# Chapter 10 Removal of Heavy Metal Ions Using Magnetic Materials



Soh-Fong Lim, Agnes Yung-Weng Lee, S. N. David Chua, and Bee-Huah Lim

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Abstract Heavy metal ions contaminate water environment through point sources and nonpoint sources. Heavy metal ions are categorized as inorganic contaminants by both the WHO and the USEPA. The heavy metal ions are increasingly being introduced into the environment as pollutants and contaminants resulting from human activities.

Magnetic particles for water treatment applications have received considerable attention from researchers due to high separation efficiency. The magnetic particles behave similar to or even better than various commercial adsorbents. The magnetic

S.-F. Lim (⊠) · A. Y.-W. Lee · S. N. D. Chua

Faculty of Engineering, Universiti Malaysia Sarawak, Sarawak, Malaysia e-mail: sfl[im@unimas.my](mailto:sflim@unimas.my); [15020101@siswa.unimas.my;](mailto:15020101@siswa.unimas.my) [csndavid@unimas.my](mailto:csndavid@unimas.my)

B.-H. Lim

Fuel Cell Institute, Universiti Kebangsaan Malaysia, Bangl, Selangor Darul Ehsan, Malaysia e-mail: [beehuah@ukm.edu.my](mailto:beehuah@ukm.edu.my)

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particles also exhibit high selectivity for the target pollutants from the environment besides enabling ease of operation for reducing the particle separation steps from the flowing stream. A comprehensive and systematic understanding of synthesis and surface modifications of magnetic particles is significant to enhance their practicability in environmental technology. Although high removal performance and reactivity can be achieved by smaller particle size, the stability, toxicity, and recovery of the particles magnetically could be challenging.

In contrast, the active surface of magnetic particles may be forfeited, while surface modifications stabilize and reduce the toxicity of the particles. Reliable surface modifications are necessarily needed for the increment of the number of active sites to remove the heavy metals. For successful environmental applications of the magnetic particles, modification on the magnetic particles is principally crucial to balance the effects on their reactivity, capacity, and reusability.

Keywords Heavy metal ions · Magnetic particles · Contaminants · Heavy metal · Adsorbent · Pollution · Removal · Separation · Magnetic sorption technology

## Nomenclature





## <span id="page-2-0"></span>1 Introduction

The conventional adsorbents, including activated carbon, silica gel, zeolite, and clay minerals, which have been widely used to remove heavy metals suffer from high generation costs. The attention was then shifted to the use of adsorbent derived from agricultural waste such as sawdust, orange peel, ground coffee, and almond shell for the heavy metal removal due to their low cost and high abundance. Although these adsorbents were reported to be very useful for water purification, separation of these powdered adsorbents from wastewater in a continuous flow system tends to be very challenging. In recent years, magnetic sorption technology has become one of the emerging technologies in solving environmental problems. Exploration of magnetic materials permits the tendency of applications in water treatment extensively. After the usage, the magnetic particles which act as adsorbent are separated from the solution by magnetic force. Thus, it receives considerable attention due to ease in separation after usage.

## <span id="page-2-1"></span>2 Magnetic Materials

Magnetic materials are materials that display magnetic response in the presence of a magnetic field. Mitchell [\[1](#page-14-1)] claimed that magnetic materials are categorized into two major groups: (1) soft magnetic materials and (2) hard magnetic materials based on their magnetic properties such as remanence  $(B_r)$ , coercive force  $(H_c)$ , and Curie

<span id="page-3-1"></span>

Fig. 10.1 Developments of (a) soft magnetic material and (b) hard magnetic material. (Source: Dobrzański et al. [[7\]](#page-14-7))

temperature  $(T_c)$ . In other words, magnetic materials are classified as being magnetic or nonmagnetic. A material which is easily magnetized and demagnetized is referred to as soft magnetic material, whereas hard magnetic material is challenging to be demagnetized [[2,](#page-14-2) [3\]](#page-14-3). The hard magnetic materials remain strongly magnetized after the applied magnetic field is removed and become to be permanent magnets. Iron, steel, and alloy bars are the most common magnetic materials.

Typically, soft magnetic materials denote permeable magnets or electromagnets. Electromagnets (artificial magnets) are constituted of soft-iron cores around which are wound coils of insulated wire [\[4](#page-14-4)]. The core becomes magnetized when an electric current flows through the coil; the core loses most of the magnetism when the current ceases to flow. The soft magnetic materials have coercive force less than 1000 A/m and high magnetic permeability. Examples are Si steels, permalloys, Mn-Zn soft ferrites, amorphous Fe-based, and Co-based.

On the other hand, hard magnetic materials denote permanent magnet. Permanent magnets as another type of artificial magnets are hardened steel or certain alloys that have been permanently magnetized. They are distinctive for their excellent magnetic properties such as remanence and coercive force [[5,](#page-14-5) [6\]](#page-14-6). Examples of this material include Co and W steels, alnico bars, ferrite magnets, magnets from the cobalt alloys with the rare earth group elements, and magnets from the Nd-Fe-B alloys. The evolution of the magnetic material is illustrated in Fig. [10.1.](#page-3-1) Despite that, some commercially available magnetic materials are tabulated in Table [10.1](#page-4-0) with their respective characteristics.

