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Preparation and Potential Applications of Super Paramagnetic Nano-Fe$_3$O$_4$

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Abstract: Ferroferric oxide nanoparticle (denoted as Nano-Fe$_3$O$_4$) has low toxicity and is biocompatible, with a small particle size and a relatively high surface area. It has a wide range of applications in many fields such as biology, chemistry, environmental science and medicine. Because of its superparamagnetic properties, easy modification and function, it has become an important material for addressing a number of specific tasks. For example, it includes targeted drug delivery nuclear magnetic resonance (NMR) imaging in biomedical applications and in environmental remediation of pollutants. Few articles describe the preparation and modification of Nano-Fe$_3$O$_4$ in detail. We present an evaluation of preparation methodologies, as the quality of material produced plays an important role in its successful application. For example, with modification of Nano-Fe$_3$O$_4$, the surface activation energy is reduced and good dispersion is obtained.

Keywords: Nano-Fe$_3$O$_4$; super paramagnetic; water; environment remediation

1. Introduction

Recently, adsorption has become widely used in industrial wastewater treatment technology. In the process, many adsorbents have been synthesized and applied to the treatment of pollutants that contain metallic elements, synthetic dyes and pharmaceutical products [1–4]. However, the removal of suspended adsorbent in wastewater is still a challenge. If it can be handled properly, it allows the effective recycling of the adsorbent with a reduction in operational costs. The addition of magnetic adsorbents has been studied to help efficient removal from wastewater. The use of magnetic Nano-Fe$_3$O$_4$ as an effective means for separating suspended sorbents has been identified [5,6].

As society develops, the water environment and its protection is increasingly more complex and treatment demands are much more changeable. Conventional water treatment materials are not able to satisfy the long term requirements of water treatment processes. Consequently, there is considerable interest in the development of multi-performance materials. Among them, Nanoadsorption materials have been considered to be an effective and environmentally friendly high-performance water treatment material [7]. Compared with atomic or larger scale systems, nanoscale materials have excellent physical and chemical properties from its mesoscopic effect, small objects effect, quantum size and surface effect. Nano-Fe$_3$O$_4$ has attracted wide attention because of its small size, large surface area (BET), super magnetic properties and easy recycling. In addition, it also has the non-toxic and biocompatible characteristics. Nano-Fe$_3$O$_4$ has diverse applications in new biomedical biosensors [8], contrast agent in magnetic resonance imaging [9], magnetic targeting for drug delivery system [10],

tissue engineering [11]. New preparation systems and methods of modification have been developed during its application. Prabha et al. [12] studied the preparation of polymer nanocomposite coated magnetic nanoparticles. Compared with the traditional preparation method, this method can increase the reactivity of the nanoferroferric oxide by changing the active groups such as the amino group and the carboxyl group on the surface to increase the surface-active sites.

The application of Nano-Fe_3O_4 has many advantages but it is easy to coalesce and oxidize in the water environment, resulting in limited development. A modification to the Nanomagnetic particles can prevent agglomeration, thus increasing its dispersion in water resulting in broader opportunities for application [13]. To date, superparamagnetic Nano-Fe_3O_4 has been applied to the preparation of magnetic fluid material such as ink. These materials in damping device, rotating seal, magnetic drug target cells, magnetic separation, magnetic card and other fields play an important role [14]. They are also being used in environmental remediation. Given the critical dependence of properties on preparation methodology, it is useful to provide an overview of the Nano-Fe_3O_4 in its preparation, modification and application.

2. Methods for Preparation of Nano-Fe_3O_4

The methods for the preparation of Nano-Fe_3O_4 usually consists of co-precipitation [15], hydrothermal [16], sol-gel [17], micro-emulsion [18], high temperature thermal decomposition [19], solvothermal [20] and a number of less common approaches, which aim to obtain nanometer sized magnetic adsorption material. The performance of Nano-Fe_3O_4 is critically dependent on its particle size and specific surface area. Fuskele et al. [21] focused on the preparation and stability of nanofluids, studied the synthesis methods of various nanoparticles and found that the particle size of ferroferric oxide has a great influence on its performance. As the particle size decreases, the specific surface area increases, the specific saturation magnetization decreases but the coercive force does not change substantially. For example, Dutta et al. [22] proposed a simple method for preparing PEGylated Fe_3O_4 cubic magnetic nanoparticles using iron acetylacetonate thermal decomposition methods and discussed its application in drug release and hyperthermia. The results show that Nano-Fe_3O_4 has good crystallinity and there are active groups such as carboxyl groups on the surface, which provide colloidal stability, low toxicity and anti-protein properties. The modified Nano-Fe_3O_4 has high electrostatic binding affinity with the positively charged anti-cancer drug doxorubicin hydrochloride and which provides useful pH release characteristics.

2.1. Hydrothermal Method

The hydrothermal method—also called hot solvent synthesis—refers to a chemical reaction in a sealed pressure vessel with water as a solvent and under high temperature and pressure. The nanocrystals prepared by the hydrothermal method have relatively advanced development, wide distribution range and do not require high-temperature calcination and treatment. However, because the reaction is carried out at higher temperatures and pressures, the requirements for equipment are more extreme [23,24]. Yang et al. [25] used iron acetylacetonate as the only iron source to prepare magnetite nanoparticles under simple hydrothermal conditions and chose polyacrylic acid as a stabilizer to provide good hydrophilicity. High-water-dispersed Nano-Fe_3O_4 with a particle size of about 50 to 100 nm was obtained. The Nano-Fe_3O_4 was composed of monodispersed magnetite with a size of about 6 nm and had high magnetic properties. The content of magnetite was over 70%. Wu et al. [26] used $FeCl_2$, $FeCl_3$ and glucose as raw materials at 160 °C in water to prepare Fe_3O_4@C composite nanoparticles, as shown in Figure 1. The adsorption behavior of methylene blue on Fe_3O_4@C was studied. The results showed that Fe_3O_4@C prepared by hydrothermal method could adsorb methylene blue effectively and the maximum adsorption capacity was 117 mg/g.
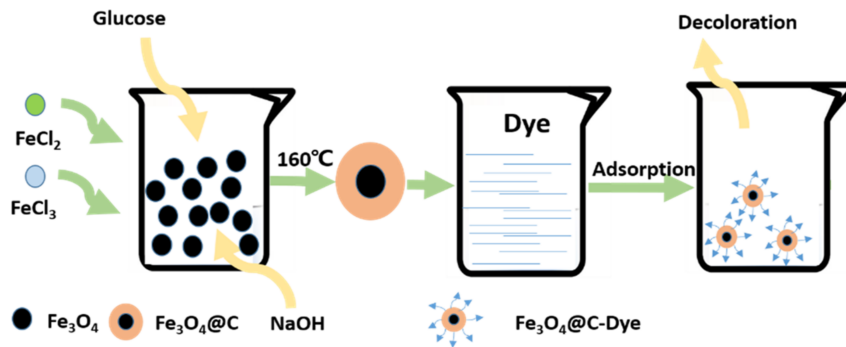
Figure 1. Scheme of the hydrothermal preparation process of Fe_3O_4@C composite particles and its adsorption on dyes.

