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Chapter 3

Applications of Magnetite Nanoparticles for Heavy Metal Removal from Wastewater

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1. Introduction

Because access to safe drinking water is the key to protect public health, clean water has become a basic need of all properly functioning societies [1]. Despite their presence at low concentration ranges, environmental pollutants possess serious threats to freshwater supply, living organisms, and public health [2].

Contamination of water with toxic metal ions (Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III)) is becoming a severe environmental and public health problem. In order to achieve environmental detoxification, various techniques like adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation and biosorption processes are extensively used [3-5]. Among these, adsorption is a conventional but efficient technique to remove toxic metal ions and bacterial pathogens from water.

Development of novel and cost-effective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention. Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology [6-7].

The synthesis of magnetite nanoparticles has been intensively developed not only for its fundamental scientific interest but also for many technological applications: such as magnetic resonance imaging, ferrofluids for audio speakers, magnetic targeted drug delivery, and magnetic recording media [8]. In particular, the use of magnetite nanoparticles as adsorb-

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ents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields.

Bare magnetite nanoparticles are susceptible to air oxidation and are easily aggregated in aqueous systems [9]. Thus, for the application of these nanoparticles in various potential fields the stabilization of the iron oxide particles by surface modification is desirable. The magnetic structure of the surface layer, which is usually greatly different from that in the core of the nanoparticles, can have a notable effect on the magnetic properties of nanoparticles [10]. The control of the size and the polydispersity are also very important because the properties of the nanocrystals strongly depend upon the dimension of the nanoparticles. It is interesting to mention that only magnetite particles with size of less than 30 nm have a large surface area and exhibit super paramagnetic properties that make them prone to magnetic fields and they do not become permanently magnetized without an external magnetic field to support them [11]. These properties are highly useful in the development of novel separation processes [12].

To understand the behavior of the colloidal ferrofluids of the particles and to improve their applications or develop new ones, careful studies related to fluid stability, control of surfactants, particle sizes and physical behavior are essential [8].

We here present recent developments on the use of magnetite nanoparticles (NPs) and magnetite-containing composite nanomaterials for the removal of heavy metals from waters.

2. Synthesis of Fe_3O_4 nanoparticles

For different applications, several chemical methods can be used to synthesize magnetic nanoparticles: co-precipitation, reverse micelles and micro-emulsion technology, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, and electrospray syntheses [8]. The synthesis of superparamagnetic nanoparticles is a complex process because of their colloidal nature. For metal removal applications, an adequate surface modification of the nanoparticles is a critical aspect regarding both selectivity and aqueous stability of these materials. To this end, in the last decade, organic and inorganic functionalized Fe_3O_4 nanoparticles have been developed and modifications of the synthesis methods mentioned above have been proposed. A brief description of the methods most widely used for preparing materials with applications in metal removals is given below:

Co-precipitation: This method is probably the simplest and most efficient chemical pathway to obtain magnetic particles. Magnetite is usually prepared by an aging stoichiometric mixture of ferrous and ferric salts in aqueous medium. The precipitation of Fe_3O_4 is expected at a pH between 8 and 14. The size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature and nature of the salts [13-14]. Particles with sizes ranging from 5 to 100 nm have been obtained using this method. The addition of chelating organic anions, such as carboxylate ions (e.g. citric, gluconic, or oleic acid) or polymer sur-

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face complexing agents (e.g. dextran, carboxydextran, starch, or polyvinyl alcohol) during the formation of magnetite can help to control the size of the nanoparticles [8].

Reverse micelles and micro-emulsion technology: This method includes amphoteric surfactants to create water-swollen reversed micellar structures in nonpolar solvents. Surfactant molecules may spontaneously form nanodroplets of different sizes, micelles (1-10 nm) or water-in-oil emulsions (10-100 nm) [15-16]. In these nanodroplets, aqueous iron salt solutions are encapsulated by a surfactant coating that separates them from a surrounding organic solution. Thus, this system act as nanoreactor for synthesizing nanoparticles as provides a confinement that limits particle nucleation and growth. The main advantage of the reverse micelle or emulsion technology is the diversity of nanoparticles that can be obtained by varying the nature and amount of surfactant and cosurfactant, the oil phase, or the reacting conditions. In addition, the size of the magnetite particle can be controlled by the temperature and the surfactant concentration [15].