#### <span id="page-3-0"></span>3 Aspect of Magnetism

Magnetism is a remarkable physical property that can be exploited in water treatment by manipulating the physical properties of the pollutants in water. In combination with other processes, it facilitates the efficiency of water purification. The concept of the use of magnetism for water treatment such as anti-scaling technique in boilers, pipelines in factories, coagulation, and biological processes has been extensively reported.

| Characteristic  | Ceramic   | Alnico    | <b>Bonded</b><br>$Nd$ -Fe-B | $Sm-C0$         | Nd-<br>$Fe-B$  |
|---|-----------|-----------|-----------------------------|-----------------|----------------|
| Highest energy product, $BH_{\text{max}}$<br>$(kJ/m^3)$ | 32        | 59        | 79                          | 254             | 382            |
| Maximum operating temperature<br>$(^{\circ}C)$          | 300       | 550       | 150                         | 300             | 150            |
| Resistance to demagnetization                           | Moderate  | Low       | High                        | Very<br>high    | High           |
| Corrosion resistance [uncoated]                         | Excellent | Excellent | Good                        | Good            | Poor           |
| Mechanical toughness                                    | Moderate  | Tough     | Moderate                    | Very<br>brittle | <b>Brittle</b> |
| Relative cost   | Very low  | Moderate  | High                        | Very<br>high    | High           |

<span id="page-4-0"></span>Table 10.1 Comparison of key characteristics of commercially available magnetic materials

Source: Hatch and Stelter [[8\]](#page-14-9)

<span id="page-4-1"></span>

Fig. 10.2 The periodic table showing the types of the magnetic behavior of each element at room temperature. (Source: Harris and Willams [\[2](#page-14-2)])

Magnetism is defined as a phenomenon associated with magnetic fields. It has the power to attract magnetic materials such as iron, steel, nickel, or cobalt. There are five types of magnetism: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism [[9,](#page-14-8) [10](#page-15-0)]. In magnetic materials, a magnetic field is formed due to the movement of electrons within the material. However, ferromagnetic materials exhibit magnetism on a microscopic scale even without an applied field [\[11](#page-15-1)].

Based on Fig. [10.2,](#page-4-1) diamagnetism and paramagnetism account for the magnetic behavior of most of the elements in the periodic table at room temperature. These elements are indicated as nonmagnetic material. Meanwhile, those elements which are referred to as magnetic are categorized as ferromagnetic. Another type of

| Type of magnetism  | Atomic/magnetic behavior  |   | Susceptibility, $\chi$  | Typical materials   |  |
|--------------------|---|---|---|---|--|
| Diamagnetism       | Atoms have no<br>magnetic moment  | $^{\circ}$<br>$^{\circ}$<br>$^{\circ}$<br>$\bullet$ $\bullet$ | Small and<br>negative   | Organic mate-<br>rials.<br>superconducting<br>metals, and other<br>metals       |  |
| Paramagnetism      | Atoms have ran-<br>domly oriented<br>magnetic<br>moments                        | $\bullet$ $\bullet$   | Small and positive  | Alkali and tran-<br>sition metals.<br>rare earth<br>elements                    |  |
| Ferromagnetism     | Atoms have paral-<br>lel aligned mag-<br>netic moments                          |   | Large and posi-<br>tive, function of<br>applied field,<br>microstructure<br>dependent | Some transition<br>metals (Fe, Ni,<br>Co) and rare<br>earth metals (Gd)         |  |
| Antiferromagnetism | Atoms have<br>mixed parallel and<br>antiparallel<br>aligned magnetic<br>moments |   | Small and positive  | Salts of transi-<br>tion elements<br>(MnO)                                      |  |
| Ferrimagnetism     | Atoms have anti-<br>parallel aligned<br>magnetic<br>moments                     |   | Large and posi-<br>tive, function of<br>applied field,<br>microstructure<br>dependent | Ferrites<br>(MnFe <sub>2</sub> O <sub>4</sub> )<br>$ZnFe2O4$ ) and<br>chromites |  |

<span id="page-5-1"></span>Table 10.2 Classification of magnetic material

Source: Mitchell [\[1](#page-14-1)]

magnetism observed in pure elements is antiferromagnetism. Additionally, magnetic materials can also be classified as ferromagnetic. This material is not detected in any pure element but can be found in compounds such as the mixed oxides (ferrites).

The magnetic properties of materials are mostly determined by their structure and the several magnetic interactions between neighboring atoms. There are only 16 elements that have magnetically ordered ground state, and all but oxygen belongs to the 3d or 4f transition series [[12\]](#page-15-2). The magnetic materials are divided into few categories in terms of their magnetic behavior as presented in Table [10.2](#page-5-1).