2.2. Coprecipitation Method

The co-precipitation method involves the mixing of Fe^{2+} and Fe^{3+} in 1:2 proportion, precipitation under alkali conditions followed by filtering, washing and drying to generate Nano-Fe_3O_4. Due to its simple procedure, low cost and rapid reaction co-precipitation methods have been widely used [27,28], (see Figure 2). Qin et al. [29] adopted the chemical coprecipitation method, taking $NH_3 \cdot H_2O$ as the precipitant, which was added to a mixed solution of Fe^{2+} and Fe^{3+}. The particle size of $NanoFe_3O_4$ could be controlled within 20 nm under appropriate experimental conditions. Meng et al. [30] used $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and deionized water to prepare an iron salt solution and a ferrous salt solution. At the same time, the two solutions were mixed and heated to prepare Nano-Fe_3O_4 with $NH_3 \cdot H_2O$ as a precipitant in the mixed solution. The results showed that the concentration of Fe^{2+}/Fe^{3+} in the mixed solution had the greatest effect on the yield of Nano-Fe_3O_4. In addition, the temperature has an effect on the particle size, indicating that as the temperature increases, the Nano-Fe_3O_4 particle size increases first and then decreases.
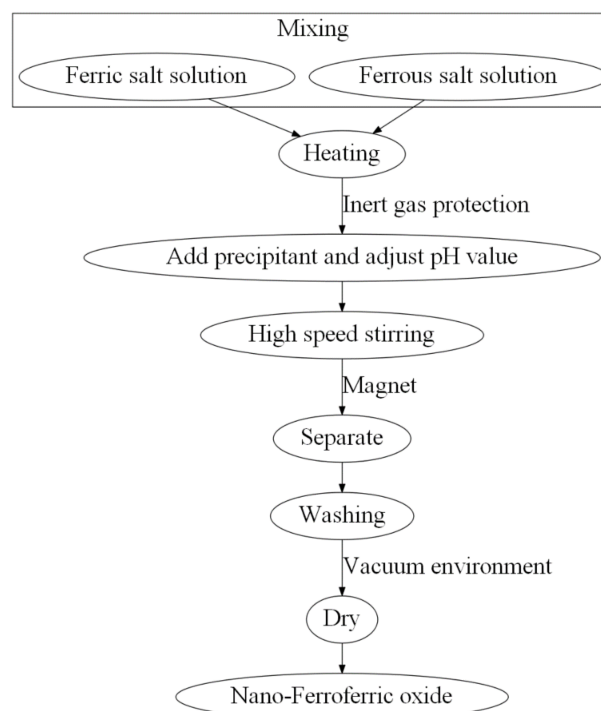

Figure 2. Scheme of co-precipitation synthesis of Nano-Fe_3O_4.

2.3. Sol-Gel Method

The sol-gel method typically utilizes iron sulfate, metal alkoxide hydrolysis and metal oxide or metal hydroxide sol as the raw material and a clean oxide powder [31,32] is then obtained after drying, as shown in Figure 3. The Fe_3O_4 synthesized by the sol-gel method has high purity but the gelation process is slow, the overall period of synthesis is long, with high temperature calcination needed [33]. Zhang et al. [34] prepared Fe_3O_4 aerogels by sol-gel method using $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and propylene oxide as precursors and gel promoters, respectively. The results show that Fe_3O_4 aerogel has lower density, larger specific surface area, higher saturation magnetization and its structure and magnetic properties are controlled by factors such as solution concentration, propylene oxide and Fe^{3+} molar ratio and calcining temperature and Fe_3O_4 aerosol is prepared. The gel has certain electromagnetic properties in the 2–18 GHz frequency range. Guo et al. [35] used the sol-gel method for preparation of a Nano-Fe_3O_4 coated with tetraethyl orthosilicate under a constant temperature of 380 °C. It showed a good particle size of 15~20 nm and uniform dispersion.
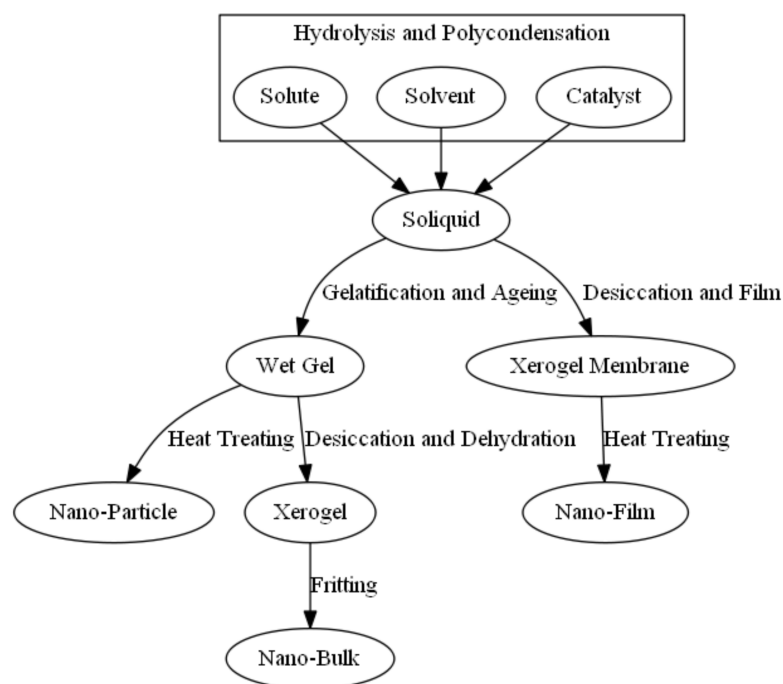

Figure 3. Scheme of sol-gel synthesis of Nano-Fe_3O_4.