Thermolysis of precursors: Organic solution-phase decomposition of the iron precursor at high temperatures (higher than 200 °C) has been widely used in iron oxide nanoparticle synthesis [8]. This method has improved significantly the control of the mean size, the size distribution and the crystallinity of magnetic iron nanoparticles. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products. Many iron precursors have been tested. For example, Sun and Zeng [17], have prepared monodisperse magnetite nanoparticles with size of 3 to 20 nm by reaction at high-temperature (265 °C) of iron acetylacetonate, $Fe(acac)_3$, in phenyl ether in the presence of alcohol, oleic acid, and oleylamine.

Hydrothermal reactions: Hydrothermal syntheses of Fe_3O_4 nanoparticles have been reported in the literature during the last decade [18-20]. These reactions are performed in aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200 °C. There are two main routes for the formation of magnetite via hydrothermal conditions: hydrolysis and oxidation or neutralization of mixed metal hydroxides. These two reactions are very similar, except that only ferrous salts are used in the first method. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products. In the hydrothermal process, the particle size is controlled mainly through the rate processes of nucleation and grain growth.

Magnetic nanocomposites: Fe_3O_4 nanoparticles can be coated with inorganic material such as silica, gold or silver [21-23]. These coatings not only improve the stability of the nanoparticles in solution but also provide sites for covalent binding with specific ligands to the nanoparticle surface. These nanoparticles have an inner iron oxide core with an outer shell of inorganic materials. For example, the use of silica confers great stability to the nanoparticles dispersion against changing of pH and concentration of electrolytes [24]. Chang et al. [25] prepared three types of nano-scale composites comprised of magnetite, silica and aluminosilicate as SPASMs (i.e., aluminosilicate materials incorporated with superparamagnetic particles) via three sequential steps: formation of magnetite by chemical precipitation, coating of silica on magnetite through the acidification method or the sol–gel route, and development of aluminosilicates via the sol–gel route.

3. Characterization of Fe_3O_4 nanoparticles

Among the methods widely used in the literature for Fe_3O_4 nanoparticle characterization and surface determination are: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Powder X-ray Diffraction (XRD) Technique, Atomic Absorption Spectroscopy (AAS), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Electrical Conductivity Measurement.

Among the methods used for the determination of the size and size distribution of nanoparticles, a few are applicable in various chemical environments, i.e. small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS). One particular advantage of SAXS is that it can be used to analyze dispersions as well as powders or solids, whereas DLS is limited to dilute solutions. Comparing SAXS with an image-guided method like transmission electron microscopy (TEM), SAXS benefits from a higher statistical quality in the size distribution determination providing information about primary particles and aggregates from a single scattering experiment. Additionally, no high vacuum is required, which limits the samples to solid state samples. TEM has its specific benefits as it delivers direct images and local information on size and shape of nanoparticles. Therefore, these two techniques are complementary and combining both methods can lead to superior information with regard to shape and size of nanoparticles in dispersions or powders [26]. A less common technique to obtain a particle size distribution is the analysis with nitrogen sorption. The evaluation according to BET theory (Brunauer–Emmet–Teller) allows obtaining information on the size of non-agglomerated and dense particles [27].

Comparison between the results obtained by the different techniques in the literature seem to support the view that comprehensive information on particle size, size distribution and shape require the use of more than one characterization technique. Each of the techniques has its specific advantages: TEM delivers direct images, from which information on size and shape of nanoparticles is obtained, SAXS is able to measure powders, solids and also particles in solution, DLS is a fast and cheap method to measure a high number of samples, and BET give the size of nanoparticles as a by-product from the main aim of the method, e.g. the determination of phases within a sample or the specific surface. For many nanomateriales it is observed that DLS exceeds SAXS and TEM by a factor of two or higher. Significantly larger values from DLS might be attributed to larger hydrodynamic shells, as a complex shape of particles as well as their aggregation can influence the numerical evaluation from DLS.

Powder XRD and electronic diffraction patterns (ED) are used to determine the crystal structure and characterization of the bulk Fe_3O_4 nanoparticles. Elemental analysis and surface coverage of magnetite particles may be measured by energy dispersive X-ray spectroscopy (SEM/EDS, EDAX). XPS is used for the analysis of the surface chemistry. Raman and Fourier transform infrared (FTIR) spectroscopy have been used to characterize the phase of the magnetic core of magnetite nanoparticles [28-29]. FTIR spectra yield information on the chemical bonds between the Fe_3O_4 core and the organic surface coverage [30].