## <span id="page-5-0"></span>3.1 Diamagnetism

Diamagnetism which is usually very weak is a fundamental property of all matter. In a diamagnetic material, the atoms have no net magnetic moment in the absence of applied field [[13,](#page-15-3) [14\]](#page-15-4). Nevertheless, a negative magnetization is produced in the opposite direction from the applied magnetic field, resulting in negative susceptibility of approximately  $-10^{-6}$ . The susceptibility of the diamagnetic materials is temperature independent. These materials are very weakly affected by magnetic

fields. Therefore, the contribution of diamagnetism is insignificant unless it is the only magnetism present. Materials such as acetone, alumina, carbon dioxide, copper, lead, quartz, silver, and water are diamagnetic.

#### <span id="page-6-0"></span>3.2 Paramagnetism

Paramagnetism results from the magnetic forces on unpaired electrons. In paramagnetic materials, some of the atoms or ions have a net magnetic moment due to unpaired electrons in partially filled orbitals [[15\]](#page-15-5). Under the influence of an applied field, there is a partial alignment of the atomic magnetic moments parallel to the direction of the field, resulting in a net positive magnetization and positive susceptibility lies between  $10^{-3}$  and  $10^{-5}$ . The net magnetization of the atom is small due to random ordering of moments but more significant than the diamagnetic contribution. Similar to diamagnetism, the magnetization is zero when the field is removed. Materials such as clay, carbonate, silicate, sodium, and platinum are paramagnetic.

#### <span id="page-6-1"></span>3.3 Ferromagnetism

Ferromagnetism occurs when there are exchange interactions among the electrons in the material. In ferromagnetic materials, the atomic magnetic moments align parallel or antiparallel to each other due to an interaction between neighboring moments or mutual reinforcement of the dipoles. Unlike paramagnetic materials, the atomic moments in these materials exhibit powerful exchange forces, equivalent to a field on the order of 1000 Tesla or around 100 million times the strength of the earth's field [[16\]](#page-15-6). The parallel alignment of moments results in large net magnetization even in the absence of a magnetic field, giving high susceptibility approaching  $10^6$ . Above the Curie temperature, ferromagnetic materials exhibit paramagnetic behavior. Iron, nickel, and cobalt and many of their alloys are typical ferromagnetic materials.

## <span id="page-6-2"></span>3.4 Antiferromagnetism

Antiferromagnetism occurs when the magnetic moments produced in neighboring atoms line up in opposition to one another in the magnetic field. This magnetic ordering cancels out the magnetic moments, and net magnetization is zero. The magnetic susceptibility is positive and small, approximately  $10^{-5}$  to  $10^{-3}$ . Moreover, these materials exhibit paramagnetic behavior like ferromagnetic materials above a transition temperature, Néel temperature [[17\]](#page-15-7). Cobalt oxide, chromium, manganese chloride, manganese oxide, and nickel oxide are examples of antiferromagnetic materials where chromium is the only element exhibiting antiferromagnetism in the periodic table at room temperature.

#### <span id="page-7-0"></span>3.5 Ferrimagnetism

Ferrimagnetism is observed in more complex crystal structures than pure elements. The magnetic structure is composed of two magnetic sublattices separated by oxygen. In a ferromagnetic material, some atoms are in parallel alignment while others are in antiparallel alignment. The magnetic moments of the sublattices are not equal and result in a net magnetic moment. The magnetic susceptibility is similar to ferromagnetic materials, but ferrimagnetic materials usually have lower saturation magnetizations. The material breaks down into magnetic domains where the diluting effect of those atoms in antiparallel alignment keeps the magnetic strength of this material generally less than that of purely ferromagnetic solids, a relatively low magnitude as only one-eighth of the ions contribute to the magnetization of the material  $[2]$  $[2]$  $[2]$ . A well-known ferrimagnetic material is a magnetite,  $Fe<sub>3</sub>O<sub>4</sub>$ .

## <span id="page-7-1"></span>4 Synthesis of Magnetic Particles

According to Thanh [[18\]](#page-15-8), the materials fabricated in the laboratory are mainly composed of magnetite ( $Fe<sub>3</sub>O<sub>4</sub>$ ), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), greigite ( $Fe<sub>3</sub>S<sub>4</sub>$ ), and several types of ferrites (MeO Fe<sub>2</sub>O<sub>3</sub>, where Me = Ni, Co, Mg, Zn, Mn, and others). Iron oxide nanoparticles (Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) have shown the most promise as potential environmental magnetic sensing materials by way of the synthesis, tuning of physical properties, and surface functionalization [[19\]](#page-15-9).

Numerous methods of synthesizing magnetic particles such as coprecipitation, hydrothermal, thermal decomposition, and sol-gel method have been so well established. Some common methods to synthesize magnetic iron oxide nanoparticles for versatility in tuning the characteristics of the nanomaterials are described in Table [10.3](#page-8-0). Furthermore, common inorganic coatings for magnetic nanoparticles are presented in Table [10.4.](#page-9-1)

In order to be successfully exploited in applications, prerequisites such as good dispersibility, nano-sized distribution, highly uniformed superparamagnetic properties, hydrophilic surface with different functional groups, as well as homogenous physical and chemical properties are emphasized for the synthesis of iron oxide nanoparticles [\[20](#page-15-10)]. The synthesis of the magnetic particles is divided into two groups: in situ methods and ex situ methods.