2.4. Micro-Emulsion Method

Micro-emulsion method using two kinds of mutually miscible e solvents under the action of surfactant, forms a homogeneous emulsion. The solid phase is subsequently precipitated from the emulsion and the complete process consisting of nucleation, growth, coalescence and agglomeration finally forms spherical particles in a spherical droplet, as shown in Figure 4. The microemulsion method can prevent the agglomeration of particles while synthesizing Fe_3O_4 but the yield of nanoparticles prepared by a single synthesis is low, the separation and purification process of particles is complicated and the water solubility is poor [36,37]. Sun et al. [38] synthesized monodisperse Fe_3O_4 and polyaniline core-shell nanocomposites by microemulsion polymerization. Before the polymerization of aniline, Fe_3O_4 nanoparticles were prepared by thermal decomposition of acetylacetone and oleic acid using benzyl alcohol as solvent. Surface modification was carried out, then sodium dodecylbenzenesulfonate was used as surfactant, ammonium persulfate was used as oxidant and microemulsion was polymerized on the surface of Fe_3O_4 nanoparticles to obtain aniline monomer. Studies have shown that the oleic acid-modified Fe_3O_4 nanoparticles have good dispersion and the

particle size is about 10 nm. Lv et al. [39] used the microemulsion hydrothermal method to prepare a new type of tower-like Fe_3O_4 particles. Through experiments, it was found that the reaction time has important influence on the final product. The key factors, such as NaOH concentration and the formation of tower-like Fe_3O_4 microstructures, are very large. The relationship and the micro-scale pagoda-like Fe_3O_4 crystals were grown from the Fe_3O_4 rod structure by an etching process and lithium air cells prepared with a pagoda-type Fe_3O_4 air electrode had a higher specific capacity at 100 mA g^{-1}. The specific capacity is up to 1429 mA h g^{-1}.
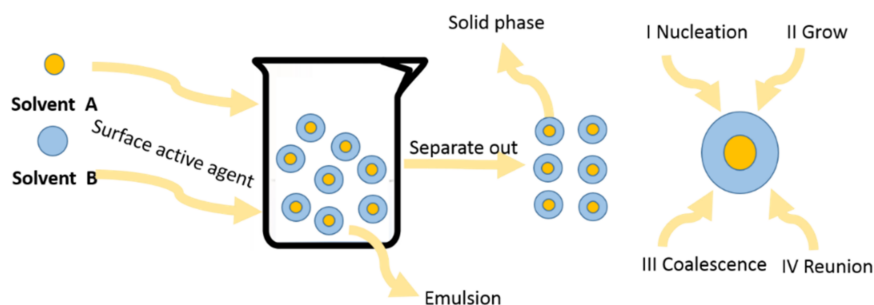

Figure 4. Scheme of Micro-emulsion synthesis of Nano-Fe_3O_4.

2.5. Solvent Heat Method

The solvent heat method is similar to the hydrothermal method but the water is replaced by organic solvents. The solvo-thermal method can precisely regulate the morphology and properties of Fe_3O_4 but it requires stringent preparation conditions [40]. Jiang et al. [41] synthesized monodisperse mesoporous Fe_3O_4 hollow microspheres with a diameter of 220 nm and a shell thickness of 50 nm using the trisodium citrate-assisted solvothermal method. The reaction time was good for this kind of mesoporous structure. The formation method influences the final product. Through experimental studies, it has been found that the synthesized Fe_3O_4 hollow microspheres have superparamagnetism, high saturation magnetization at room temperature, mesopores and high dispersibility. Zeng et al. [42] used ferric chloride hexahydrate as the sole iron source and sodium dodecylbenzenesulfonate as the surfactant. A uniform hollow Fe_3O_4 submicron sphere with a particle size of 350–450 nm was prepared by solvothermal synthesis. And it has high saturation magnetization and very low coercivity. The results show that the addition of sodium dodecylbenzenesulfonate is beneficial to the formation of monodisperse Fe_3O_4 hollow particles with a narrow particle size distribution, a high specific capacitance of 294 F g^{-1} at 0.5 A g^{-1} and good cycle stability. It maintained about 90.8% of the original capacitance after 500 charge and discharge cycles.

Table 1 summarizes the particle sizes of Fe_3O_4 prepared by several commonly used chemical methods; the substances added during the synthesis process and the optimal synthesis conditions; by optimizing the experimental conditions. The adsorption of pollutants and chemical adsorption properties are identified and the difference in the physical and chemical properties of Fe_3O_4 before and after the experimental conditions were optimized are highlighted.

Table 1. Optimization of Experimental Conditions in the Synthesis of Nano-Fe_3O_4 and Its Effect.

Preparation Methods	Particle Size	Additive	Optimum Ratio	Pollutants	Adsorption Manner	Optimization Effect	References
Coprecipitation method	35 nm	Ethylenediaminetetraacetic acid	15 mol $FeCl_3 \cdot 6 H_2O$, 7.5 mol $FeCl_2 \cdot 4 H_2O$,150 mL deionized water	Ag(I), Hg(II), Mn(II), Zn(II), Pb(II) and Cd(II)	Chemical adsorption and physical adsorption	The Fe_3O_4 modified by ethylenediaminetetraacetic acid had reactive functional groups such as carboxyl groups and amino groups on its surface and could undergo chemical ligand exchange with heavy metal ions in water.	[43]
Coprecipitation method	60 nm	Soluble starch	Reaction time = 2 h, pH = 3, equilibrium concentration = 1.0 mg/L	P	Physical adsorption	The Fe_3O_4 modified by starch has good dispersion, shown a monolayer disperse. The starch coats on the surface of Fe_3O_4 nanoparticle through steric hindrance and charge repulsion overcome the van der Waals force and magnetic attraction force.	[44]
Sol-gel method	-	Activated carbon fiber	pH = 2.0–6.0 at room temperature	P	Chemical adsorption	After modification through activated carbon fiber, the Fe_3O_4 had a significant increase in surface area and total pore volume. The modified Fe_3O_4 was positively charged and negatively charged by the electrostatic adsorption of phosphate ions. The ion exchange reaction occurred between phosphate and hydroxide. The prepared Fe_3O_4 particle had a larger BET.	[45]
Coprecipitation method	Around 25 nm	-	pH = 6.0 at 25 °C, 4.0 g/L Fe_3O_4	Pb and Cr ions	Single phase adsorption Pb ion, multiphase adsorption for Cr ion	Under the van der Waals force and magnetic attraction, it had the link structure of the polygon, which increased the three-dimensional space between the particles.	[46]
Solvent heat method	-	Bentonite	Heating for 8 h at 200 °C	Pb^{2+}, Cd^{2+} and Cu^{2+} ions	Chemical adsorption	It had a spinel structure and high crystallization degree. The composites composed of Fe_3O_4 and bentonite had reactive functional groups such as hydroxyl and carboxyl groups on the surface, which exhibited better adsorption of heavy metal ions. The specific surface area and total pore volume of composites were larger than those of pure Fe_3O_4, with higher magnetization saturation and lower remanence.	[47]
Coprecipitation and Sol-gel method	1–100 nm	Cellulose	4.0 g $FeCl_2 \cdot 4H_2O$, 8.0 g $FeCl_3 \cdot 6H_2O$, 150 mL deionized water, Reaction temperature = 60 °C stirring time = 60 min	Mercury ion	Chemical adsorption	Cellulose slender nanostructures were more likely to adsorb mercury ions. Cellulose-modified Fe_3O_4 has a reactive functional group such as CH_2 on its surface and interacts with mercury ions.	[48]

3. The Modification of Nano-Fe$_3$O$_4$

Magnetic attraction is often present in the Nano-Fe$_3$O$_4$ colloidal solution, which has obvious aggregation effect because of the large BET and small diameter. At the same time, the Nano-Fe$_3$O$_4$ is easily oxidized in the air during the preparation process. It is of great importance to modify the surface of the Nano-Fe$_3$O$_4$ by using physical and chemical methods to solve the problem that agglomeration and oxidation in Nano-Fe$_3$O$_4$. The common surface modification methods include surface chemical reaction [49], surface polymerization reaction [50], ultrasonic chemistry-method [51], surface adsorption deposit [52] and others. According to the different classification of modified raw materials, the package materials on Nano-Fe$_3$O$_4$ are generally classified into 3 kinds [53] including inorganic small molecules [54], organic small molecules [55] and organic polymers [56]. The specific classification was shown in Table 2.

