II)	4	Adsorption	Langmuir &Freundlich	pseudo-2nd order	60	83.5	32.6	[72]
	methylene blue (MB)	10.1	Adsorption	langmiur		120		273	[189]
	BTEX (benzene, toluene…)	3–7	Photocatalytic			5 day	95visible light		[112]
						90	97(UV)		
γ-Fe_2O_3@starch (starch based)	As(III)		Adsorption	–	pseudo-2nd order		–	8.60	[190]
γ-Fe_2O_3-functionalized with glycine	Cu(II)	6	Adsorption	Langmuir	pseudo-2nd order			625	[191]

Table 8   Removal mechanism, efficiency, and capacity of Hematite nanoparticle (α-Fe$_2$O$_3$) for different contaminants.

Iron nanoparticle type	Removed pollutant	Opt. pH	Mechanism	Isotherm/kinetic model	Contact time (min)	Removal capacity		Reference
						(%)	mg/g	
α-Fe$_2$O$_3$	As(III)	5.6	Adsorption	Pseudo 2nd order / Langmuir	30	100	95	[194]
	malachite green (MG)		Adsorption	Pseudo 2nd order/ Freundlich	45	86.13		[75]
	Congo red			Langmuir		–	253.8	[193]
	Crystal violet (CV)		photocatalytic degradation	first order	30	100	–	[73]
	methylene blue (MB)		photocatalytic degradation	first order	40	100	–	
	reactive blue		photocatalytic degradation	—	56	95.08	–	[115]
	Cr(VI)		Adsorption	——			17.0	[193]
			Adsorption	——	1800	100	–	[114]
	Cd(II)	5	photocatalytic reduction	—	150	97.02	–	[113]
	direct red 28 dye (DR28)	2	Adsorption	pseudo-second-order	20	97	1.252	[127]

was studied and the removal was higher in acidic pH as compared to that exhibited in the basic medium. The sorption of Cr(VI) ion by obtained nanoparticle followed pseudo-second-order kinetics and the adsorption isotherm data fits well the Freundlich adsorption isotherm. Here the process of adsorption was spontaneous and endothermic from thermodynamics studies [111].

Siddiqui et al. (2020) studied both γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$@starch could efficiently be used in the removal of arsenite from water. The γ-Fe$_2$O$_3$@starch showed higher Langmuir adsorption capacity (8.60 mg/g) than virgin γ-Fe$_2$O$_3$ (7.15 mg/g) as observed in table 7, which revealed that the functionalization of γ-Fe$_2$O$_3$ enhanced the adsorption capacity. The possible removal mechanisms, adsorption phenomenon, of arsenite onto surface-functionalized maghemite has been reported including various isotherms and kinetic models. The adsorption process followed the pseudo-second-order kinetics, with film diffusion being the rate-determining step [190]. These pieces of evidence confirmed the chemical interaction between arsenic and γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$@starch. Therefore, γ-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$@starch are efficient materials for arsenic removal from water. Further research on the mechanism is recommended and careful modification of Maghemite nanoparticles should be conducted for the effective elimination of contaminants from waste effluents.

3.1.6. Hematite (α-Fe$_2$O$_3$) nanoparticle

Hematite (α-Fe$_2$O$_3$) is the most known oxide form of iron and the most frequent polymorph of Fe$_2$O$_3$ which exists naturally as a mineral, occurring commonly in rocks and soils, and has a weak ferromagnetic or antiferromagnetic behavior at room temperature [187]. Hematite (α-Fe$_2$O$_3$) is the utmost stable form of iron oxide. It is eco-friendly, non-toxic, biocompatible, and is economical, and highly resistant to corrosion [31]. Synthesis of the hematite-based calcium-rich hydroxyapatite nanomaterial (CRHAP) by co-precipitation
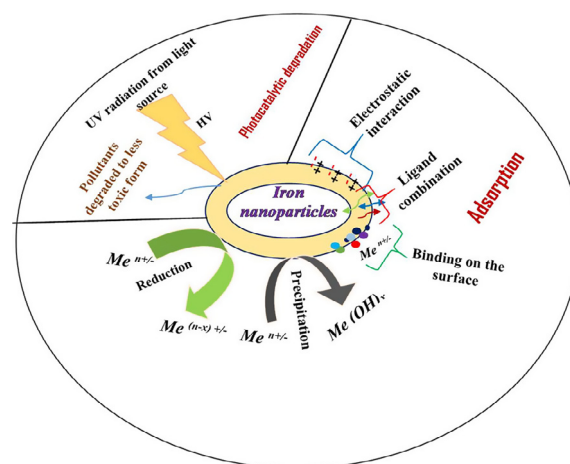
Fig. 6   Adsorptive and photocatalytic mechanisms of pollutant removal by iron-based nanoparticles. Modified from [28].