Synthesis methods Size (nm) Shape Benefits Drawbacks Coprecipitation 15–200 Spherical/ rhombic Conventional Low reaction temperature Rapid synthesis with high yield Not suitable for the preparation of highly pure, accurate stoichiometric phase Unprotected magnetite vulnerable to oxidation or aggregation Hydrothermal 27 Spherical Highly crystalline Pure iron oxide nanoparticles Simple and scalable Good morphological control Hydrothermal slurries are potentially corrosive Harsh reaction conditions Long reaction times Thermal decomposition 4–20 Spherical Reasonable control of size and shape with high yields Narrow size distribution Ability to quickly make different mixed metal oxide nanoparticles Complicated and harsh preparation procedures The surfactant used hinders subsequent surface modification High decomposition temperature Microemulsion  $|4-12|$  Spherical (inverted), cubic, lamellar phases, cylindrical micelles A simple and versatile method Reproducible Using surfactant limits particle nucleation, growth, and aggregation Better morphological control Homogenous particle size distribution Low crystallinity of SPIONs on a large scale due to low-temperature usage Complicated purification methods for separation of surfactants Poor yield A large number of solvents required Sol-gel  $\vert$  20–200  $\vert$  Spherical Pure amorphous phases Homogeneity and phase purity Low-temperature procedure Moderate morphological control Useful for hybrid nanoparticles' fabrication High cost Close monitoring is needed due to the several steps Challenging to obtain monodispersed nanoparticles through hydrolytic sol-gel route Broad size distribution Sonochemical 5–30 Spherical Shortened reaction time Uniform particle size Higher surface area Better thermal stability Improved phase purity Particle agglomeration Not energy efficient Particle size tunability is not readily achievable Use of organometallic precursors causes in vivo toxicity

<span id="page-8-0"></span>Table 10.3 The comparison between various common synthesis methods of magnetic iron oxide nanoparticles

| Inorganic<br>coating |   |   |  |
|----------------------|---|---|--|
| material             | Conditions                                    | <b>Benefits</b>   | <b>Drawbacks</b>   |
| <b>Silica</b>        | Sol-gel/Stöber<br>method, reverse<br>micelle  | Good dispersion in<br>aqueous solutions<br>Surface silanols for<br>easy siloxane modifi-<br>cation<br>Ability to incorporate<br>dyes and <i>quantum</i><br>dots       | Drastic loss of core magnetic<br>character                               |
| Carbon               | Hydrothermal,<br>pyrolysis                    | Biocompatible<br>High chemical and<br>thermal stability   | Few synthetic methods/lack of<br>understanding of formation<br>mechanism |
| Gold                 | Microemulsion.<br>solution-based<br>reduction | Chemical inertness<br>Thiol surface ligand<br>modification<br>Minor loss of core<br>magnetic susceptibil-<br>ity<br>Surface plasmon<br>peaks for optical<br>detection |  |
| Silver               | Solution-based<br>reduction                   | Surface plasmon<br>peaks for optical<br>detection   | Difficult functionalizing with the<br>Ag surface                         |
| CdSe or<br>CdS       | Solution-based<br>shell growth                | Tunable fluorescent<br>shell  |  |

<span id="page-9-1"></span>Table 10.4 Common inorganic coatings for magnetic nanoparticles

Source: Kumar [\[24\]](#page-15-13)

# <span id="page-9-0"></span>4.1 In Situ Methods

In situ methods refer to the formation of nanostructures from precursor with the presence of another phase material [\[21](#page-15-11), [22\]](#page-15-12). The most common method for the synthesis of magnetic particles in the literature is the coprecipitation method. In this method, divalent and trivalent iron salts are condensed in the presence of hydroxide bases. This method is relatively simple, cheap, and reproducible and results in high yield besides keeping the surface of particles free for any subsequent functionalization. However, the particles obtained in the first stage might agglomerate due to the neutralization of counter cations such as  $Na<sup>+</sup>$  and the negative charge of  $FeO<sup>-</sup>$  groups on the surface. Moreover, the pH value and the required time to accomplish the transformation of the particle crystal structure are the crucial factors for the synthesis of iron oxides.

Other than that, hydrothermal is another method that has been investigated extensively for the synthesis of magnetic nanoparticles. The hydrothermal method is a process where the iron precursors in aqueous solution are heated at high temperature and pressure followed by crystallization of the dissolved material from the fluid [\[23](#page-15-14)]. The water can be replaced by other polar or nonpolar solvents such as benzene. The combination of microwave and hydrothermal method reported for the preparation of superparamagnetic iron oxide nanoparticles is advantageous for scaleup and fabrication of uniform particles.

#### <span id="page-10-0"></span>4.2 Ex Situ Methods

Ex situ methods refer to the blending of pre-synthesized nanostructures with polymer using specific techniques such as ball milling, melt blending, and thermal curing. Unlike in situ methods, it is relatively challenging to handle the nanoparticle agglomeration due to the high surface energy of nanoparticle in preparing highperformance magnetic particles.