Table 2. Modification of Nano-Fe$_3$O$_4$ by different substances.

Type	Materials	Advantages	References
Inorganic small molecules	(1) SiO$_2$ and other oxides; (2) Au, Co, Ni and other inorganic metals	The modification of SiO$_2$ and other oxides can shield the dipole interaction between the magnetic nanoparticles to prevent the particles from agglomerating and facilitate further functionalization of the particle surface. At the same time, it had a good biocompatibility, hydrophilicity and stability. Encapsulation of inorganic metals can synthesize composite particles of core-shell structure, giving the magnetic nanoparticles rich and excellent physical properties.	[57]
Organic small molecules	(1) Ethanol, organic carboxyl, sulfur and silane coupling agent oil-soluble substances; (2) Sodium oleate, sodium carboxymethylcellulose, β-cyclodextrin, citric acid, amino acids	Particle oil-soluble conversion to water-solubility was achieved by the interaction between the modifier and the stabilizer and the ligand exchange reaction resulting in water-soluble, oil-soluble and amphiphilic nanoparticles. Surfactant modification could control nanoparticle size and shape and changed surface properties of nanoparticle. Modification of silane coupling agents introduces reactive groups on the surface of nanoparticles to provide chemical selectivity for their further functionalization.	[58]
Organic polymers	(1) Glucose, starch, protein, peptides and other natural polymers; (2) Polyethylene glycol, polyvinyl alcohol and other synthetic polymers	Natural biomolecules had a good biodegradability and biocompatibility, greatly improving the biocompatibility of magnetic particles and giving them special biological activity. Synthetic polymer modification could give the material a variety of different properties to meet the actual requirement. Biomacromolecules had excellent bioactivity and were a synthetic polymer-rich chemical-selective organic combination.	[59]

3.1. Modification of Small Inorganic Molecules

Currently, there are two types of materials for Nano-Fe$_3$O$_4$ surface modification. The first includes SiO$_2$ and other oxides and the second is a metal such as Au, Co, Ni. There are also other inorganic materials used to modify Nano-Fe$_3$O$_4$, for example, the introduction of carbon to ferrosoferric oxide can increase its electrochemical performance. Han et al. [60] prepared a series of Fe$_3$O$_4$/C nanocomposites with nanoholes of 5 to 10 nm using a cotton assisted combustion reaction. The particle size of Fe$_3$O$_4$ nanoparticles is less than 10 nm and it is well embedded in the carbon matrix, making Fe$_3$O$_4$/C have good electrochemical performance. At a current of 0.4 A g^{-1}, the presence of carbon favors good dispersion and minimal agglomeration of Fe$_3$O$_4$ nanoparticles, with higher conductivity and buffer volume change.

Coating the Nano-Fe$_3$O$_4$ with a layer of silicon dioxide can effectively improve its corrosion resistance and dispersion. For example, Wang et al. [61] found that Fe$_3$O$_4$ without silica is highly susceptible to corrosion by acidic solutions. However, the silica-coated Fe$_3$O$_4$ forms a shell structure that blocks the contact with the solution. To a large extent, Fe$_3$O$_4$ is protected, which improves its acid resistance. Mostafaei et al. [62] first synthesized Nano-Fe$_3$O$_4$ by chemical precipitation. It was found through analysis that its small particle size was easily modified without precipitation and the dispersion effect was poor before the surface was modified with silica. From the experimental results, it can be seen that the spherical structure did not change. Each of the microspheres covered with SiO$_2$ has a small number of magnetic particles and has a good dispersion. The reason for this phenomenon

after modification may be that the SiO$_2$ core shell blocks the dipole interaction between Nano-Fe$_3$O$_4$ to make the particle distribution more uniform.

The surface of mesoporous SiO$_2$ had Si-OH structure and its surface was easy to be modified after the Nano-Fe$_3$O$_4$ coated with SiO$_2$, further grafting other active functional groups [63–66]. Xue et al. [67] used the hydrothermal method to prepare Nano-Fe$_3$O$_4$, compounding a magnetic shell composite microsphere by coating SiO$_2$ on its surface. It had a unique channel structure and a large BET based on SiO$_2$ groups in the surface. Finally, through the comparison of its performance in adsorption, they concluded that the adsorption effect for Cr ions by SiO$_2$ on the Nano-Fe$_3$O$_4$ coating was poor. After introducing -NH$_2$ groups, the attraction of negatively charged CrO$_4^{2-}$ by the positively charged -NH$_2$ through electrostatic attraction, significantly improved the absorption of Cr ions. Scanone et al. [68] synthesized Nano-Fe$_3$O$_4$ by co-precipitating Fe^{2+} and Fe^{3+} in ammonia solution and then modified the surface of SiO$_2$ with sodium silicate and passed 3-aminopropyltriethoxysilane. After the alkylsilane (APTS) treatment, the amino group was introduced onto the surface of SiO$_2$ by grafting. Then use 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (TCPP) activated by carbondiamine (NHS/EDC) and triiron tetraoxide (MNPNH) and coated with silica. The tri-iron oxide (MNPSINH) is covalently bonded. The photodynamic activities of MNPNH-TCPP and MNPSINH-TCP in the presence of different photo-oxidation substrates and in microbial cell suspensions were compared. The main difference is that the silica coating on the surface of mnpnh-tcpp produces O$_2$ in water. The photodynamic effect of TCPP linked to MNP is very sensitive to the decomposition of tryptophan. The last study showed that the MNPSINH-TCPP as an antibacterial material can control the proliferation of microorganisms under visible light and can maintain the sterilization state and has potential value in the medical field.

Nano-Fe$_3$O$_4$ BET surface area can be controlled in the presence of certain heavy metals. Sun et al. [69] studied composite Fe$_3$O$_4$ particles under the influence of Ag. The results of the experiment showed that after coating Ag on Fe$_3$O$_4$, the specific surface area had a significant increase, the same as its average pore size and total pore volume. In addition, the modification Fe$_3$O$_4$ by Ag provided excellent physical and chemical properties, with good stability even under high temperature and also improved its adsorption capacity in heavy metal removal application.