Because of the peculiar magnetic properties of magnetite, the particles magnetization as a function of temperature and the hysteresis cycle of both magnetite and composite particles is also used for the characterization of the particle. Normally, magnetite nanoparticles exhibit overall magnetic behavior characteristic of soft magnetic particles, with a narrow hysteresis cycle, and a small coercive field and remnant magnetization. The presence of nonmagnetic shells covering the nanoparticles is evidenced by the fact that magnetization is reduced compared to that of pure magnetite and the initial magnetization field dependence is steeped in the latter case [31]. In general, particle intrinsic coercivity (Hc) and the saturation magnetization are determined by vibrating sample magnetometer (VSM) [32]. However, the effective magnetic core size of the particles may be measured by magnetic relaxometry (MRX) investigating the relaxation behavior in liquid suspensions [33].

Mössbauer spectroscopy analysis may also be performed to distinguish crystallographic phases [34]. Magnetite particles exhibit ferromagnetic properties for observation times shorter than the relaxation time, while superparamagnetic properties are exhibited in the opposite case. Since the time of relaxation increases with the particle size, the Mössbauer spectrum of a dispersed system of magnetic nanocrystals is usually a superposition of a Zeeman sextet, corresponding to the large-size ferromagnetic particles, with a superparamagnetic doublet, corresponding to the particles of smaller size. However, since the time of relaxation in the system of interacting superparamagnetic particles can change due to correlation bonds arising between magnetization vectors of neighboring particles, the shape of the Mössbauer spectra depends both, on the inter-particle interaction and on the superparamagnetic properties of an individual particle. Therefore, interpretation of Mössbauer spectra yields information on particle size and on strong inter-particle interactions [34].

FTIR spectra yield information on the chemical bonds between the Fe_3O_4 core and the organic surface coverage [30].

Thermogravimetric and differential thermal analyses are essential for the determination of the weight of surfactant covering the particle surface per mass of magnetite, and for the determination of desorption binding heat of the covering layers [35-36].

Given that the surface properties of oxides are extremely sensitive to pH variations in the dispersion medium, determinations of the electrophoretic mobility and zeta-potential of the particles are also of importance for their technological applications [28].

4. Metal removal

In the present section we will describe recent literature results related to the application of magnetite nanomaterials for the removal of heavy metals and metalloids from water, mainly copper, chromium, mercury and arsenic.

Yantasee et al. [12] prepared superparamagnetic iron oxide (Fe_3O_4) nanoparticles with a surface functionalization of dimercaptosuccinic acid (DMSA) and employed them as an effective sorbent material for toxic soft metals such as Hg(II), Ag(I), Pb(II), Cd(II), and Tl(I) ions which effectively bind to the DMSA ligands and for As(III) which binds to the iron oxide lattices. The nanoparticles could be separated from solution within a minute with a 1.2 T magnet. The authors compared the chemical affinity, capacity, kinetics, and stability of the magnetic nanoparticles to those of conventional resin based sorbents (GT-73), activated carbon, and nanoporous silica (SAMMS) of similar surface chemistries in river water, groundwater, seawater, and human blood and plasma. DMSAFe_3O_4 showed a capacity of 227 mg of Hg/g, a 30-fold larger value than that of GT-73.

Singh et al [37] prepared magnetite nanoparticles functionalized with carboxyl (succinic acid), amine (ethylenediamine) and thiol (2,3-dimercaptosuccinic acid) groups These nanoparticles were used for removal of toxic metal ions (Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II) and As(III)) and bacterial pathogens (Escherichia coli) from water.

Liu et al. [38] developed humic acid (HA) coated Fe_3O_4 nanoparticles (Fe_3O_4/HA) for the removal of toxic cations such as Hg(II), Pb(II), Cd(II), and Cu(II) from water. Fe_3O_4/HA were prepared by the coprecipitation method. TOC and XPS analyses showed that the as-prepared Fe_3O_4/HA contains ~11% (w/w) of HA fractions abundant in O and N-based functional groups. TEM images and laser particle size analysis revealed that the Fe_3O_4/HA (with ~10 nm Fe_3O_4 cores) aggregated in aqueous suspensions to form aggregates with an average hydrodynamic size of ~140 nm. Sorption of the heavy metals to Fe_3O_4/HA reached equilibrium in less than 15 min, and agreed well to the Langmuir adsorption model with maximum adsorption capacities ranging from 45 to 100 mg/g. The Fe_3O_4/HA was able to remove over 99% of Hg(II) and Pb(II), and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH.