#### <span id="page-10-1"></span>5 Magnetic Separation for Water Purification

Ideal water purification techniques at a low cost have attracted broad interest to be affordable for developing countries as well. Adsorption technology using an adsorbent satisfies the requirement due to its high performance, ease of operation, and insensitivity to toxic substances [\[25](#page-15-15)]. An optimal adsorbent ought to have the following characteristics: (1) high performance, (2) fast kinetics, (3) cost-efficient, (4) environmentally friendly, (5) reusability, and (6) ease of separation to be applied commercially. The most problematic issue for the removal process is the effectiveness of particle separation from aqueous solution. Water purification process has to implicate recyclable materials for successive treatment cycles and evade generation of secondary waste on an industrial scale. Among the adsorbent materials established, the feasibility of magnetic nano-adsorbents that have a high surfaceto-volume ratio, tunable morphology, and excellent removal performance besides the magnetism property shows the most promising application for water and wastewater treatment systems. It is anticipated that magnetic separation can emerge to be a more cost-effective and expedient process for separating tiny powdered particles than sophisticated membrane filtration.

In the year 1995, magnetic ion exchange resins (MIEX) with the magnetic beads were introduced for the removal of natural organic matter [[26\]](#page-15-16). Later, the removal of bromide ion was claimed to varying degrees by using MIEX, but the process was highly dependent on the alkalinity of the water and concentrations of the competing ion [\[27](#page-15-17)]. The small resin beads with a high surface area allow rapid exchange kinetics of selective ions, enabling a suitable usage in a continuous process. Agglomeration of the magnetic beads leads to flocculation, which allows higher settling velocity than for the single particles or fluidization at higher hydraulic loading rates.

On the application of an external magnetic field, the magnetic adsorbents can be rapidly and easily separated from water due to the presence of the metal components which are oxides of metals such as Fe, Co, Ni, and Cu in the adsorbent. Since magnetic particles were modified with polymer, carbon nanotubes deserve due attention to be used commercially for water treatment due to chemical stability, mechanical and thermal stability, and high surface area.

In addition, spinel ferrite magnetic materials with the general structural formula  $MFe<sub>2</sub>O<sub>4</sub>$  (M = Ca, Co, Cu, Mg, Mn, Ni, Zn) are becoming more popular for remediation of metal ions due to their tunable sizes, diverse structures, high surface areas, excellent chemical and thermal stabilities, ease of separation, high sorption performance, and wide pH ranges [[49\]](#page-16-0). A ferromagnetic  $NiFe<sub>2</sub>O<sub>4</sub>$  which is synthesized by a sol-gel method using egg white shows high adsorption capacity for  $Cu^{2+}$ .  $Cr^{4+}$ , and  $Ni^{2+}$  because its 3D interconnected porous structure was reported to keep high removal efficiency (>97%) during seven reusable cycles [[28\]](#page-15-18). Some other findings on the removal of heavy metals by using magnetic particles are presented with their respective synthesis methods in Table [10.5](#page-11-0).

| Magnetic particles  | Pollutants                                    | Synthesis<br>methods                   | References         |
|---|---|--|--------------------|
| Maghemite nanoparticles   | $Cr^{\overline{6+}}$                          | Sol-gel                                | $\left[29\right]$  |
| Carbon nanotubes-iron oxide magnetic<br>composites  | $Cu^{2+}$ , $Pb^{2+}$                         | Catalytic<br>pyrolysis                 | $\lceil 30 \rceil$ |
| Magnetic alginate microcapsules containing the<br>extractant Cyanex 272                                     | $\overline{\mathrm{Ni}^{2+}}$                 | Coprecipitation                        | [31]               |
| Alginate encapsulated magnetic sorbent  | $As(V)$ ,<br>organic arse-<br>nate, $Cu^{2+}$ | Encapsulation                          | $[32 - 34]$        |
| Zirconium-based magnetic sorbent  | As(V)   | Coprecipitation                        | $\lceil 21 \rceil$ |
| Thiourea-modified magnetic chitosan<br>microspheres   | $Cu^{2+}$ , Hg <sup>2+</sup> ,<br>$Ni2+$      | Coprecipitation<br>and<br>hydrothermal | $\left[35\right]$  |
| Amino-functionalized $Fe3O4@SiO2$ core-shell<br>magnetic nanomaterial                                       | $Cu^{2+}$ , $Cd^{2+}$ ,<br>$Pb^{2+}$          | Coprecipitation                        | $\left[36\right]$  |
| Magnetic chitosan nanoparticles   | $\overline{\mathrm{Cu}^{2+}}$                 | Coprecipitation<br>and<br>hydrothermal | $[37]$             |
| Superparamagnetic iron oxide nanoparticles<br>(SPIONs) modified with $poly(\gamma$ -glutamic acid)<br>(PGA) | $Cd^{2+}$ , $Pb^{2+}$                         | Coprecipitation                        | $\left[38\right]$  |
| Magnetic $Fe3O4$ @ silica-xanthan gum<br>composite  | $Pb^{2+}$                                     | Coprecipitation                        | [39]               |
| Magnetic chitosan/cellulose hybrid<br>microspheres  | $Cu^{2+}$ , $Cd^{2+}$ ,<br>$Pb^{2+}$          | Sol-gel                                | [40]               |

<span id="page-11-0"></span>Table 10.5 Magnetic particles for heavy metal removal with their respective synthesis methods

### <span id="page-12-0"></span>6 Recovery of Magnetic Particles

Although abundant experimental photographic results were reported for the prospect of separation and recovery of magnetic nanoparticles from water or wastewater, there is no successful industrial application of magnetic particles for water or wastewater treatment that have been published. The discrete magnetic particles which are prone to agglomerate due to the magnetism property were believed to decrease the heavy metal removal capacity. The problem has become a prodigious limitation for recovery and reuse of the magnetic particles. Several conditions are manipulating the applicability of magnetic particles in a sustainable treatment process.