3.2. Modification of Small Organic Molecules

Inorganic nanomaterials have many advantages in the modification of Nano-Fe$_3$O$_4$ but in some systems (water phase system, oil phase system, oil and water system), their impact is limited. The modification of Nano-Fe$_3$O$_4$ by small organic molecule can provide good performance in both the water and oil phase systems. Modification by small organic molecules is divided into two, using either coupling agents or surfactants. The most common coupling agent is silane and surface-active agents include β-cyclodextrin [70], sodium carboxymethylcellulose [71], citric acid [71], amino acids [72,73] and other small organic molecules.

Surfactant-treated Nano-Fe$_3$O$_4$ often has lipophilic and hydrophilic groups forming micelles in the solution and on this basis, can achieve nanoparticle size and morphology control. The modification by surfactants can be to form a coating layer of long chain hydrocarbon on the Fe$_3$O$_4$, with the surface of Fe$_3$O$_4$ as the polar end for adsorption [74]. For example, Zhu et al. [75] modified the ferroferric oxide with oleic acid and found that the unmodified Nano-Fe$_3$O$_4$ was easy to reunite and the Nano-Fe$_3$O$_4$, which was modified by oleic acid, had large particle diameter and better dispersion. The reason for this phenomenon was that oleic acid on the Nano-Fe$_3$O$_4$ surface became a layer which effectively prevented the aggregation of particles. The hydrophilic group of oleic acid exposed to air turned the hydrophilic surface of Nano-Fe$_3$O$_4$ into a lipophilic surface. In addition, the modified Nano-Fe$_3$O$_4$ had more active sites on its surface. Wang et al. [70] synthesized a new cyclodextrin(-CD) polymer adsorbent-cyclodextrin/ethylenediamine/magnetic oxide graphene (CD-E-MgO) to extract Cr(VI) from aqueous solution. The adsorption mechanism was also analyzed: (a) electrostatic

attraction; (b) subject-object interaction; (c) Cr (VI), (HCrO$_4^-$) icons and CD-E-MgO combined with hydrogen bonding.

Nano-Fe$_3$O$_4$ after being modified by a silane coupling agent, can undergo further surface modification introducing higher selectivity. Shi et al. [76] used a silane coupling agent as modification material in the process of synthesizing magnetic microspheres. The results showed that the hydroxyl group of the Nano-Fe$_3$O$_4$ and the hydroxyl group were dehydrated, so the coupling agent could be adsorbed on the Nano-Fe$_3$O$_4$ surface. In addition, the surface of the modified Nano-Fe$_3$O$_4$ increases the relative concentration of oxygen atoms on the silane coupling agent, so that it can better integrate with other reactive groups and enhance its surface activity. Gui et al. [77] used a coupling agent to surface-treat Nano-Fe$_3$O$_4$ synthesized by the co-precipitation method and found that the coupling agent bonds well to the surface of Nano-Fe$_3$O$_4$. In addition, studies have shown that lipophilic and hydrophilic amphiphilic Nano-Fe$_3$O$_4$ can be obtained on the surface of Nano-Fe$_3$O$_4$ treated with coupling agent and the coupling agent is chemically bound in the dehydration reaction of the coupling agent and Nano-Fe$_3$O$_4$ to give new surface activity.

The modification of the coupling agent can improve the surface performance of Nano-Fe$_3$O$_4$. Lou et al. [78] compared the properties of the Nano-Fe$_3$O$_4$ had coupling agent on the surface and the unmodified Nano-Fe$_3$O$_4$. The results showed that after modified by coupling agent, the dispersity of Nano-Fe$_3$O$_4$ was greatly improved and the settlement was difficult to occur with the same magnetic responsiveness. The methanol formed during the hydrolysis of coupling agent also increased the hydroxyl groups on the Nano-Fe$_3$O$_4$ surface which is helpful for further modification.

3.3. Modification of Organic Polymers

There are still many deficiencies in aspects of the biocompatibility and stability in the modification of inorganic nanomaterials using small organic molecule in the case of Nano-Fe$_3$O$_4$. Modification of Nano-Fe$_3$O$_4$ by an organic polymer provides a special nucleation, shell structure, which also has the surface functionality and biological activity of the polymer. The modification using an organic polymer is typically divided into two: a natural biological molecule or a synthetic polymer. The natural polymers commonly used include: glucan [79], proteins [80], starch [81] and polypeptides [82]. The synthetic polymers usually used include: polyethylene glycol [83] and polyvinyl alcohol [84,85].

After the modification of natural biomolecules, the biocompatibility of Nano-Fe$_3$O$_4$ can be improved with new biological activity also established. For instance, as a natural, non-toxic protein macromolecule, gelatin has two segments, which can provide Nano-Fe$_3$O$_4$ with micellar encapsulation and water dispersion. The synthesis of magnetic nanoparticles and the stabilizing effect on Fe$_3$O$_4$ nanoparticles were proposed in the polyacrylamide hydrogel gel network by Reddy et al. [86] The study found that the presence of biocompatible gelatin in magnetic hydrogel enhanced the absorption of Nano-Fe$_3$O$_4$ and in vitro blood compatibility by thrombus and hemolysis test to study the biocompatibility of the gel. In addition, drug release was studied under an external magnetic field. The results showed that the hydrogel prepared in this way can be used for magnetic control drug release system and had potential application value in magnetic sensor, actuator and pseudo muscle. The water dispersible Fe$_3$O$_4$ nanoparticles were prepared with the method of gelatin embedding by Cheng et al. [87] and the surface coated with micellar was analyzed. At the same time, because the gelatin contained a large number of active groups, the nanocomposites could be prepared by fluorescent labeling and low-toxic platinum-precursor drugs, which could be applied in anti-cancer therapies.

After the surface modification of Nano-Fe$_3$O$_4$, various copolymers can be introduced to give Nano-Fe$_3$O$_4$ a variety of better and richer properties. For example, Hu et al. [88] looked at polyethylamine (PEI). The Fe$_3$O$_4$ modified by PEI was significantly more dispersed than pure Fe$_3$O$_4$ and the modified Fe$_3$O$_4$ particles were more spherical. The explanation was that the made increased the repulsive effect of charges and increased the steric resistance [89]. He et al. [90] first prepared ferroferric oxide by coprecipitation method at 90 °C, then the ferroferric oxide was coated with sodium polyacrylate by solution dispersion polymerization and surface Ca^{2+} crosslinking. The composite

materials prepared had good adsorption properties for Pb^{2+} and Cd^{2+}, which had the highest adsorption rate when the dosage of adsorbent was 1.0 g/L and 1.6 g/L to 200 mg/L Pb^{2+} solution and 100 mg/L Cd^{2+} solution. Yan et al. [91] used catalytic polymerization of aniline to load polyaniline on the surface of Fe_3O_4 to prepare a highly efficient complex catalyst. In a simulated wastewater treatment, COD removal was highly effective. In addition, the hydrogen ions provided by polyaniline can form coordination bonds with iron ions and reduce the loss of iron into the aqueous phase.