Badruddoza et al. [39] fabricated carboxymethyl-β-cyclodextrin modified Fe_3O_4 nanoparticles (CMβCD-MNPs) for removal of copper ions from aqueous solution by grafting CMβCD onto the magnetite surface via carbodiimide method. The characteristics results of FTIR, TEM, TGA and XPS show that CM-β-CD is grafted onto Fe_3O_4 nanoparticles. The grafted CM- β -CD on the Fe3O4 nanoparticles contributes to an enhancement of the adsorption capacity because of the strong abilities of the multiple hydroxyl and carboxyl groups in CM- β -CD to adsorb metal ions. The adsorption of Cu(II) onto CMCD-MNPs was found to be dependent on pH and temperature. The thermodynamic parameters reveal the feasibility, spontaneity and exothermic nature of the adsorption process. FTIR and XPS reveal that Cu(II) adsorption onto CMCD-MNPs mainly involves the oxygen atoms in CM-β-CD to form surface-complexes. In addition, the copper ions can be desorbed from CMCD-MNPs by citric acid solution with 96.2% desorption efficiency and the CMCD-MNPs exhibit good recyclability.

Goon et al. [40] studied the controlled adsorption of polyethylenimine (PEI) onto 50 nm crystalline magnetite nanoparticles (Fe_3O_4 NPs) and how these PEI-coated Fe_3O_4 NPs can be used for the magnetic capture and quantification of ultratrace levels of free cupric ions. The authors were able to systematically control the amount of PEI adsorbed onto the Fe_3O_4 mag-

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netic nanoparticle surfaces by varying the concentration of polymer during the adsorption process. This work demonstrated that the NPs ability to bind with copper is highly dependent on the amount of PEI adsorbed on the NP surface. It was found that PEI-coated Fe_3O_4 NPs were able to capture trace levels (~2 ppb) of free cupric ions and concentrate the ions to allow for detection via ICP-OES. They also showed that due to the amine-rich structure of PEI, the PEI-coated Fe_3O_4 NPs selectively adsorb toxic free cupric ions but not the less toxic EDTA complexed copper.

Chou and Lien [41] prepared dendrimer-conjugated magnetic nanoparticles (Gn-MNPs) combining the superior adsorbent of dendrimers with magnetic nanoparticles (MNPs) for effective removal and recovery of Zn(II). The adsorption efficiency increases with increasing pH. At pH less than 3, Zn(II) is readily desorbed. Hence, the Gn-MNPs can be regenerated using a diluted HCl aqueous solution (0.1 M) and Zn(II) can be recovered in a concentrated form. It was found that the Gn-MNPs still retained the original removal capacity of Zn(II) after 10 consecutive adsorption–desorption stages.

Wang et al. [42] developed amino-functionalized Fe_3O_4@SiO_2 magnetic nanomaterial with a core–shell structure to remove heavy metal ions from aqueous media. The structural, surface, and magnetic characteristics of the nanosized adsorbent were investigated by elemental analysis, FTIR, N_2 adsorption–desorption, transmission electron microscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, vibrating sample magnetometry, thermogravimetric analysis, and zeta-potential measurement. The amino-functionalized Fe_3O_4@SiO_2 nanoadsorbent exhibited high adsorption affinity for aqueous Cu(II), Pb(II), and Cd(II) ions, resulting from complexation of the metal ions by surface amino groups. Moreover, the adsorption affinity for heavy metal ions was not much affected by the presence of a cosolute of humic acid or alkali/earth metal ions (Na^+, K^+, etc.). The metal-loaded Fe_3O_4@SiO_2–NH_2 nanoparticles could be recovered readily from aqueous solution by magnetic separation and regenerated easily by acid treatment.

Shishehbore et al. [43] reported a method for the pre-concentration of trace heavy metal ions in environmental samples. The method is based on the sorption of Cu(II), Cd(II), Ni(II) and Cr(III) ions with salicylic acid as chelate on silica-coated magnetite nanoparticles. The adsorbent was characterized by XRD, SEM, BET and FT-IR measurements. The method was successfully applied to the evaluation of these trace and toxic metals in various waters, foods and other samples.