Several studies have indicated that the nanoscale iron oxide, which behaves as superparamagnetic material, can offer high accessibility and reusability for water or wastewater treatment systems  $[21, 41-43]$  $[21, 41-43]$  $[21, 41-43]$  $[21, 41-43]$  $[21, 41-43]$  $[21, 41-43]$  $[21, 41-43]$ . Majority of the systems require centrifugation or filtration process to separate solid wastes. Magnetic nanoparticles, however, can be separated and recovered easily with the aid of an external magnetic field due to the inherent characteristic of the nanoparticles, magnetism [\[44](#page-16-9)].

Magnetic separation is a technique to collect or separate magnetic substances from flowing streams. High-gradient magnetic separation (HGMS) device comprises of a bed of magnetically susceptible filling placed inside an electromagnet usually practiced in magnetic separations. Scientific literature has indicated that magnetic field-enhanced process with magnetite and HGMS offers substantial improvement for the removal of heavy metals from wastewater [[45\]](#page-16-10). The generation of significant magnetic field gradients, size and magnetic properties of particles, and the area of magnetized surfaces are the crucial factors for effective particle collection. When the particle suspension flows through the separation unit, the magnetic force attracting particles must be on top of the gravitational, fluid drag, buoyancy, inertial, and diffusion forces.

Separation of magnetic nanoparticles with a low-gradient magnetic field or a handheld permanent magnet (usually made of Fe and Nd) from solution has been regularly conveyed [\[46](#page-16-11)]. However, a higher magnetic force for a superconducting magnet in HGMS instead of an electromagnet is required when the particle size is reduced to the nanoscale. Complementary to this, aggregation due to strong magnetic dipole-dipole interactions between particles can either be coated with a surfactant to provide steric stability or particle surfaces be modified to produce a repulsive electrostatic force [[47,](#page-16-12) [48](#page-16-13)]. In short, an optimum particle size, synthesis methods of magnetic nanoparticles, and fluid properties are the aspects needed to be considered to design an effective recovery and high removal performance system.

#### <span id="page-13-0"></span>7 Environmental Application of Magnetic Particles

Magnetic particles such as nano zerovalent iron, magnetite, and maghemite and composite magnetic nanoparticles have been extensively utilized in environmental applications. These particles demonstrated favorable performance for eradicating pollutants from waterway systems. These promising findings have laced an alternative solution for the removal of heavy metal ions from contaminated water using magnetic adsorption technology [[50\]](#page-16-14).

Remediation of heavy metal pollution is possible by immobilizing them in a non-bioavailable form or re-speciating them into fewer toxic forms with nano zerovalent iron (nZVI). Several practical experiences of site remediation using nZVI have been established in the USA, and this remediation technique is expected to phase out in the coming decades. In Europe, many pilot test projects with the application of nZVI for different pollutants through three full-scale applications were merely conveyed. The pilot studies of 7 kg nZVI were reported to treat  $1-5$  g/L of Cr (VI) at Permon, Czechia [[51\]](#page-16-15). Furthermore, macroscale zerovalent iron has been documented as a suitable electron donor in aquatic environments.

Economic constraints and the precautionary attitude in Europe raise concerns regarding the feasibility of nZVI as a cost-effective technique for aquifer remediation. Nontechnical aspects, including the probability of negative repercussions and the novelty of the technology for consultancy, governments, as well as the public, tend to be significant challenges for the commercialization of nZVI.