of the leach liquor from waste recycling plant scrap material is reported as an effective synthesis method of hematite-based nanoparticle [192].

The hematite nanoparticles had been also prepared effectively via an additive-free hydrolysis process at 75 °C for half-day with a large surface area of 164.1 m^2/g. it was applied to take away Congo red and chromium ions from the waste stream [193]. The result showed that the capacity of hematite nanoparticles on Congo red and hexavalent chromium ion have been examined using the Langmuir isotherm and the capacities were 253.8 and 17 mg/g respectively. In another finding, the α-Fe$_2$O$_3$ Nanoparticles were successfully prepared by the Sol-Gel method and the powder was calcinated at 400 °C having a crystalline size of 11.55 nm. Synthesized Hematite nanoparticle was utilized in the reduction of Cd(II) ion study. It was observed that photocatalytic reduction by

hematite was more successful at a metal concentration of 4 ppm, α-Fe$_2$O$_3$ dosage of 100 mg, pH of 5, and contact time of 150 min with 97.02% reduction of Cadmium (II) [113] as shown in Table 8.

The porous sphere-like micron-sized α-Fe$_2$O$_3$ can be easily attained by calcination of a bundle like a β-FeOOH precursor [163]. The obtained porous hematite microspheres, which are micro-sized in diameter, showed great potential for identifying ethanol [170].

4. Mechanisms of treating pollutants by iron nanoparticles

Several studies explained the mechanism of iron-based nanomaterials for the removal of numerous contaminants. Existing applications of various iron-based nanoparticles in the treatment of wastewater are based on adsorptive techniques that use different iron nanoparticles as a type of nano-adsorbent to enhance the efficient removal of pollutants or photocatalytic technologies that use them as semiconductor photocatalysts to converts contaminants into less toxic compounds [55,195].

4.1. Adsorptive mechanisms

The adsorption mechanisms or principles from polluted places or wastewater streams include electrostatic interaction(attraction between opposite charges), ligands ion combination, and binding on surfaces [195]. Ali et al. (2019) also mentioned five types of adsorptive removal mechanisms as shown in Fig. 6; namely, electrostatic interaction between pollutants and magnetic nanomaterial owing to the availability of different biomolecules on magnetic nanoparticle surfaces; chemical diffusion between adsorbent and adsorbate; surface precipitation; redox reactions; and ion exchange mainly because of the presence of hydroxyl/OH$^-$ functional groups [48]. Moreover, Iron-based nanomaterials prepared by green methodologies are to be probed as adsorbents for the successful removal of different pollutants by evoking redox, complex formation, and ion-exchange tendencies towards the pollutants [55,196]. Mostly, the removal mechanism of a certain contaminant is achieved simultaneously (a combination of physic-chemical adsorption, reduction, precipitation, and disinfection) by iron-based nanoparticles due to having various properties such as surface modifiability by various substances and functional groups [44,197].

The physicochemical adsorption is resulted due to the residual valences or imperfections in the iron oxide matrix. Redox tendencies of the ferrous and ferric ions may also contribute to the adsorption process. The nanoform of zerovalent iron when in contact with water and dissolved oxygen gets oxidized to oxyhydroxides of iron. The product of oxidation can 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 [55].