3.4. Structure of Nano-Fe₃O₄ Composite Materials

There were four basic sub-structures for ferroferric oxide modified by inorganic or organic substances. These include: core-shell [92], shell-core [93], diffuse [94] and sandwich [95] and are shown in Figure 5a–d. Figure 5a is the core-shell structure, with Nano-Fe_3O_4 as centrally, surrounded by a polymer shell. The Nano-Fe_3O_4 is completely embedded in the polymer. Figure 5b is the shell-core structure, in which the polymer acts as the core and Nano-Fe_3O_4 surrounds as the shell. This kind of composite microsphere is combined with Nano-Fe_3O_4 by complexation or electrostatic adsorption. Figure 5c is the diffuse structure, with the Nano-Fe_3O_4 evenly distributed within the polymer. Figure 5d is the sandwich structure and inner and outer layers of the complex are organic polymers, while the middle layer is Nano-Fe_3O_4. These microspheres are usually coated with organic polymers in the shell-core structure microspheres [96,97]. In addition, magnetic complexes after modification are found to have super paramagnetism, which was faster and easier to separate from the reaction system under the action of magnetic field. Moreover, magnetic compounds can be rapidly dispersed in the reaction system after removing the external magnetic field, which can assist in the recycling of materials and reduce its application costs [98,99].
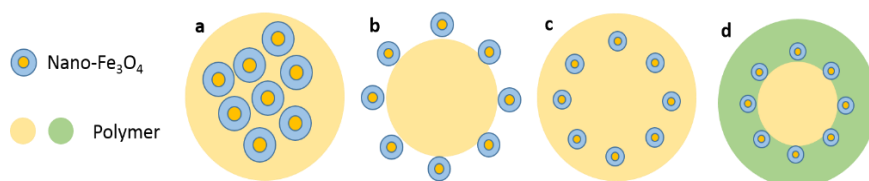

Figure 5. Four different structures of magnetic polymer composite microspheres: (**a**) Core-shell structure; (**b**) Shell-core structure; (**c**) Diffusion structure; (**d**) Sandwich structure.

The magnetic properties of these four different structures varies. The core-shell structure has a number of advantages over the other three structures. It is easier to modify the magnetic complex of the core-shell structure and introduce additional functional groups such as hydroxyl, mercapto and carboxyl group [100,101]. Compared with the diffuse structure and the shell-core structure, the environmental stability and thermal stability of the core-shell structure magnetic complex were improved. At the same time, this structure can prevent Nano-Fe_3O_4 from contacting with air and other substances, which can avoid its core being oxidized and corroded [102]. Compared with the sandwich structure, the core-shell structure magnetic complex was easier to prepare and the surface modification of Nano-Fe_3O_4 can be completed by a one-step method [103], which produced a superparamagnetic product and easier to be separated. For example, Kalska et al. [104] prepared nuclear shell nanoparticles with different magnetic core diameters and different thickness, who used Ag, Au and Cu as spacer metal. The influence of the thickness and composition of the particles in the structure were studied, together with the Cu, Au and Ag on the structure of core crystal magnetite. The results showed that the existence of the precious metal shell and the dipole interaction between the magnetic particles made the magnetic complex separation better. The presence of Cu, Ag and Au in magnetic particles leaded to the addition of superfine magnetic fields, which made them superparamagnetic.

4. Applications of Nano-Fe$_3$O$_4$

4.1. Biomedical Sciences

The Nano-Fe$_3$O$_4$ had more selective and catalytic activity than general materials because of its characteristics of small particle size, BET and surface activity center [105]. At the same time, the modified Nano-Fe$_3$O$_4$ can be used as an anti-tumor drug carrier, which had good specificity and targeting in the field of external magnetic field [106]. The Fe$_3$O$_4$ nanoparticles modified by sodium oleate were expected to do drug carrier for osteosarcoma chemotherapy. It could be combined with anticancer drugs targeting tumor body parts through the magnetic field and the basic physiology of the human body with added benefit of low toxicity [107]. For example, Isiamian et al. [108] studied the enhanced radio sensitivity of breast cancer cells with the combination of 2-deoxy-D-glucose and doxorubicin plus superparamagnetic Fe$_3$O$_4$ nanoparticles. At the same time, it was also found that doxorubicin and 2-deoxy-D-glucose combined with targeted magnetic Fe$_3$O$_4$ nanoparticles can promote breast cancer radiotherapy by improving the localization of chemotherapy, increasing the cytotoxicity of tumor cells and reducing the single therapeutic dose.

With good biocompatibility and magnetic effect, Nano-Fe$_3$O$_4$ had a wide application in the treatment of tumors and magnetic resonance imaging [109]. Zhang et al. [110] studied the application of Nanoferroferric oxide in rats' hydrocrania CT imaging, which could be used as a photographic developer. They also analyzed the Nano-Fe$_3$O$_4$ distribution in rat various organs and found that there was no accumulation in different organs. This phenomenon showed that the Nano-Fe$_3$O$_4$ had biocompatibility.

4.2. Removal of Heavy Metals from Aqueous Systems

Modified Nano-Fe$_3$O$_4$ surfaces reacts with heavy metal ions and have been studied in the removal for treatment of aqueous systems. For example, Cui et al. [111] synthesized a new magnetic nanocomposite material (MgHAP/Fe$_3$O$_4$) by adding Fe$_3$O$_4$ into magnesium hydroxyapatite (MgHAP), which can remove the Cu^{2+} from the aqueous solution. The adsorption of Cu^{2+} by MgHAP/Fe$_3$O$_4$ was mainly by chemical adsorption, with the sharing or exchange of electrons between adsorbent and Cu^{2+}, in which the valence state is important. Because of this chemical interaction, the combination of MgHAP/Fe$_3$O$_4$ and Cu^{2+} had stable chemical and physical properties. In addition, Mg^{2+} and Cu^{2+} in MgHAP had the same charge and similar ionic radius, promoting their exchange in hydroxyapatite. After adsorption, the properties of the material were very stable, which would not cause secondary pollution to the environment, making it advantageous for water treatment.