#### <span id="page-13-1"></span>Glossary





#### <span id="page-14-1"></span><span id="page-14-0"></span>**References**

- 1. Mitchell BS (2004) An introduction to materials engineering and science for chemical and materials engineers. Wiley, New Jersey, USA
- <span id="page-14-2"></span>2. Harris IR, Willams AJ (2009) Magnetic materials. In: Rawlings RD (ed) Materials science and engineering – volume II. EOLSS, UK, pp 49–83
- <span id="page-14-3"></span>3. Birčáková Z, Kollár P, Füzer J, Bureš R, Fáberová M (2020) Magnetic properties of selected Fe-based soft magnetic composites interpreted in terms of Jiles-Atherton model parameters. J Magn Magn Mater 502:166514
- <span id="page-14-4"></span>4. Spellman FR (2014) Fundamentals of electricity, 3rd edn. CRC Press, Boca Raton, FL, USA
- <span id="page-14-5"></span>5. Spellman FR, Bieber RM (2011) The science of renewable energy. CRC Press, Boca Raton, FL, USA
- <span id="page-14-6"></span>6. Allia P, Barrera G, Tiberto P (2020) Hysteresis effects in magnetic nanoparticles: a simplified rate-equation approach. J Magn Magn Mater 496:165927
- <span id="page-14-7"></span>7. Dobrzański LA, Drak M, Ziębowicz B (2006) Materials with specific magnetic properties. J Achiev Mater Manuf Eng 17(1–2):37–40
- <span id="page-14-9"></span>8. Hatch GP, Stelter RR (2001) Magnetic design considerations for devices and particles used for biological high-gradient magnetic separation (HGMS) systems. J Magn Magn Mater 225:262–276
- <span id="page-14-8"></span>9. Buschow KHJ, de Boer FR (2004) Physics of magnetism and magnetic materials. Kluwer Academic, Moscow
- <span id="page-15-0"></span>10. Acharya SS, Medicherla VRR, Bapna K, Ali K, Biswas D, Maiti K, Rawat R (2020) Exchange correlation and magnetism in bcc Fe 0.8 Ni 0.2 alloy. J Electron Spectrosc Relat Phenom 240:146933
- <span id="page-15-1"></span>11. Czichos H, Saito T, Smith LE (2011) Springer handbook of metrology and testing. Springer Handbook of Metrology and Testing, New York
- <span id="page-15-2"></span>12. Coey JMD (2009) Magnetism and magnetic materials. Cambridge University Press, New York
- <span id="page-15-3"></span>13. Callister WDJ (2007) Material science and engineering an introduction. Wiley, USA
- <span id="page-15-4"></span>14. Chen Q (2020) Nanobismuth enhanced plasmonic, emission and faraday rotation properties of diamagnetic tellurite glasses. J Alloys Compd 828:154448
- <span id="page-15-5"></span>15. Rao RS (2012) Electromagnetic waves and transmission lines. PHI Learning, New Delhi, India
- <span id="page-15-6"></span>16. Pal M, De A (2009) Polymer-iron oxide based magnetic nanocomposites. In: Merhari L (ed) Hybrid nanocomposites for nanotechnology: electronic, optical, magnetic and biomedical applications. Springer Science+Business Media, New York, pp 455–506
- <span id="page-15-7"></span>17. Buschow KHJ, de Boer FR (2003) Physics of magnetism and magnetic materials, Springer, US
- <span id="page-15-8"></span>18. Thanh NT (2012) Magnetic nanopartic. Ramimoghadam D, Bagheri S, Hamid SBA (2015) Stable monodisperse nanomagnetic colloidal suspensions: an overview. Colloids and Surfaces B: Biointerfaces 133:388–411. Les: from fabrication to clinical applications. Florida: Taylor & Francis, USA
- <span id="page-15-9"></span>19. Wu W, He QG, Jiang CZ (2008) Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies. Nanoscale Res Lett 3:397–415
- <span id="page-15-10"></span>20. Ramimoghadam D, Bagheri S, Hamid SBA (2015) Stable monodisperse nanomagnetic colloidal suspensions: an overview. Colloids Surf B: Biointerfaces 133:388–411
- <span id="page-15-11"></span>21. Zheng YM, Lim SF, Chen JP (2009) Preparation and characterization of zirconium based magnetic sorbent for arsenate removal. J Colloid Interface Sci 338(1):22–29
- <span id="page-15-12"></span>22. Zhu JH, Wei SY, Chen MJ, Gu HB, Rapole SB, Pallavkar S, Ho TC, Hopper J, Guo ZH (2013) Magnetic nanocomposites for environmental remediation. Adv Powder Technol 24:459–467
- <span id="page-15-14"></span>23. Byrappa K, Adschiri T (2007) Hydrothermal technology for nanotechnology. Prog Cryst Growth Charact Mater 53:117–166
- <span id="page-15-13"></span>24. Kumar CSSR (2009) Magnetic nanomaterials. Wiley-VCH, Weinheim
- <span id="page-15-15"></span>25. Dauda KT, Atasie VN, Adeoye OB (2015) The kinetics and equilibrium studies of the adsorption of  $(Cu^{2+}, Pb^{2+})$  from industrial wastewater using rice husk as adsorbent. Int J Adv Res Chem Sci (IJARCS) 2(4):13–21
- <span id="page-15-16"></span>26. Ambashta RD, Sillanpää M (2010) Water purification using magnetic assistance: a review. J Hazard Mater 180(1–3):38–49
- <span id="page-15-17"></span>27. Boyer TH, Singer PC (2005) Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. Water Res 39(7):1265–1276