The surface binding mechanism implies contaminants either diffuse into the adsorbent or are adsorbed via electrostatic interactions for additional interactions with functional groups [195]. It has been demonstrated that the dyes containing a hydroxyl (–OH) group have been adsorbed in higher amounts with maximum adsorption capacity as compared to the non-OH$^-$ group, as the dye-containing the OH$^-$ group can easily form hydrogen/electrostatic bonding with the surface hydroxyl group of magnetite, which leads to the enhanced adsorption of these dyes. The adsorption study has shown that a double effect of electrostatic attraction during the adsorption process and ionic exchange was observed for maghemite-covered cationic resin [198].

The mechanism of contaminant by iron-based nanoparticle is multiple due to the presence of several functional groups obtained from the nanoparticle surface and the surface modification practices (i.e. stabilizing agent, capping agent, and antioxidant). The chemisorption mechanism of dyes by ZVI NPs involves three simple steps as; first, dyes are reduced by ZVI into dyes with −4 charges, while the iron is oxidized into Fe^{2+}. Next, the chromophore group and conjugated systems of these dyes are destroyed, generating hydrogen atoms, in a reaction between FeO and water. Finally, dyes adsorb on the intermediate products of FeO (Fe^{2+}, Fe^{3+}) and the passive iron oxides layers [199], For example, reactive black 5 and reactive red 198 were removed by these mechanisms [200]. Nanoscale zero-valent iron (nZVI) assisted biochar (BC) composites were studied for Cr(VI) removal. XRD, XPS, FTIR, and TEM analysis explained the mechanisms of Cr(VI) removal were due to electrostatic force, complexes, metal reduction, and precipitates on the edges [201]. Moreover, a nanocomposite prepared using zero-valent iron (ZVI) nanoparticles supported by acid-modified waste rock wool (ARW) was used to remove hexavalent chromium (Cr(VI)) from water and soil through adsorption and reduction mechanisms, and the resulting ARWZ-Cr could be easily collected under a magnetic field. Importantly, when nanomaterial was loaded in filter cotton with a micro/nanonetworks structure, the resulting system could be conveniently used as an excellent filter layer to control the migration of Cr(VI) [202].

Maghemite nanoparticles (MNPs) were functionalized with glycine for efficient removal of copper ions from water. The efficiency of these functionalized nanoparticles for removal of Cu (II) from water has been explored and showed that adsorption is highly dependent on pH and that it occurs either by forming chelate complexes and/or by electrostatic interaction [191].

A study of α-Fe$_2$O$_3$- citric acid assisted system reported that the mechanisms were ascribed to the auto-reduction of aqueous Fe(III)-citrate complexes and the subsequent Fe(III)/Fe(II) redox cycle. Adsorbed Cr(VI) on iron oxide surfaces indicated the formation of inner-sphere complexes on the surfaces [203]. Nizamuddin et al. (2018) summarized a mechanism of flowerlike α-Fe$_2$O$_3$ nanostructures for removing As(V) and Cr(VI) that started with the electrostatic attraction of α-Fe$_2$O$_3$ and As(V)/Cr(VI) ions for surface bonding. The mechanism of adsorption between Fe$_2$O$_3$ and Cr(VI) is mainly because of ion exchange and electrostatic attraction activities. On the other hand, the organic contaminants exchange ions (OH$^-$) with iron oxide or hydroxide by finding inner-sphere complexes [7].

Razzouki et al. (2015) studied the mechanisms of As (III) adsorption on the surface of iron (III)hydroxide by using the surface complexation model. The model proficiently supposed that the complexation occurs through an inner-sphere legend exchange mechanism (ligand combination) with a surface

functional group of FeOH. Their result showed that the co-precipitation of As(III) with $Fe(OH)_3$ was more dependent on the concentration of iron and H^+ ions. Ligand exchange in a mono-dentate part was more significant than the bi-dentate throughout the pH examined, but the bi-dentate complex-ion has a vital role near a pH of 8 [152].