Wu et al. [44] showed that Fe_3O_4 can be used to disperse nano-Fe^0 and thus sustain Cr(VI) mitigation by nano-Fe^0. Fe^0 nanoparticles can attach to the surface of Fe_3O_4 by addition of large Fe_3O_4-NPs into the reaction solution during the preparation of Fe^0 nanoparticles. The introduction of Fe_3O_4 prevents the aggregation of Fe^0 nanoparticles and keeps the high efficiency of the nanocomposite for Cr(VI) reduction. Their results suggest that higher proportions of Fe_3O_4 in the nanocomposites could increase the rate of Cr(VI) reduction, and the optimal ratio of Fe_3O_4:Fe^0 for Cr(VI) reduction was determined to be 40:1. The authors also showed that solution pHs significantly affect the rate of Cr(VI) reduction, with reactions occurring faster under acidic or neutral than basic conditions.

Cutting et al. [45] showed that nanomagnetites produced by the bacterial reduction of schwertmannite powder were more efficient at reducing Cr(VI) than either ferrihydrite "gel"-derived biomagnetite or commercial nanoscale Fe_3O_4. Schwertmannite-derived biomagnetite proved capable of retaining more (~20%) ^{99}mTc(VII) than ferrihydrite-derived biomagnetite, confirming that the production of biomagnetite can be fine-tuned for efficient environmental remediation through careful selection of the Fe(III) mineral substrate supplied to Fe(III)-reducing bacteria.

Wang et al. [46] investigated As(V) speciation resulting from different sorption processes on magnetite nanoparticles, including both adsorption and precipitation. Using X-ray absorption fine structure (XAFS) spectroscopy and transmission electron microscopy (TEM), they conclude that As(V) could form complexes at the surfaces of the small nanoparticles and could be progressively incorporated in their structure with increasing As loading. These results provide some of the fundamental knowledge about As(V)-magnetite interactions that is essential for developing effective water treatment technologies for arsenic.

Chen et al. [47] synthesized multiwalled boron nitride nanotubes (BNNTs) functionalized with Fe_3O_4 nanoparticles (NPs) for arsenic removal from water solutions. Adsorption experiments conducted at neutral pH (6.9) and room temperature using the developed nanocomposites revealed effective arsenic (V) removal. The Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms were tested for a range of As(V) initial concentrations from 1 to 40 mg/L under the same conditions. The equilibrium data well fitted all isotherms, indicating that the mechanism for As(V) adsorption was a combination of chemical complexation and physical electrostatic attraction with a slight preference for chemisorption.

Chowdhury and Yanful [48] investigated the adsorption of arsenic and chromium by mixed magnetite and maghemite nanoparticles from aqueous solution. These authors employed a commercially grade nanosize 'magnetite', later identified in laboratory characterization to be mixed magnetite-maghemite nanoparticles in the uptake of arsenic and chromium from different water samples. Their results showed 96-99% arsenic and chromium uptake under controlled pH conditions. The maximum arsenic adsorption occurred at pH 2 with values of 3.69 mg/g for As(III) and 3.71 mg/g for As(V) when the initial concentration was kept at 1.5 mg/L for both arsenic species, while at the same pH Cr(VI) sorption capacity was 2.4 mg/g with an initial Cr(VI) concentration of 1 mg/L. Their results also showed the limitation of arsenic and chromium uptake by the nano-size magnetite-maghemite mixture in the presence of a competing anion such as phosphate.

Yang et al. [49] studied the effect of Zn(II) on both the kinetic and equilibrium behavior of arsenic adsorption to magnetite nanoparticles in the pH range 4.5-8.0. At pH 8.0, adsorption of both arsenate and arsenite to magnetite nanoparticles was significantly enhanced by the presence of small amount of Zn(II) in the solution. The adsorption rate also increased signifi-

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cantly in the presence of Zn(II). The adsorption enhancement effect of Zn(II) was not observed at pH 4.5-6.0, nor with ZnO nanoparticles, nor with surface-coated Zn-magnetite nanoparticles. The enhanced arsenic adsorption in the presence of Zn(II) cannot be due to reduced negative charge of the magnetite nanoparticles surface by adsorption of Zn(II) because other cations, such as Ca(II) and Ag(I), failed to enhance arsenic adsorption. Formation of a ternary surface complex by zinc, arsenic and magnetite nanoparticles was proposed as a possible mechanism controlling the observed zinc effect. Zinc-facilitated adsorption provides further advantage for magnetite nanoparticle-enhanced arsenic removal over conventional treatment approaches.