The modified Nano-Fe$_3$O$_4$ can also reduce the reactivity of heavy metals and produce stable hydroxide and iron oxide precipitation on its surface. Tian et al. [112] modified the Nano-Fe$_3$O$_4$ by using a kaolin with better functional properties after comparing various modifiers. Based on this, the pH was studied in the process of removing heavy metal chromium. At higher concentrations, the kaolin-modified Nano-Fe$_3$O$_4$ forms hydroxides of iron and chromium on the surface, so that the particles are in a stable state and passivated and their surface almost loses reactivity. Chang et al. [113] used coprecipitation to wrap the γ-polyglutamic acid (γ-PGA) on the Nano-Fe$_3$O$_4$ surface successfully. The results showed that the γ-PGA/Fe$_3$O$_4$ particle size was smaller than that of the Nano-Fe$_3$O$_4$, which also had larger surface area. The removal rate of Cr^{3+}, Cu^{2+} and Pb^{2+} by γ-PGA/Fe$_3$O$_4$ in the deionized water was more than 99%, which was because of the larger specific surface area of the γ-PGA/Fe$_3$O$_4$ mNPs. The experimental results showed that γ-PGA/Fe$_3$O$_4$ was better performance than Fe$_3$O$_4$ and γ-PGA/Fe$_3$O$_4$ in heavy metal removal. The adsorption of heavy metal ions got through the membrane by means of γ-PGA and the unabsorbed ions removal activity was reduced through the membrane.

The heavy metal ions could react with the function group on the modified Nano-Fe$_3$O$_4$ surface. For instance, Jin et al. [114] analyzed the process of adsorption of heavy metals by the Nano-Fe$_3$O$_4$ surface loaded amino functional group. The study found that the Nano-Fe$_3$O$_4$ coated with a single

silicon dioxide had a low adsorption capacity of heavy metals and when its surface is modified with amino functional group, faster and more effective removal of heavy metal ions occurred. As a result of the interaction between lewis acid-alkali, amino groups can strengthen the introduction of SiO_2 for heavy metal ions, such as Hg^{2+}, Pb^{2+} and Ag^+. The reason of this phenomenon maybe is the amino changed the silica shell with Nano-Fe_3O_4 nuclear structure, increasing the BET and pore size. Shen et al. [115] investigated the fungi and ferroferric oxide compound material. Using a kind of rice root mildew derived biomaterial to modify Fe_3O_4 and analyzed adsorption mechanism. They concluded that the rhizopus oryzae surface functional groups can readily react with metals, promoting enhanced adsorption of metals from water.

The removal activity of modified Nano-Fe_3O_4 for heavy metals is strongly pH dependent. For example, Zhao et al. [116] successfully synthesized Fe_3O_4-MnO_2 magnetic nanoplates using a simple hydrothermal method to remove divalent heavy metals in water. The modification of amorphous MnO_2 can significantly increase the specific surface area of Fe_3O_4-MnO_2 and reduce the zero-charge point, thus ensuring good adsorption capacity for metal cations. Experiments show that the acid-alkaline environment affects the surface charge of Nano-Fe_3O_4 during the adsorption of divalent heavy metal by Nano-Fe_3O_4. The reason is that at low pH, H^+ ions easily combine with the hydroxyl groups on the surface of Nano-Fe_3O_4, which increases the positive charges and groups on the surface and the negatively charged divalent heavy metal ion complexes are electrostatically attracted to the surface of Nano-Fe_3O_4. At the same time, the ability to adsorb divalent heavy metals is increased. Kilianová et al. [117] reported a simple and cheap synthesis of ultra-fine Nano-Fe_3O_4 with narrow particle size distribution and its application in the field of arsenic removal in a water environment. The study showed that the mesoporous arrangement of nanoparticles in their system enhanced the adsorption capacity, which was due to the strong magnetic interaction between nanoparticles. As (V) would be removed totally when the pH value was in the acid range. At this time, the Zeta potential of Nano-Fe_3O_4 adsorbent was 7.6; pH value was 5–7.6; Fe/As was approximately 20/1 and the balance of arsenic removal was 45 mg/g.

Table 3 lists the modification of Fe_3O_4 by surface chemical physical methods for different substances. After modification, Fe_3O_4 can increase the adsorption efficiency of heavy metal ions and the mechanism of removal of metal ions also differs between them. The three main mechanisms are electrostatic adsorption, surface reaction and chemical ligand exchange.

Table 3. Methods for the modification of Nano-Fe_3O_4 and mechanism for the removal of heavy metals.

Heavy Metal	Methods	Removal Mechanism	References
Pb	With different amounts of glycerol	Surface coordination, chemical adsorption.	[118]
As	With manganese dioxide and graphene oxide	Manganese dioxide can oxidize arsenic into pentavalent arsenic and graphene oxide can increase adsorption ability.	[119]
Cr	With Reduced graphene oxide	Electrostatic adsorption and acid groups adsorption.	[120]
Hg	With cellulose	The complex of mercury ion and cellulose on the surface of Fe_3O_4.	[48]
Pb and Cr	With micrococcus	Weak electrostatic forces between cadmium ions (II) and carboxyl groups or hydroxyl groups; chemical bonding of lead (II) ions and amino groups.	[121]
U and Cu	With calcium alginate containing-chitosan hydrogel beads	Chemical interaction of NH_3-groups in Chitosan with -COOH groups in calcium alginate. Physical pore adsorption and electrostatic adsorption.	[122]

4.3. Electrochemical Sensor and Energy Storage

Complex Nano-Fe_3O_4 had shown excellent charge-discharge cycling stability [123]. For example, composite material combined by Nano-Fe_3O_4 and Graphene after modification had good

electrochemical sense performance. The modified graphene can enhance its stability and conductivity and Fe_3O_4 has a reversible capacity synergistic effect [124]. Peng et al. [125] synthesized a novel multifunctional magnetic biomolecule with Fe_3O_4 as the core, and heme protein and polydopamine as shells, using a one-pot chemical polymerization method. The results showed that the synthesized biomacromolecules not only possess the magnetic properties of Fe_3O_4 but also maintain the native structure of the heme protein under the action of an external magnetic field. Polydopamine and Au nanoparticles have good biocompatibility and conductivity. At the same time, due to the presence of Au nanoparticles, the exchange of electrons between the hemoprotein and the electrode is enhanced. Zheng et al. [126] synthesized magnetic Fe_3O_4 nanoparticles using chemical co-precipitation method and mixed Fe_3O_4 nanoparticles with chitosan to form a matrix of immobilized hemoglobin to prepare a hydrogen peroxide biosensor. In the pH range of 4–10, the potential of the Fe(III)/Fe(II) couples changes linearly with increasing pH, indicating that electron transfer is accompanied by transport of single protons in the electrochemical reaction. At the same time, it also has a certain effect on the storage of electrical energy.

After secondary modification, the dispersion of the composite particles was better and graphene had a stronger protective effect on granules, which was of great practical significance. Zhu et al. [127] studied a lab prepared Nano-Fe_3O_4 compound rich in amino and carboxyl groups on the rheophore. After testing the content of the alpha fetoprotein antibody absorbed by amino and electrostatic forces, they concluded that alpha fetoprotein immune sensor had high sensitivity and stability. In addition, the adsorption capacity of nanometer compound to the antibody was increased compared with the traditional method.