Once magnetic nanomaterials are used to purify water from pollutants, magnetic separation could be performed to separate the nanomaterial from treated media by applying an external magnetic field [7]. The general treatment path seems as; initially, a magnetic adsorbent is added to a solution of a sample, and the mixture is stirred for a certain time necessary for the sorption of analytes. The adsorbent (nanoparticle) is then recovered from the final solution by applying an external magnetic field. After the field is removed, the adsorbent loses immediately its magnetic properties, and it is converted again into a suspension. The suspension is first washed with a proper solution, and then a concentrated eluent is added to desorb the pre-concentrated impurities [121].

4.2. Photocatalysis process

The other promising mechanism of pollutant/contaminant removal from wastewater is the photocatalysis process by introducing UV/Visible radiation and appropriate nanoparticle on the contaminated site [76], in which the contaminants can be gradually oxidized into low molecular weight intermediate products and eventually transformed into CO_2, H_2O, and anions (NO_3^-, PO_4^{3-}, and Cl^-) [204]. The photo-Fenton process is documented as an effective and promising technique for the microorganisms, existing in water and/or wastewater, disinfection. However, its effectiveness is near-neutral pH values rather than the far basic and acidic solution [205]. Giannakis et al. (2017) overwhelmed these obstructions by utilizing the heterogeneous photo-Fenton procedure as the default purifying strategy, directing MS2 coliphage in wastewater [206].

TiO_2 is the most widely used semiconductor photocatalyst in water/wastewater treatment owing to its low toxicity, chemical stability, low cost, and abundance as raw material [16], but, Iron oxide NM can be a good photocatalyst absorbing visible light. Compared with commonly applied TiO_2, which mainly absorbs UV light with wavelengths of 380 nm (covering only 5% of the solar spectrum) due to its wide band-gap of 3.2 eV, Fe_2O_3 with a band-gap of 2.2 eV is an interesting n-type semiconducting material and a suitable candidate for photodegradation under visible light condition [56].

Many species of Fe(III) oxides have been proposed, such as α-Fe_2O_3, γ-Fe_2O_3, α-FeOOH, β-FeOOH, and γ-FeOOH, to degrade organic pollutants and reduce their toxicity due to enhanced photocatalysis effect [194]. These NMs are illustrative of a new way to manipulate the catalytic properties of iron oxide for photocatalysis, towards a safe and effective wastewater treatment nanotechnology. An example is the photodegradation of Congo red (CR) dye ($C_{32}H_{24}N_6O_6S_2$) by iron oxide nanoparticles which were synthesized by thermal evaporation and co-precipitation approach [207]. The maximum removal efficiency was 96% at a size of 100 nm.

Particularly, Bibi et al. (2019) demonstrated the degradation of dye using Fe_2O_3 nanoparticles as shown in Fig. 7.

When the Fe_2O_3 nanoparticle was irradiated, an electron (e^-) and hole (h^+) pair are produced and the electron is excited from the valence band to the conduction band, leaving the h^+ in the VB. This hole (h^+) is responsible for the conversion of water into hydroxyl radical, which is responsible for the oxidative degradation of dye. On the other hand, free-electron combines with molecular oxygen and is converted into superoxide radicals. The superoxide radical is also converted into hydroxyl radicals. The hydroxyl radical is a strong oxidizing agent and degrades the organic species non-selectively into harmless end products [115].
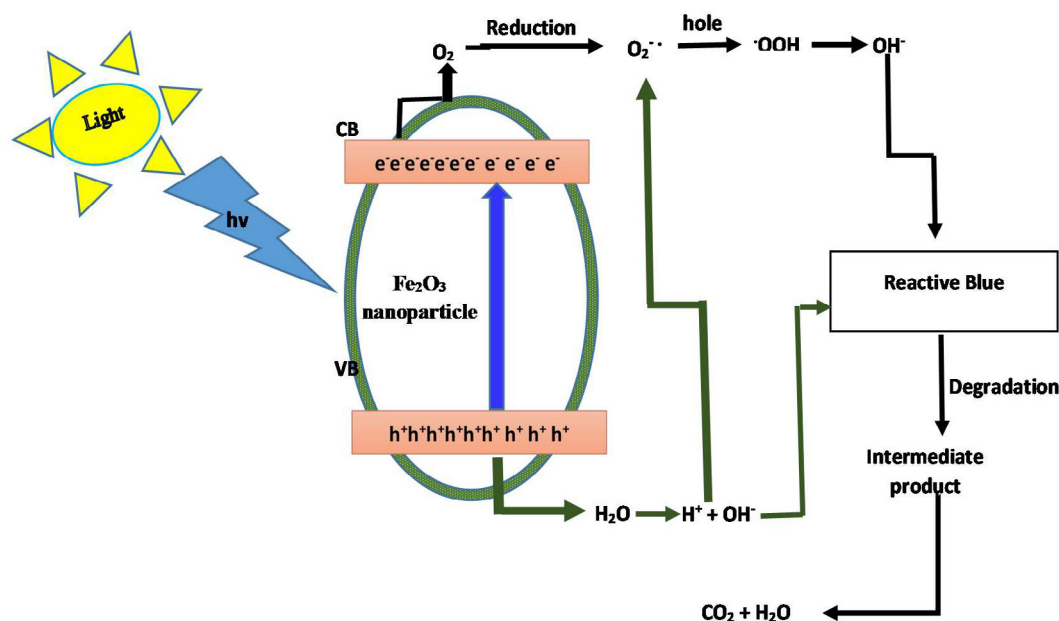