Zhang et al. [50] showed that the application of starch as a stabilizer in preparation of the Fe_3O_4 particles is able to efficiently reduce particle aggregation, and thus, effective particle size, resulting in much greater specific surface area and adsorption sites. Moreover, the presence of starch leads to the formation of more effective adsorbing sites on magnetite particle surfaces. By employing the XAFS technique, the authors showed that arsenate is adsorbed on starch-stabilized magnetite nanoparticles mainly as inner-sphere bidentate and monodentate complexes. The coordination numbers of As-Fe binding increases with increasing starch concentration, which indicates that the arsenate is more firmly adsorbed at higher starch concentrations.

An et al. [51] prepared and tested a new class of starch-bridged magnetite nanoparticles for removal of arsenate from spent ion exchange brine. Maximum uptake was observed within a pH range of 4-6. The Langmuir capacity coefficient was determined to be 248 mg/g at pH 5.0. The final treatment sludge was able to pass the TCLP (Toxicity Characteristic Leaching Procedure) based leachability of 5 mg/L as As.

All the results described in this section are summarized in Table 1.

5. Perspectives

As illustrated in this book chapter, the use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields. In particular, technologies based on the utilization of magnetite nanoparticles for the removal of heavy metals from wastewaters are under active development as highly effective, efficient and economically viable nanoadsorbents. Among the main advantages of these nanomaterials is the possibility of surface modifications with different organic or inorganic coating agents to allow the removal of a wide range of heavy metals with specificity. However, the application of these methods is still limited in the early stage and more research in the field is certainly necessary.

In conclusion, there is much recent interest in the use of engineered magnetite nanoparticles in wastewater treatment. However, uncertainties over the health impacts and environmental fate of these nanomaterials need to be addressed before their widespread application. Research on their fate and impact in the environment is required due to the discharges already occurring to the environment.

Synthesis Method	Coating agents	Surface functionalized group	Metal removed	Ref.
Thermolysis of precursors	dimercaptosuccinic acid	Thiol group	Hg(II), Ag(I), Pb(II), Cd(II), Tl^+	[12]
Co-precipitation	succinic acid	Carboxylic group	Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), As(III)	[37]
Thermolysis of precursors	ethylenediamine	Amine group		
Thermolysis of precursors followed by ligand exchange process	dimercaptosuccinic acid	Thiol group		
Co-precipitation	Humic acid	Carboxylic and phenolic group	Hg(II), Pb(II), Cd(II), Cu(II)	[38]
Co-precipitation	carboxymethyl-β-cyclodextrin	Carboxylic group	Cu(II)	[39]
Crystallization from ferrous hydroxide gels	polyethylenimine	Amine group	Cu(II)	[40]
Co-precipitation	dendrimers	Amine group	Zn(II)	[41]
Co-precipitation followed by a sol-gel process using sodium silicate (Fe_3O_4@SiO_2)	(3-aminopropyl) trimethoxysilane	Amine group	Pb(II), Cd(II), Cu(II)	[42]
Co-precipitation followed by hydrolysis of TEOS, (Fe_3O_4@SiO_2)	salicylic acid functionalized silica	Carboxylic group	Cu(II), Cd(II), Ni(II), Cr(III)	[43]
Stabilization of Fe^0 nanoparticles with Fe_3O_4	-	-	Cr(VI)	[44]
Bacterial reduction of schwertmannite	-	-	Cr(VI), Tc(VII)	[45]
Co-precipitation	-	-	As(V)	[46]
BNNTs functionalized with Fe_3O_4 nanoparticles	-	-	As(V)	[47]
Commercially available magnetite-maghemite mixture nanoparticles	-	-	As(V), As(III), Cr(VI)	[48]
Commercially available magnetite.	-	-	As(V), As(III)	[49]
Modification of co-precipitation method	Starch	hydroxyl group	As(V)	[50]
Modification of co-precipitation method	Starch	hydroxyl group	As(V)	[51]

Table 1. Application of magnetite nanomaterials for the removal of heavy metals from water.

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