4.4. Chemical Catalysis

Cai et al. [128] found that when Ag was loaded on the surface of Fe_3O_4, the effect on the catalytic reduction of nitrophenol was greater than in its absence and that this effect increased with the increase in Ag concentration. Zou et al. [129] used $PdCl_2$, $SnCl_2 \cdot 2H_2O$ as precursors to prepare different Fe_3O_4 catalysts with different Fe_3O_4 content. They found, using cyclic voltammetry and timing current tests, that the catalyst had a good electrocatalytic activity for ethanol oxidation and the charge transfer resistance had a strong relationship with the Pd/Sn content.

Coupling agents were used to connect the heavy metal bridge on the Nano-Fe_3O_4 surface, effectively inhibiting the agglomeration of Fe_3O_4 and enhance its stability. Gu et al. [130] prepared Au/Fe_3O_4 by ultrasound in the presence of 3-aminopropyl triethoxysilane, which had high catalytic activity and did not agglomerate because of the action of the amino containing 3-aminopropyl triethoxysilane. Its rate constant can reach 0.2256 min^{-1} in the catalytic reduction of 4-nitrophenol. After nine cyclic reactions, the catalytic conversion rate was still very high. Gao et al. [131] utilized Nano-Fe_3O_4 as a filler for polytetrafluoroethylene and the linear expansion coefficient of composite material was greatly reduced. When the mass fraction of Fe_3O_4 was 15%, the linear expansion coefficient decreased by $40.1 \times 10^{-6}/°C$ compared with the single polytetrafluoroethylene.

4.5. Others

The use of Nano-Fe_3O_4 has great practical value in other applications (as shown in Table 4). In addition, to the water environment, a number of studies had shown that Nano-Fe_3O_4 can effectively remove heavy metals from sewage and also remove organic, inorganic compounds, dyes, algae [132] and other environmental pollutants in water. Ito et al. [133] studied the effect of $ZrFe_2(OH)_8$ as adsorbent on phosphorus removal in wastewater. According to the study, $ZrFe_2(OH)_8$ was a good phosphate adsorbent. More than 90% of the phosphate can be removed within 5 min. It can effectively prevent the eutrophication of polluted water and is straight forward to recycle. Phenol was widely used in rubber, pesticides, dyes, plastics and other fields but its toxicity led to significant environmental pollution and subsequent restriction. Nano-Fe_3O_4 shows good adsorption for phenol, for example, Jiang et al. [134] in studies of fungal degradation, compared Nano-Fe_3O_4 immobilized cells to

isolated fungal cells without nucleus, free floating cells and calcium alginate immobilized cells without nanoparticles. The results showed that the immobilized dedoxycycline strain had better biodegradability than the free cells and the Nano-Fe_3O_4 immobilized cells had the highest rate of removal of phenol. In addition, when the initial phenol concentration was higher than 900 mg L^{-1}, the Nano-Fe_3O_4 immobilized cells could degrade over 99.9 percent of phenol in 80 h and had good stability in the saline environment. On the contrary, the free cells removal rate of phenol was 34.5% and immobilized cells without Nano-Fe_3O_4 was 81.3%.

Table 4. The application of modified Nano-Fe_3O_4 in treatment of other environmental pollutants.

Pollutants	Methods for Modification of Nano-Fe_3O_4	Removal Principles	References
Congo red	With hydroxyapatite and zeolite	The interaction of the dye and Nano-Fe_3O_4 through Surface coordination, hydrogen bonding, Lewis acid base reaction.	[135]
Natural rubber	With silane coupling agent	The Fe_3O_4 has high binding energy after modification and it was much easier to bond with rubber.	[136]
Rhodamine B	With Fenton reaction in the presence of H_2O_2	The surface of Fe_3O_4 formed complexes and hydroxyl radicals, resulting of degradation of dye.	[137]
Methylene blue	With natural eloise under vacuum impregnation and high temperature pyrolysis	A large number of hydroxyl groups on the surface of rocky oxidized methylene blue.	[138]
Acid orange	With Chitosan	Interacting of ions of dye with the protonated amino ions of chitosan	[139]
Methylene blue	With Graphene	The positive charged oxygen-containing groups in Graphene attracted a negatively charged methylene blue.	[140]
Bisphenol A	With amine-containing β-cyclodextrin	Hybrid effects of electrostatic, hydrophobic and van der Waals.	[141]
Organics 2,4,6-trinitrophenol	With activated carbon	Porous physical adsorption on the surface of activated carbon; Electrostatic adsorption and hydrogen bonding; Surface reaction; In the presence of dissolved oxygen, the phenols on the surface of activated carbon are gathered.	[142]

Due to having a magnetic property, some materials are likely to combine with it and enhance their functions. They often show a combination performance other than individual. For example, in order to short settling time of flocs in coagulation-flocculation, with the help of external magnetic fields, the coagulation by magnetic coagulant consisting of Nano-Fe_3O_4 and conventional coagulants (e.g., polyaluminum chloride [143], chitosan [144,145], polyacrylamide [146] et al.) is easy to achieve the purpose. In fact, it is far more than the effect in settling speed enhancement because the presence of Nano-Fe_3O_4 is likely to enhance original functions of coagulant in charge neutralization, netting adsorption-bridging [147]. Therefore, Nano-Fe_3O_4 is helpful in improving performance of coagulation. Magnetic separation is a green technology and its development is more tempting. Research on the magnetic coagulant is, however, quite deficient. How to ensure its stability and effectiveness is an important problem. In on another part, the Nano-Fe_3O_4 has also received wide attention. A typical example is the metal-organic frameworks (MOFs) being powder materials means that they have a small Nanosize, which means they are often difficult to separate from liquid phase. With the help of Nano-Fe_3O_4, this difficulty can be overcome. The hybridized materials of Nano-Fe_3O_4 and MOFs were able to show more special functions than their individual [148]. Overall, the composite material of Nano-Fe_3O_4 and other functional materials may be a better solution in overcoming their shortcomings or obtaining their expected functions.

5. Conclusions

Because Nano-Fe_3O_4 has the excellent chemical properties, it has been an important research focus in recent years. It is different from general magnetic materials due to unique features which include simple preparation and lower requirements for equipment compared with the traditional adsorbents. Although Nano-Fe_3O_4 has been widely applied in many fields, some problems still need to be addressed. For example, its dispersion and stability. Through modification, iron oxide has multidimensional functional properties such as oxidation, adsorption, catalysis, magnetic separation.

If the Nano-Fe$_3$O$_4$ was applied to different fields, the morphology, structure and surface properties are the main factors controlling their successful application. Further research on their modification is still needed. Finding a more convenient and more economical way to prepare and modify good Nano-Fe$_3$O$_4$ should be addressed to fully exploit their potential in the diverse fields of application.

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