Fig. 7   An example of the mechanism of pollutants (dye) removal by Fe_2O_3 nanoparticles. Reproduced with modification from [115].

5. Limitation of using Iron-based nanoparticles

The impact of nanoparticles on health and the environment has not been studied deeply. The negative impacts of some nanoparticles are due to their size or particular chemical properties, particularly those that are freely mobile and not incorporated into a material [208,4]. The growing utilization of iron-based nanomaterials will certainly cause releasing trace amounts into the aquatic environment and consequently cause contact with living organisms that may made health problems [209]. As discussed in the above sections, iron oxide nanoparticles are effective nanomaterials for various contaminant removal from wastewater and other applications. However, the inherent disadvantage of using nanosized iron particles as adsorbent is that water flow in continuous columns through the bed of nanosized particles needs a pressure head. Hence, methodologies have to be developed with open columns wherein the nanoparticles are embedded in the matrix of synthetic or natural inorganic or organic polymers or beads. The host matrix may also alter the structural characteristics of the nanoparticles, and they have to be exploited for the advantage of pollutants removal from wastewater [55]. Moreover, recent research suggested the potential cytotoxicity of iron-based nanomaterials along with the potential implications in medicine, chemistry, and biology [210].

Till now, regeneration and reusing of nanomaterials synthesized from a green approach, are the major contests to researchers for developing them from pilot or laboratory scale to commercialization [40]. The major demerits of these bio-based syntheses are that the composition (chemical) of the extracts could be altered in the biomasses, even in the same species, with different environmental weathering. For example, seasonal variation, different geography, and growth stage of each other, 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 components existing in the bio extracts and then using them for water remediation purposes. Thus, investigations have to be undertaken in this direction.

The main drawbacks of nanoscale ZVI are the release of soluble iron ions and its susceptibility in surface oxidation [200] and separation of iron ox-hydroxide (FeOOH) nanoparticles in the final solution after treatment is another effort seeking issue of using it as an adsorbent, due to fine collide in water matrix are formed from FeOOH suspension that is hard and expensive to accumulate FeOOH nanoparticles from final wastewater stream [167].

Zhao et al. (2016) studied the limitations of using zero-valent iron (ZVI) nanoparticles in wastewater treatment. They reported that some drawbacks are associated with the process and need to be addressed. For example, when iron nanoparticles are subjected to magnetic attraction, rapid aggregation of particles resulted. Moreover, the ZVI nanoparticle is more likely to react with oxygen and oxygen-containing compounds. Meantime, ZVI nanoparticles could exert some degree of toxicity towards microbial species, and the effects of it at the cellular and community levels are progressively being explained. To avoid these difficulties, the ZVI nanoparticle was supported with suitable solid supports, adjust the parameters affecting the Fenton reaction particularly pH. They also identify problems that may occur as a result of changes in the physicochemical properties of ZVI nanoparticles due to their modification. Toxicity studies suggest that cell membrane disruption and oxidative stress through the generation of Fe^{2+} and oxygen-rich species by ZVI nanoparticle leads to the contribution of ZVI cytotoxicity[211].