- <span id="page-15-18"></span>28. Hou X, Feng J, Liu X, Ren Y, Fan Z, Wei T, Meng J, Zhang M (2011) Synthesis of 3D porous ferromagnetic NiFe2O4 and using as novel adsorbent to treat wastewater. J Colloid Interface Sci 362(2):477–485
- <span id="page-15-19"></span>29. Hu J, Chen GH, Lo IMC (2005) Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. Water Res 39(18):4528–4536
- <span id="page-15-20"></span>30. Reng XJ, Luan ZK, Di ZC, Zhang ZG, Zhu CL (2005) Carbon nanotubes-iron oxides magnetic composites as adsorbent for removal of Pb(II) and Cu(II) from water. Carbon 43:855–894
- <span id="page-15-21"></span>31. Ngomsik A, Bee A, Siaugue J, Cabuil V, Cote G (2006) Nickel adsorption by magnetic alginate microcapsules containing an extractant. Water Res 40(9):1848–1856
- <span id="page-15-22"></span>32. Lim SF, Zheng YM, Zou SW, Chen JP (2008) Characterization of copper adsorption onto an alginate encapsulated magnetic sorbent by a combined FT-IR, XPS, and mathematical modeling study. Environ Sci Technol 42(7):2551–2556
- 33. Lim SF, Zheng YM, Chen JP (2009) Organic arsenic adsorption onto a magnetic sorbent. Langmuir 25(9):4973–4978
- <span id="page-15-23"></span>34. Lim SF, Zheng YM, Zou SW, Chen JP (2009) Uptake of arsenate by an alginate-encapsulated magnetic sorbent: process performance and characterization of adsorption chemistry. J Colloid Interface Sci 333(1):33–39
- <span id="page-16-1"></span>35. Zhou LM, Wang YP, Liu ZR, Huang QW (2009) Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres. J Hazard Mater 161:995–1002
- <span id="page-16-2"></span>36. Wang JH, Zheng SR, Shao Y, Liu JL, Xu ZY, Zhu DQ (2010) Amino-functionalized Fe3O4@SiO2 core–shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. J Colloid Interface Sci 349(1):293–299
- <span id="page-16-3"></span>37. Chen YW, Wang JL (2011) Preparation and characterization of magnetic chitosan nanoparticles and its application for Cu(II) removal. Chem Eng J 168(1):286–292
- <span id="page-16-4"></span>38. Inbaraj BS, Chen BH (2012) In vitro removal of toxic heavy metals by poly( $\gamma$ -glutamic acid)coated superparamagnetic nanoparticles. J Int J Nanomed 7:4419–4432
- <span id="page-16-5"></span>39. Peng XL, Xu F, Zhang WZ, Wang JY, Zeng C, Niu MJ, Chmielewská E (2014) Magnetic Fe3O4 @ silica–xanthan gum composites for aqueous removal and recovery of Pb2+. Colloids Surf A Physicochem Eng Asp 443:27–36
- <span id="page-16-6"></span>40. Zhao MH, Xu Y, Zhang CS, Rongm HW, Zeng GM (2016) New trends in removing heavy metals from wastewater. Appl Microbiol Biotechnol 100(15):6509–6518
- <span id="page-16-7"></span>41. Yantasee W, Warner CL, Sangvanich T, Addleman RS, Carter TG, Wiacek RJ, Fryxell GE, Timchalk C, Warner MG (2007) Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. Environ Sci Technol 41(14):5114–5119
- 42. Mahdavian AR, Mirrahimi MA (2010) Efficient separation of heavy metal cations by anchoring polyacrylic acid on superparamagnetic magnetite nanoparticles through surface modification. Chem Eng J 159:264–271
- <span id="page-16-8"></span>43. Feng LY, Cao MH, Ma XY, Zhu YS, Hu CW (2012) Superparamagnetic high-surface-area  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles as adsorbents for arsenic removal. J Hazard Mater 217–218:439–446
- <span id="page-16-9"></span>44. Lim SF, Lee AYW, Kam YS, Chua SND (2018) Synthesis and characterization of alginate encapsulated zirconium-based ferromagnetic sorbent for adsorptive removal of dyes. Int J Eng Technol 7(3.18):87–90
- <span id="page-16-10"></span>45. Navratil JD, Shing Tsair MT (2003) Magnetic separation of iron and heavy metals from water. Water Sci Technol 47(1):29–32
- <span id="page-16-11"></span>46. Lim SF, Lee AYW, Chua SND, Lim BH, Jain P (2020) Kinetic study on heavy metal divalent ions removal using zirconium-based magnetic sorbent. Int J of Integr Eng 12(3):225–234
- <span id="page-16-12"></span>47. Low KG, Lim SF (2014) Study on electrostatic extrusion method for synthesizing calcium alginate encapsulated Iron oxide. J Appl Sci Process Eng 1:1
- <span id="page-16-13"></span>48. Moore TL, Rodriguez-Lorenzo L, Hirsch V, Balog S, Urban D, Jud C, Rothen-Rutishauser B, Lattuada M, Petri-Fink A (2015) Nanoparticle colloidal stability in cell culture media and impact on cellular interactions. Chem Soc Rev 44:6287–6305
- <span id="page-16-0"></span>49. Reddy DHK, Yun YS (2016) Spinel ferrite magnetic adsorbents: alternative future materials for water purification? Coord Chem Rev 315:90–111
- <span id="page-16-14"></span>50. Anuradha Jabasingh S, Ravi T, Yimam A (2018) Magnetic hetero-structures as prospective sorbents to aid arsenic elimination from life water streams. Water Sci 32(1):151–170
- <span id="page-16-15"></span>51. Mueller NC, Braun J, Bruns J, Černik M, Rissing P, Rickerby D, Nowack B (2012) Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. Environ Sci Pollut Res 19(2):550–558