6. Conclusion and future perspectives

Nanotechnology is an interesting discipline that had been supporting novel innovation in our lives and is changing the entire social development. Nowadays, it imposes great opportunities in various areas like agriculture, food, environment, medicine, and many others. Wastewater generation is one of the most environmental issues that need wastewater treatment to be employed in everyday activities to overcome damage to humans, animals, soils, and plants, and the spread of various diseases. Currently, several ways of wastewater treatment are applied and reported and the utilization of nanomaterials for pollutant removal is an emerging new treatment technology. Nanomaterials, particularly iron-based nanoparticles, have several priorities among conventional adsorbents with effective and efficient performance in wastewater remediation. Good specific surface area, high reactivity, surface functionalization, size-dependent properties, etc., are the most common characteristics. Iron-based nanoparticles have tremendous commercial and industrial applications. For example, they have been used as a catalytic material, as an adsorbent in water and wastewater treatment. Moreover, they are essential in pigments, flocculants, coatings, gas sensors, ion exchangers, magnetic recording devices, magnetic data storage devices, magnetic resonance imaging in the manufacturing industry, bio-separation, and medicine. In the case of wastewater treatment using IONPs, the mechanisms of removals of contaminants from the waste stream are based on adsorptive mechanisms including electrostatic interaction, ligand combination, surface binding, and also photocatalytic degradation.

The preparation methods of iron-based nanoparticles can be categorized into either physical, chemical, and biological techniques in the top-down and bottom-up approaches. Each synthesis methods have their own merits and demerits. Co-precipitation, hydrothermal, thermal decomposition, microemulsion, and sol–gel are the most commonly employed chemical synthesis methods. Iron oxides are a combined term for oxides, hydroxides and oxy-hydroxides with Fe(II) and/or Fe(III) cations and O^{2-} and/or OH^- anions. Currently, sixteen pure phases of iron oxides are known. These are $Fe(OH)_3$, $Fe(OH)_2$, $Fe_5HO_8 \cdot 4H_2O$, Fe_3O_4, FeO, five polymorphs of FeOOH, and four of Fe_2O_3. In this review, we have discussed their synthesis methods and application for contaminant removal efficiencies of the most common iron-based nanoparticles. These various forms and several extensive properties make Iron-based nanoparticles promising and effective nanomaterials for wastewater treatment applications. Surface modifications (coating, ligand binding e.t.c..) improve the stablity against aggregation, oxidation, and corrosion by incorporation of different functional groups such as; complexion ligands, organic layers, and inorganic elements.

For future work, the toxicity effect, cost analysis study, and regeneration and reusability potential should be analyzed and checked to employ iron and other nanoparticles for wastewater treatment. The toxicity related to long-term exposure to

human beings should be considered. Process variables such as extract volume, temperature, solvent type, pH, the strength of precursor, and functional groups from plant metabolites should be optimized to avoid any change in the magnetic behavior and saturation magnetization value. Also, the cost-benefit analysis should be studied not only for green prepared iron-based nanoparticles but also for the chemically and physically synthesized iron-based nanoparticle. Moreover, despite huge applications in wastewater treatment, catalysis, removal of both organic and inorganic contaminants, recoverability of these novel nanoparticles and other challenges should be studied and explored for efficient use in waste decontamination.

Furthermore, for further contaminant removal of the iron-based nanoparticles, additional investigation must be carried out at a pilot scale, which is essential to elucidate the application in full scale. Besides, the economical, technical, and environmental feasibility of contaminant treatment using iron nanoparticles, and life cycle assessment as a comparison with other nanomaterials are relevant.

In general, this review retrieved widely essential research investigations in relation to cost-effectiveness, efficiency of different contaminant removal with different iron nanoparticles, which is relevant to unite the existing knowledge, and identified gaps that require future solution for the improvement of pollutants management in the natural environment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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